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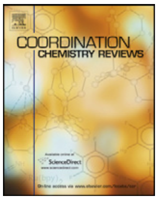

Review

Gold complexes containing organoselenium and organotellurium ligands

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Contents

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ABSTRACT

This article reviews the synthesis, structures, reactions and spectroscopic studies of gold complexes containing organoselenium and organotellurium ligands, i.e. compounds containing an Au–Se–C and Au–Te–C unit. The literature up to June 2009 has been covered. Appendix 1 lists important structural data of complexes which have been characterised by X-ray diffraction, whilst Appendix 2 contains a compilation of ^{77}Se and ^{125}Te NMR data for these compounds.

1. Introduction

Sulfur containing gold compounds date back hundreds of years and their structures, properties and applications in diverse fields are still being investigated today. In marked contrast, the chemistry of gold derivatives containing the heavier chalcogens selenium and tellurium is still an exotic and underdeveloped field of modern inorganic chemistry. Possible reasons for this may include the lack of commercially available or easily accessible Se or Te synthons as well as the often lower stability of their complexes. Some monographs of the inorganic literature give selected examples of gold complexes with selenium and tellurium ligands [1–5], but so far there is no single, comprehensive summary of this class of compounds. For the sake of brevity, we have restricted this review to cover only gold derivatives containing organoselenium and organotellurium ligands. Thus, in this review we discuss the syntheses, structures, reactivity and spectroscopic studies of complexes of the type Au–Se–C and Au–Te–C covering the literature up to June 2009.

Abbreviations: ^{t}Bu$_2$Im, 1,3-di-*tert*-butylimidazol-2-ylidine; Cp, cyclopentadienyl; Cy, cyclohexyl; Cys, cystein; DMSO, dimethyl sulfoxide; dppe, 1,2-bis(diphenylphosphino)ethane; dppee, 1,2-bis(diphenylphosphino)ethylene; dppf, 1,1′-bis(diphenylphosphino)ferrocene; dppm, bis(diphenylphosphino)methane; dppp, 1,3-bis(diphenylphosphino)propane; OTf, trifluoromethanesulfonate; PTA, 1,3,5-triaza-7-phosphaadamantane; PPN, bis(triphenylphosphine)iminium; py, pyridyl; THF, tetrahydrofuran; tht, tetrahydrothiophene.

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Purely inorganic compounds, alloys as well as Au–Se and Au–Te clusters go beyond the scope of this article. In Appendix we have included a table of important data (Au–Se/Te bond distances and angles) of all structurally characterised compounds of this class. Furthermore, we provide a compilation of ^{77}Se and ^{125}Te NMR chemical shifts, in the hope that this will serve as a useful reference for those working in the field.

2. Gold complexes with organoselenium ligands

2.1. Selenocyanate derivatives

Selenocyanate gold derivatives have been known for more than 130 years. In 1878, Clarke reported that addition of gold(I) chloride to an ethanolic solution of potassium selenocyanate gave deep red prisms which decomposed easily to elemental selenium [6]. Clarke formulated the material as $K[Au(SeCN)_2]$ but its instability hampered complete characterisation. Since then, no one has attempted to repeat this work and to confirm the identity of the reaction product. However, it was later reported that the anion $[Au(SeCN)_2]^-$ decomposes readily to give $[Au(CN)_2]^-$ and elemental selenium [7], consistent with Clarke's observations. A patent from 1997 claims that anionic gold(I) pseudohalogenato complexes are suitable for the treatment of HIV-AIDS, but only limited studies using $[Au(CN)_2]^-$ were disclosed [8].

In the following section, we will describe both, selenocyanate gold(I) and gold(III) complexes, that have been spectroscopically and structurally authenticated. These compounds are generally synthesised by mixing an alkali selenocyanate with a gold complex containing an easily substitutable group, usually chloride. In 1967, Schmidtke reported the synthesis of the tetraselenocyanatoaurate(III) salt $[Ph_4As][Au(SeCN)_4]$ from KSeCN, $K[AuCl_4]$ and $[AsPh_4]Cl$ [9,10]. This compound was characterised by elemental analysis, IR spectroscopy [ν(C–N) = 2118 cm^{-1}, ν(C–Se) = 516 cm^{-1}], and conductivity measurements (molar conductivity in DMF: $\lambda_m = 76.3\,cm^2\,\Omega^{-1}\,mol^{-1}$). The X-ray photoelectron spectrum was also measured [11]. Selenocyanate as an ambidentate ligand is a suitable model to study the hardness or softness of metal ions according to the Pearson concept [12]. The IR spectrum of $[Ph_4As][Au(SeCN)_4]$ clearly shows that gold(III) as a soft ion coordinates to the soft selenium atom of the selenocyanate and not to the hard nitrogen atom. This was further confirmed by detailed studies of the UV–vis spectra of the complex. In 1987, the crystal structure of $[Ph_4As][Au(SeCN)_4]$ (Fig. 1) was reported [13]. The square planar gold(III) centre is symmetrically surrounded by four selenocyanate anions [Au–Se, *ca.* 2.46 Å]. Overall, the $[Au(SeCN)_4]^-$ anion adopts a virtually planar swastika geometry, the angles at the selenium atom being nearly rectangular [Au–Se–C, *ca.* 103°].

The yellow mixed cyano and selenocyanato complex *trans*-$[Me_4N][Au(CN)_2(SeCN)_2]$ was synthesised by halide metathesis of *trans*-$[Me_4N][AuCl_2(CN)_2]$ with KSeCN in acetone at 0 °C in 43% yield [14]. IR spectroscopy [solid-state: ν(C–Se) = 533 cm^{-1}, ν(C–N) = 2117 cm^{-1}, 2143 cm^{-1}] and elemental analysis were used for characterisation. In nitromethane solution, a third C–N band was observed which indicates that the selenocyanate ligand is no longer bound solely *via* selenium but to some extent also *via* the nitrogen atom. Further IR spectroscopic studies to explore how pseudohalogens bind to gold were carried out with a series of phosphine gold(I) pseudohalide complexes. The selenium derivatives $[Au(SeCN)(PPh_3)]$ and $[Au_2(SeCN)_2(\mu\text{-dppe})]$ were also prepared by the halide metathesis method mentioned above [15,16] (Scheme 1).

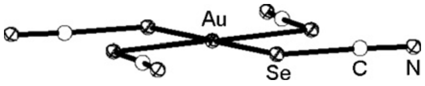


Fig. 1. Molecular structure of the $[Au(SeCN)_4]^-$ anion adapted from [13].

Far-IR measurements in solution indicated that the $SeCN^-$ ligand in the triphenylphosphine complex binds exclusively through selenium to gold [ν(Au–Se) = 218 cm^{-1}] [17]. In comparison to the thiocyanato analogue, the selenocyanate ligand is softer and therefore a stronger *trans*-director. Both $[Au(SeCN)(PPh_3)]$ and $[Au_2(SeCN)_2(\mu\text{-dppe})]$ are oxidised (accompanied by loss of the selenocyanato ligand) to the tribromogold(III) complex $[AuBr_3(PPh_3)]$ or the hexabromodigold(III) complex $[Au_2Br_6(\mu\text{-dppe})]$, respectively, by elemental bromine (Scheme 1) [16].

Schneider et al. improved the synthesis of phosphine(selenocyanato)gold(I) complexes by using a biphasic solvent system: the gold(I) halide complex was dissolved in dichloromethane and treated with an aqueous solution of potassium selenocyanate [18]. This method increased the yields of the colourless solids to over 70%. The variety of phosphine(selenocyanato)gold(I) complexes was extended to encompass other phosphines including tri(*o*-tolyl)phosphine and dimethylphenylphosphine. The complexes proved to be thermally unstable in solid and in solution depositing red selenium. In their IR spectra the ν(C–N) stretching vibrations appear at higher wavenumbers for the bound $SeCN^-$ compared to that of free $SeCN^-$, which confirms binding of the selenium to gold. The solid-state structure of the tri(*o*-tolyl)phosphine(selenocyanato)gold(I) complex $[Au(SeCN)\{P(o\text{-tolyl})_3\}]$ was determined by X-ray diffraction (Fig. 2). Isolated molecules having a propeller-type arrangement of the three *ortho*-tolyl groups are found in the lattice. The gold atom is nearly linearly coordinated by the phosphorus and selenium atoms [P–Au–Se 176.90(2)°] whilst the angle about the selenium atom is close to 90° [Au–Se–C 96.73(11)°]. The gold–selenium bond distance [Au–Se 2.4259(3) Å] is longer than that between gold and sulfur, due to the larger covalent radius of selenium.

The FAB mass spectra of the $[Au(SeCN)(PR_3)]$ [$PR_3 = P(o\text{-tolyl})_3$, $PPhMe_2$, and PPh_3] complexes showed weak $[M+H]^+$ peaks; the most intense signals being due to the phosphine gold cations. In addition, redistribution products of the type $[Au(PR_3)_2]SeCN$ and $[Au(PR_3)_2]^+$ were also observed. $[Au(SeCN)(PR_3)]$ when treated with $[Au(PR_3)]SbF_6$ in dichloromethane at −78 °C forms the extremely unstable complex $[\{(PR_3)Au\}_2SeCN][SbF_6]$ which decomposes at about −40 °C to selenium and gold(I)cyanide amongst other unidentified products. As a consequence, characterisation was limited to low temperature NMR and IR spectroscopy [18].

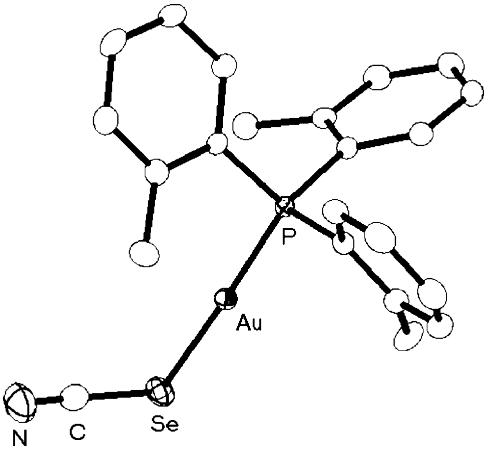
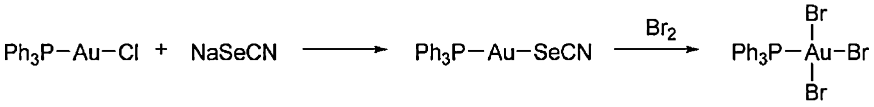


Fig. 2. Molecular structure of $[Au(SeCN)\{P(o\text{-tolyl})_3\}]$ adapted from [18]. Hydrogen atoms have been omitted for clarity.



$$\mathrm{Ph_3P{-}Au{-}Cl} + \mathrm{NaSeCN} \longrightarrow \mathrm{Ph_3P{-}Au{-}SeCN} \xrightarrow{\mathrm{Br_2}} \mathrm{Ph_3P{-}\overset{Br}{\underset{Br}{Au}}{-}Br}$$

Scheme 1.

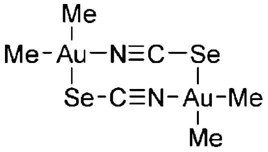


Fig. 3. Proposed structure of *cis*-$[Au(Me)_2(SeCN)]_2$ adapted from [19].

In the 1970s, Stocco et al. synthesised the dimethyl gold(III) pseudohalide complex *cis*-$[Au(Me)_2(SeCN)]_2$ by reacting $[Me_2AuI]_2$ or $[Me_2AuCl]_2$ with silver nitrate followed by addition of KSeCN at 0 °C [19]. The dimeric structure (Fig. 3) involving a bridging selenocyanato anion was proposed based on spectral data and comparison with known structures. The ^1H NMR spectrum shows two methyl group signals *trans* to nitrogen and selenium, respectively. IR and Raman data, in particular the single C≡N stretching vibration [ν(C–N): 2169 cm^{-1} (IR), 2158 cm^{-1} (Raman)], are consistent with a centric structure.

Addition of triphenylphosphine to $[Au(SeCN)Me_2]_2$ in solution induces a bridge-splitting reaction which leads quantitatively to the complex $[Au(Me)_2(SeCN)(PPh_3)]$ characterised by ^1H NMR spectroscopy *in situ* [20]. However, no pure product could be obtained by crystallisation from solution.

Schmidbaur and Dash synthesised the gold(III) complex $[Au(Me)_2(SeCN)(N\text{-}N)]$ (N-N = 2,7-dimethyl-1,8-naphthyridine) by addition of a hexane solution of $[Au(Me)_2(SeCN)]$ to a solution of 2,7-dimethyl-1,8-naphthyridine at 0 °C (Scheme 2) [21].

The colourless crystals exist as monomers in solution and are non-electrolytes at room temperature. The IR spectrum shows strong absorption bands for the selenocyanate at about 1200 cm^{-1}. The C≡N band [ν(C–N) = 2121 cm^{-1}] confirms the presence of a selenium–gold bond. For the dimethyl gold moiety intense Au–C stretching vibrations are observed in the region of 500–600 cm^{-1}. ^1H NMR spectroscopy at different temperatures showed that the 2,7-dimethyl-1,8-naphthyridine ligand is bound to the square planar gold(III) centre only *via* one nitrogen atom (Scheme 2). At −90 °C the two methyl groups of the 2,7-dimethyl-1,8-naphthyridine give two singlets of equal intensity as do the methyl groups attached to gold. The aromatic protons give two AB quartets at this temperature. Between −50 °C and room temperature the singlets of the naphthyridine methyl groups coalesce to one signal whilst those attached to gold remain unchanged. In addition, ^{77}Se satellites can be seen for the methyl group *trans* to selenium. The aromatic resonances are now observed as a single AB pattern. Increasing the temperature to +60 °C results in coalescence of the resonances due to the methyl groups attached to gold and disappearance of the selenium satellites. These data clearly illustrate the rapid exchange

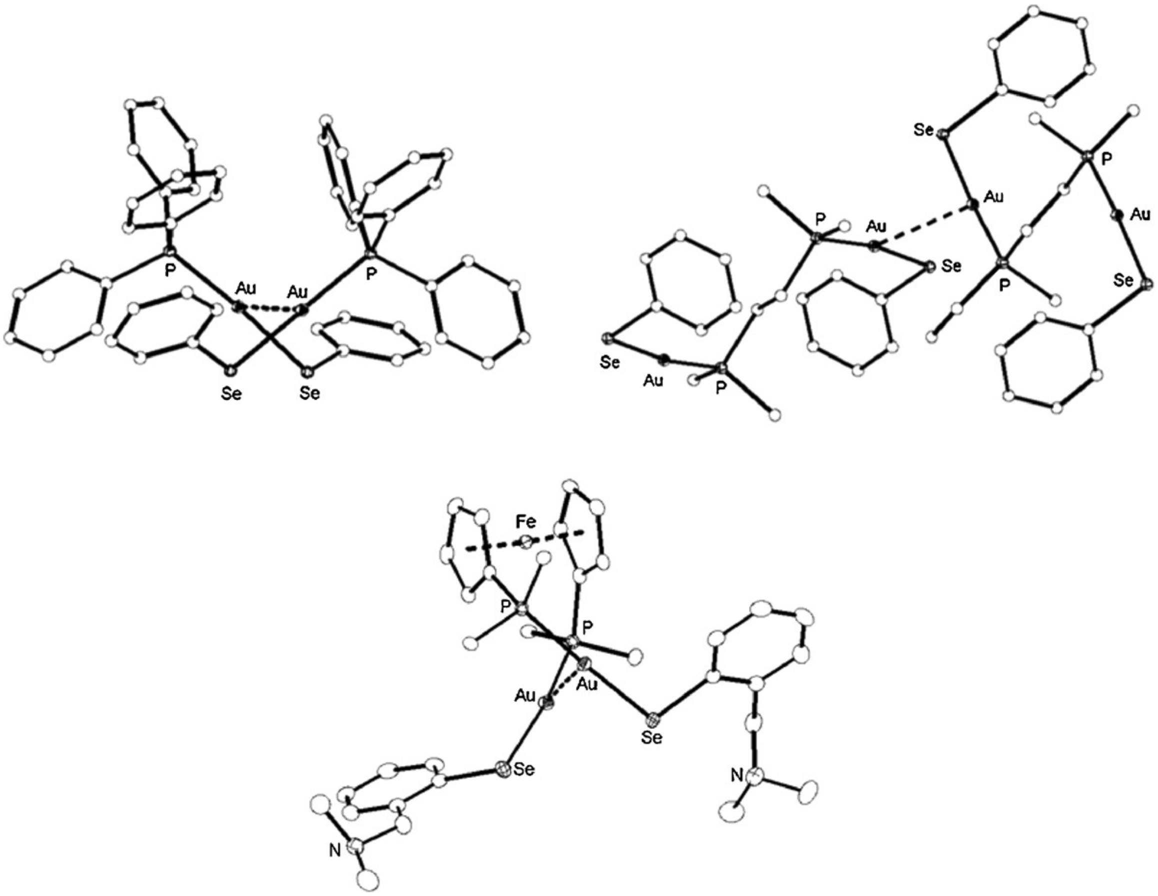
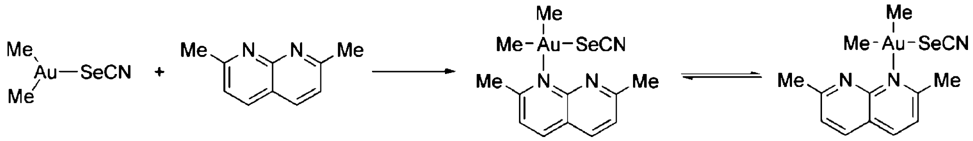
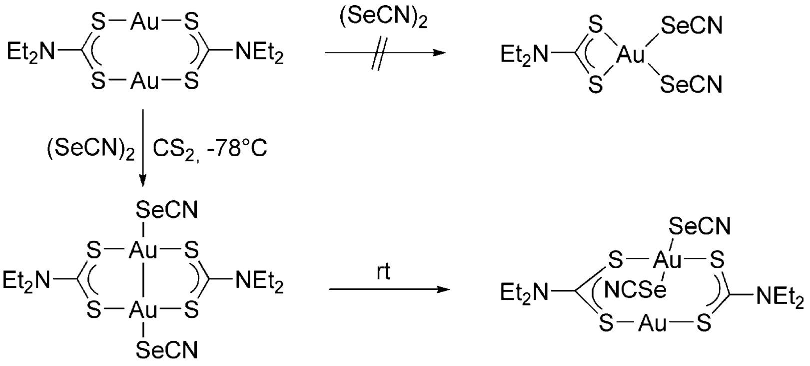


Fig. 4. Molecular structures of $[Au(SePh)(PPh_3)]$ (top left) adapted from [27], $[Au_2(SePh)_2(\mu\text{-dppe})]$ (top right) adapted from [28] and $[Au_2\{SeC_6H_4(2\text{-}CH_2NMe_2)\}_2(\mu\text{-dppf})]$ (bottom) adapted from [29]. Hydrogen atoms have been omitted for clarity. In the top right and bottom figures only the *ipso*-C of the PPh_2 groups are shown.



Scheme 2.



Scheme 3.

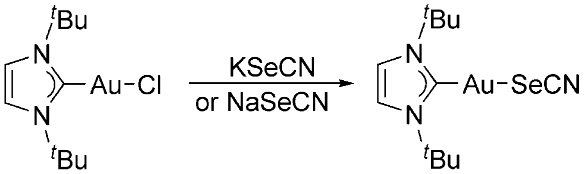
of the Au(SeCN)Me_2 unit between the two nitrogen atoms of the 2,7-dimethyl-1,8-naphthyridine.

Calabro et al. attempted to obtain the *N*,*N*-diethyldithiocarbamato(diselenocyanato)gold(III) complex [Au(S_2CNEt_2)$(SeCN)_2$] by oxidative addition of selenocyanogen $(SeCN)_2$ to the dimeric (diethyldithiocarbamato)gold(I) complex [$Au_2(S_2CNEt_2)_2$] [22]. Instead of the desired compound, they isolated a green solid, which upon warming turned yellow. Based on IR data and its diamagnetic nature, a dinuclear gold(II) structure containing a gold–gold bond was assumed for the green solid. This material undergoes an isomerisation process to give the mixed valence Au(I)/Au(III) complex as the final yellow product (Scheme 3).

The digold(II) complex is structurally related to the digold(II) bis(ylide) complex derived from oxidative addition of Ph_2Se_2 to [$Au_2\{(CH_2)_2PPh_2\}_2$], which has been structurally characterised (see Section 2.2).

Gold(I) pseudohalide complexes containing N-heterocyclic carbene ligands were investigated by Baker et al. to study of the nature of the gold–carbene bond [23]. 1,3-Di-*tert*-butylimidazol-2-ylidine selenocyanato gold(I) [Au(^{t}Bu_2Im)(SeCN)] was obtained by halide metathesis from the chloro derivative with potassium or sodium selenocyanate (Scheme 4).

Detailed characterisation was carried out using IR, UV–vis, ^{13}C, and ^{1}H NMR spectroscopies as well as X-ray diffraction. IR spectroscopy was used to prove that the selenocyanate ion binds to gold *via* selenium. By observing the chemical shift of the carbene carbon atom in the ^{13}C NMR spectrum, a correlation between the σ-donor ability of the ligands and the chemical shift was established. Weak σ-donor ligands, such as nitrate or acetate, show the most upfield chemical shift, whilst strong σ-donors, including selenocyanate, cause a downfield shift of the carbene carbon signal. In addition, there exists an approximate correlation between the carbene carbon chemical shift and the gold–carbene carbon bond length. Complexes with strong σ-donors generally have longer Au–C(carbene) bond lengths. In this case, the Au–C(carbene) bond distance was determined to be 2.049(7) Å, the Au–Se distance was 2.412(8) Å and the angle about selenium is close to 100° [Au–Se–C 97.0(3)°].



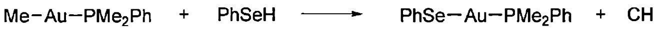
Scheme 4.

2.2. Arylselenide derivatives

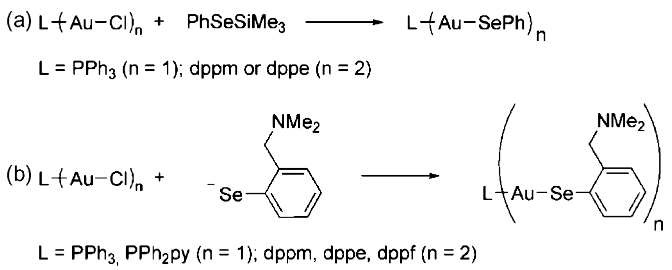
By far the biggest part of this class are gold complexes containing phenylselenolato ligands. In these complexes $PhSe^-$ can display either monodentate or bridging coordination modes. There has also been a theoretical investigation of the interaction between $PhSe^-$ and model Au surfaces consisting of one, two, and three gold atoms [24].

Puddephatt and Thompson were the first to synthesise [Au(SePh)(PMe_2Ph)] by a substitution reaction of the methyl gold compound [AuMe(PMe_2Ph)] with PhSeH (Scheme 5) [25].

Twelve years later, triphenylphosphine(phenylselenolate) gold(I) [Au(SePh)(PPh_3)] was obtained as byproduct (26% yield) from the oxidative addition of Ph_2Se_2 to the triphenylphosphine gold(I) enolate [Au{$CH_2C(O)Ph$}(PPh_3)]; the main product of this reaction was $PhSeCH_2C(O)Ph$ [26]. Jones and Thöne developed a new synthesis for this complex with a much better yield (73%) involving the chloride substitution of [AuCl(PPh_3)] with PhSeSiMe [27]. In addition, the yellow bis(diphenylphosphinomethane) derivative [$Au_2(SePh)_2$(μ-dppm)] (87%) [27] as well as the colourless bis(diphenylphosphinoethane) gold(I) complex [$Au_2(SePh)_2$(μ-dppe)] (83%) [28] were obtained by the same method (Scheme 6a). Laguna and coworkers recently reported the synthesis and characterisation of a series of mono- and dinuclear gold(I) complexes containing 2-(*N*,*N*-dimethylamino)benzylselenolato ligands [29]. Complexes of the type [AuL(P)] (P = PPh_3, PPh_2py) and [Au_2L_2(μ-P-P)] (P-P = dppm, dppe, dppf) were prepared by reacting metal (Li or K) salts of the selenium compound with the appropriate gold(I) precursors (Scheme 6b). The gold(III) salt [^{n}Bu_4N][Au{SeC_6H_4(2-CH_2NMe_2)}$(C_6F_5)_3$] was formed by a substitution reaction of [^{n}Bu_4N][AuBr$(C_6F_5)_3$] with $KSeC_6H_4(2\text{-}CH_2NMe_2)$. The complexes



Scheme 5.



Scheme 6.

were reported to be colourless or yellow stable solids which were characterised extensively including ^{77}Se NMR spectroscopy as well as detailed luminescence studies of the gold(I) derivatives.

X-ray diffraction studies of various gold complexes containing arylselenolato ligands have been carried out. The asymmetric units of [Au(SePh)(PPh$_3$)], [Au$_2$(SePh)$_2$(μ-dppe)] and [Au$_2${SeC$_6$H$_4$(2-CH$_2$NMe$_2$)}$_2$(μ-dppe)] (Fig. 4) contain independent molecules joined by intermolecular Au···Au "aurophilic" interactions [30]. The dppe derivatives form polymeric chains with gold–gold contacts of 3.044(9) and 3.0910(6) Å, respectively; the PPh$_3$ complex forms a dimer with slightly longer intermolecular gold contacts [Au···Au = 3.118(1) Å]. The dppf derivative [Au$_2${SeC$_6$H$_4$(2-CH$_2$NMe$_2$)}$_2$(μ-dppf)] (Fig. 4) contains an intramolecular aurophilic interaction of 3.0243(6) Å.

In these compounds, coordination about each gold centre is, as expected, virtually linear [P–Au–Se in PPh$_3$: 175.6(1)°; 179.6(1)°, dppe: 171.05(6)°, 172.74(6)°; dppf: 177.96(2)°, 170.61(2)°] with similar Au–Se bond distances of about 2.42 Å. It is worth noting that nearly right angles at selenium are found in the dppe complex [C–Se–Au 97.1(2)°, 94.9(3)°] whilst those of the PPh$_3$ analogue are about 10° larger [C–Se–Au 105.7(2)°, 105.3(2)°].

Puddephatt and Thompson also prepared the dinuclear tetramethyl gold(III) complex [Au$_2$Me$_4$(μ-SePh)$_2$] containing two bridging phenylselenolato ligands (Scheme 7) from [AuMe$_3$(Et$_2$O)] and PhSeH. The same product forms when *cis*-[AuMe$_2$(SePh)(PMe$_2$Ph)] is left in solution at room temperature for a period of several days. *cis*-[AuMe$_2$(SePh)(PMe$_2$Ph)] can be obtained from the reaction of [AuMe$_3$(PMe$_2$Ph)] with PhSeH [25].

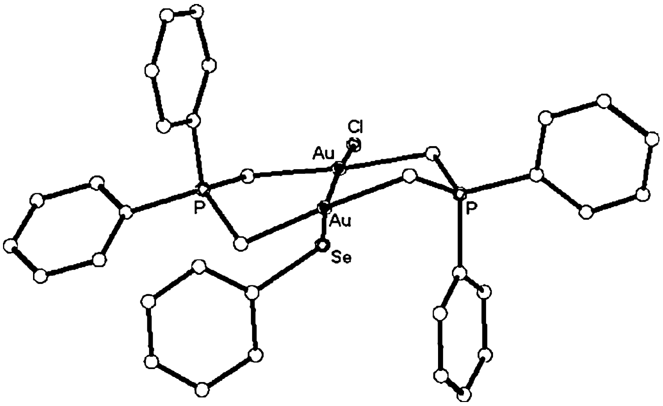


Fig. 5. Molecular structure of [AuCl(SePh){(CH$_2$)$_2$PPh$_2$}$_2$] adapted from [31]. Hydrogen atoms have been omitted for clarity.

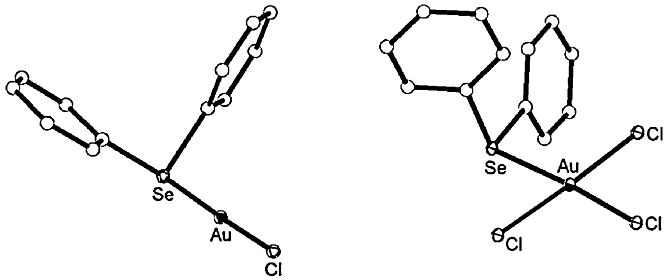


Fig. 6. Molecular structures of [AuCl(SePh$_2$)] (left) and [AuCl$_3$(SePh$_2$)] (right) adapted from [33]. Hydrogen atoms have been omitted for clarity.

In 1987, Porter and Fackler Jr. reported the preparation of the gold(II) bis(ylide) complex [Au(SePh)$_2${(CH$_2$)$_2$PPh$_2$}$_2$] by oxidative addition of Ph$_2$Se$_2$ to the dinuclear gold(I) bis(ylide) complex [Au$_2${(CH$_2$)$_2$PPh$_2$}$_2$] [31]. However, during recrystallisation of this compound in dichloromethane one of the phenylselenolato ligands was substituted by a chloride (Fig. 5). The two gold atoms are connected by a metal–metal bond [Au–Au = 2.636(1) Å] bridged by two anionic bis(ylide) ligands forming an 8-membered heterocyclic ring in a chair-like conformation. The square planar coordination geometry about gold is completed by the chloride and the phenylselenolato ligands, respectively.

The heteronuclear Pt(II)/Au(II) complex with one phenylselenolato ligand at each gold centre was synthesised by oxidative addition of Ph$_2$Se$_2$ to the heterotrinuclear Au(I)/Pt(II) complex [Au$_2$Pt{Ph$_2$P(S)CH$_2$}$_4$] [32]. The authors propose that the diselenide performs a transannular symmetric addition oxidising the [Au$_2$Pt]$^{4+}$ unit accompanied by formation of two new Au–Pt bonds. The suggested structure was however based solely on solution ^{1}H and ^{31}P NMR spectroscopy and elemental analysis.

In the 1990s, Jones and Thöne reported further studies of dinuclear gold(I) and gold(III) arylselenide compounds. Diphenylselenide complexes such as [AuCl(SePh$_2$)] or [AuCl$_3$(SePh$_2$)] were obtained by the reaction of SePh$_2$ with gold(I) or gold(III) chloride, respectively [33]. The complexes were characterised by X-ray diffraction (Fig. 6) and also for some derivatives by ^{77}Se NMR spectroscopy. The gold(I) complex exhibits an Au–Se bond distance of 2.378(1) Å, which is shorter than that of the gold(III) derivative [Au–Se = 2.445(1) Å].

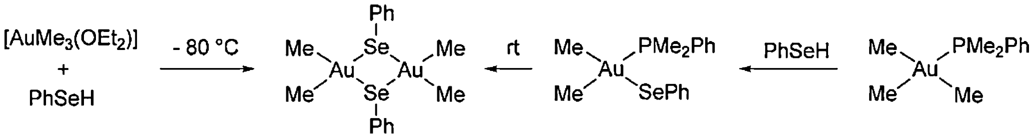
Further investigations concentrated on arylselenide ligands bridging two gold(I) phosphine moieties. The first example was the cationic phenylselenolato complex [Au$_2$(μ-SePh)(PPh$_3$)$_2$]SbF$_6$, isolated as the pale-orange hexafluoroantimonate salt in 66% yield from the oxidative addition of Ph$_2$Se$_2$ to [AuCl(PPh$_3$)] in the presence of AgSbF$_6$ [27]. Similarly, the analogous 4-chloro substituted derivative [Au$_2$(μ-4-ClC$_6$H$_4$Se)(PPh$_3$)$_2$]SbF$_6$ was also prepared [34]. In the X-ray crystal structures of both compounds (Fig. 7), the cations crystallise as dimers forming Au$_4$ squares through short intermolecular gold–gold interactions of *ca.* 3.1 Å. The intramolecular gold–gold contacts (*ca.* 3.2 Å) result in a narrow Au–Se–Au angle of about 82°.

Shortly after, a further study of cationic gold(I) phosphine complexes containing bridging arylselenolato ligands appeared (Scheme 8) [28].

All these complexes are light-sensitive and decomposition occurs in solution within hours excluding the possibility to record ^{77}Se NMR spectra. Compounds with arylselenium ligands are significantly more stable than the alkylselenium derivatives. Molecular structure analysis of the 1-naphthylselenolato derivative showed, that in the solid-state, the compound exists as an adduct of cationic [(AuPPh$_3$)$_2$(SeC$_{10}$H$_7$)]SbF$_6$ and neutral [Au(PPh$_3$)(SeC$_{10}$H$_7$)] (Fig. 8).

Intermolecular Au(I)···Au(I) contacts of *ca.* 3.2 Å link the neutral with the cationic part of the molecule. The P–Au–Se angles in the cation are strongly distorted from linearity [P–Au–Se = 167.5(2)°, 159.3(2)°] due to the presence of intermolecular Au···Se contacts of *ca.* 3.2 Å between the two components. In solution, the ^{31}P NMR spectrum shows AuPPh$_3$-group migration between the cation and the neutral component at room temperature.

The gold(I) complex [Au(2,4,6-^{t}Bu$_3$C$_6$H$_2$Se)(PPh$_3$)] containing the sterically demanding 2,4,6-tri-*tert*-butylphenylselenolato



Scheme 7.

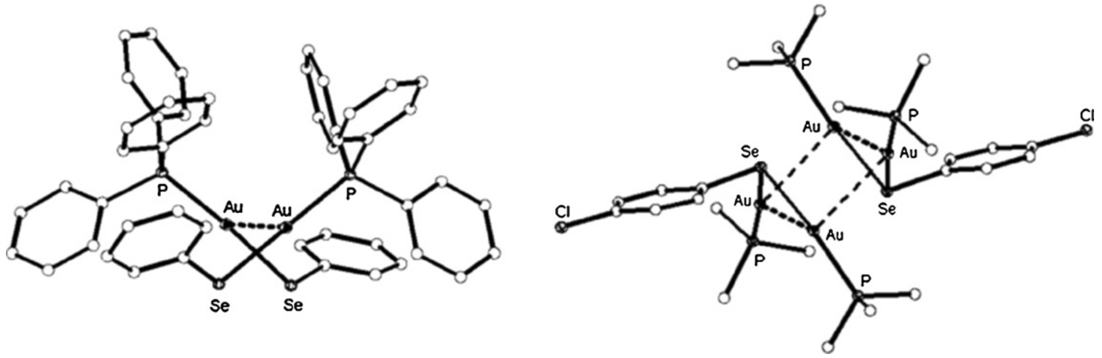
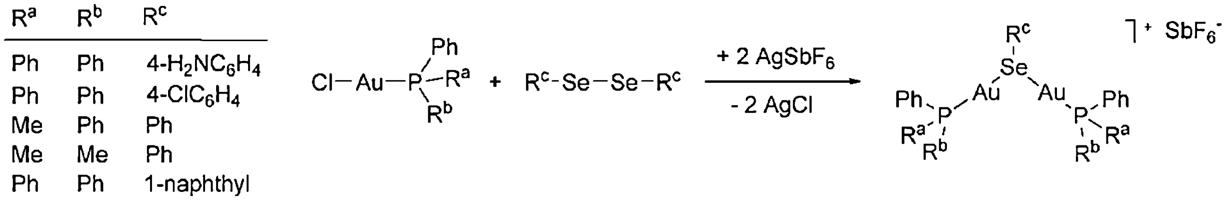


Fig. 7. Molecular structures of the cations $[Au_2(\mu\text{-SePh})(PPh_3)_2]^+$ (left) adapted from [27] and $[Au_2(\mu\text{-4-ClC}_6H_4Se)(PPh_3)_2]^+$ (right) adapted from [34]. Hydrogen atoms have been omitted for clarity. In the right hand figure only the *ipso*-C atoms of the PPh_3 group are shown.



R^a	R^b	R^c
Ph	Ph	$4\text{-}H_2NC_6H_4$
Ph	Ph	$4\text{-}ClC_6H_4$
Me	Ph	Ph
Me	Me	Ph
Ph	Ph	1-naphthyl

Scheme 8.

ligand [35,36] was synthesised by a substitution reaction of $[2,4,6\text{-}{}^tBu_3C_6H_2SeLi](THF)_x$ with $[AuCl(PPh_3)]$ (Scheme 9). The colourless crystals are thermally stable and were characterised by IR, ^1H, ^{31}P (47 ppm in C_6D_6) and ^{77}Se NMR spectroscopy (170.6 ppm, d, $^2J_{Se\text{–}P} = 41$ Hz in C_6D_6) as well as elemental analysis.

The anionic mixed sulfur–selenium gold(III) complex $[Au(\kappa^2\text{-}S,Se\text{-}1,2\text{-}SeSC_6H_4)_2]^-$ [37] was obtained from the reaction of the disodium salt of 1,2-selenothiobenzene with $K[AuCl_4]$ in the presence of a quaternary ammonium salt (Scheme 10). Instead of the desired superconducting material, an insulator was obtained as was shown by cyclic voltammetry and ESR measurements.

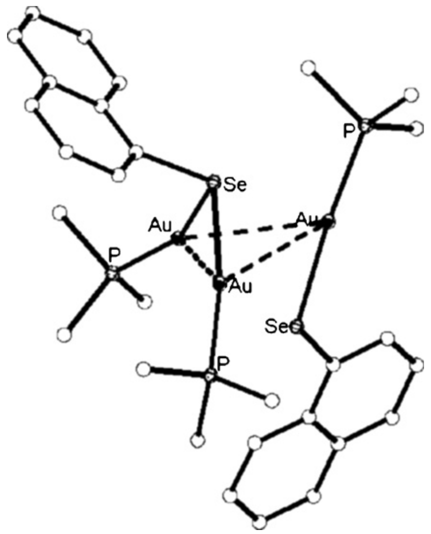
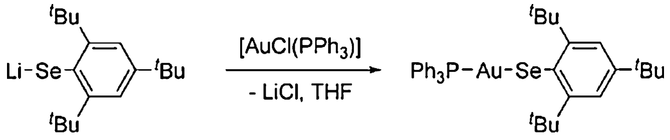


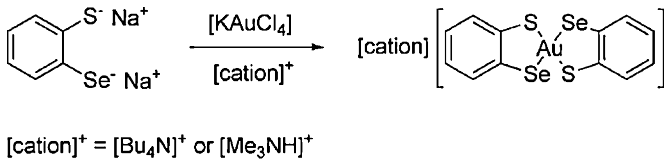
Fig. 8. Molecular structure of $[(AuPPh_3)_2(SeC_{10}H_7)]^+[Au(PPh_3)(SeC_{10}H_7)]$ adapted from [28]. Only the *ipso*-C atoms of the PPh_3 groups are shown and hydrogen atoms as well as the SbF_6 anion have been omitted for clarity.



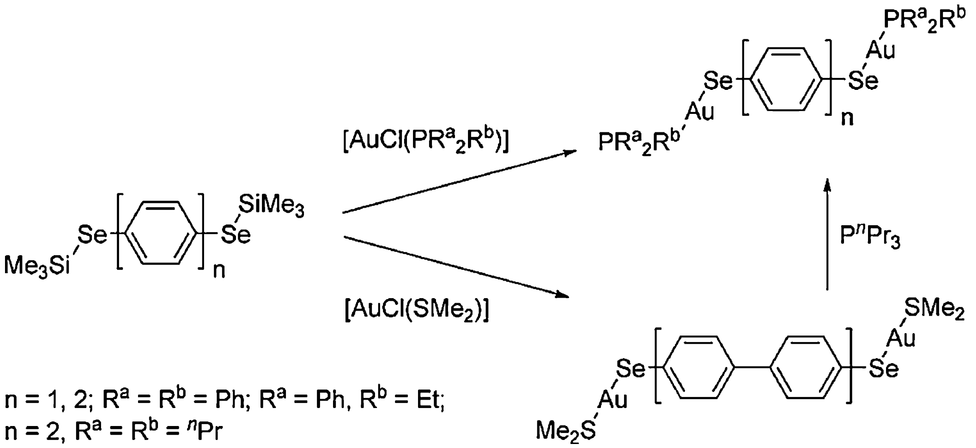
Scheme 9.

1,4-Phenylene and 4,4′-biphenylene-diselenolato bridged gold(I) complexes $[(PR^a{}_2R^b)AuSe(C_6H_4)_nSeAu(PR^a{}_2R^b)]$ were prepared by addition of $[Me_3SiSe(C_6H_4)_nSeSiMe_2]$ ($n = 1$ or 2) to the phosphine gold(I) chlorides $[AuCl(PR^a{}_2R^b)]$ [$R^a = R^b = Ph$; $R^a = Ph$, $R^b = Et$, $R^a = R^b = {}^nPr$] [38] (Scheme 11). Alternatively, $[AuCl(SMe_2)]$ was reacted with the biphenylene-4,4′-diselenolatesilane giving $[(Me_2S)AuSe(C_6H_4)_2SeAu(SMe_2)]$ whose dimethylsulfide groups are easily substituted by phosphines. This latter method gave much higher yields of the ${}^nPr_3P$ complex. Characterisation included NMR spectroscopy (^1H, ^{31}P, ^{77}Se) and X-ray diffraction of three of the compounds.

The group of Laguna carried out detailed studies of gold complexes containing selenium substituted ferrocene



Scheme 10.



n = 1, 2; $R^a = R^b = Ph$; $R^a = Ph$, $R^b = Et$;
n = 2, $R^a = R^b = {}^nPr$

Scheme 11.

derivatives. Their investigation began with symmetrically substituted 1,1′-bis(phenylseleno)ferrocene coordinated to gold [39]. In the cationic three-coordinate gold(I) complex $[Au(PPh_3)\{Fe(\eta^5\text{-}C_5H_4SePh)_2\}]OTf$, prepared by reaction of 1,1′-bis(phenylseleno)ferrocene with $[Au(OTf)(PPh_3)]$, the chelating mode of this ligand is observed [39] (Scheme 12). The compound behaves as a 1:1 electrolyte in acetone solution and the molecular ion peak of the cation is seen in the electrospray mass spectrum.

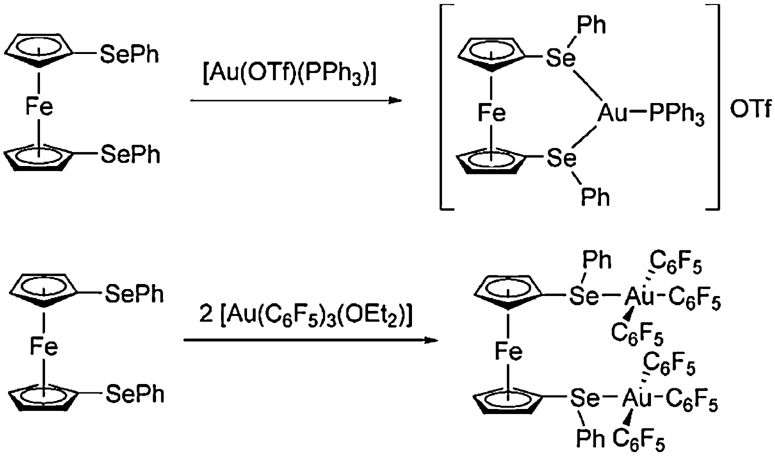
In the gold(III) derivative $[\{Au(C_6F_5)_3\}_2\{\mu\text{-}Fe(\eta^5\text{-}C_5H_4SePh)_2\}]$ the 1,1′-bis(phenylseleno)ferrocene acts as a bridging ligand. The ^{19}F NMR spectrum shows six signals in a 2:1 ratio for the mutually *trans* and *cis* pentafluorophenyl groups, respectively, typical for equivalent $Au(C_6F_5)_3$ groups. The solid-state structure of this compound was claimed to be isostructural to that of the sulfur derivative, however due to poor crystal quality, no full structure refinement could be carried out.

The same group also reported a series of gold complexes containing the phenylselenide substituted phosphinoferrocene ligand $[Fe(\eta^5\text{-}C_5H_4SePh)(\eta^5\text{-}C_5H_4PPh_2)]$ [40]. The reaction of this compound with one equivalent of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ affords the mononuclear gold(III) salt $[Au(C_6F_5)_2\{\kappa^2\text{-}P,Se\text{-}Fe(\eta^5\text{-}C_5H_4SePh)(\eta^5\text{-}C_5H_4PPh_2)\}]ClO_4$, whilst the same reaction with two equivalents of $[Au(C_6F_5)_3(OEt_2)]$ gives the dinuclear gold(III) complex $[\{Au(C_6F_5)_3\}_2\{\mu\text{-}Fe(\eta^5\text{-}C_5H_4SePh)(\eta^5\text{-}C_5H_4PPh_2)\}]$ (Scheme 13). Both air- and moisture-stable orange solids were characterised by IR, ^1H, ^{31}P and ^{19}F NMR spectroscopy and elemental analysis. These studies showed, that, given the choice between a phosphorus and selenium donor atom, gold prefers binding to phosphorus unless a vacant coordination site needs to be filled.

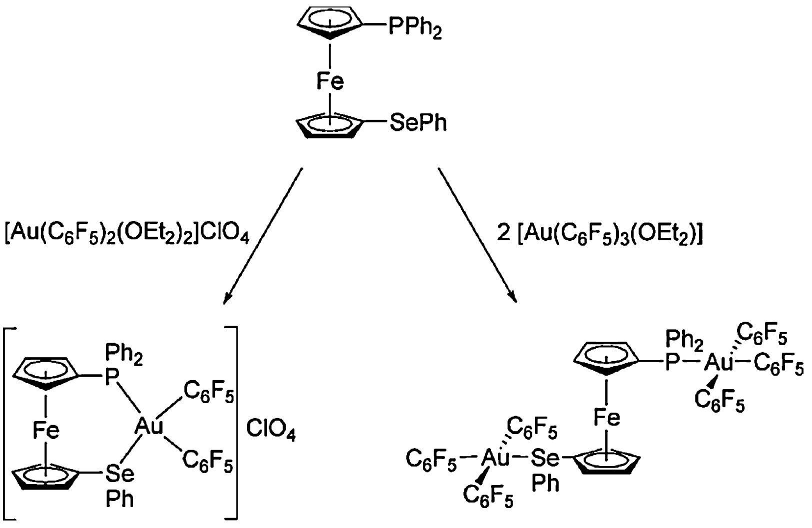
In related studies various derivatives of $[Au_2(SePh)_2(\mu\text{-dppf})]$ were synthesised in order to study aurophilic Au(I)–Au(I) and Au(I)–Au(III) interactions [41]. The complex $[Au_2(SePh)_2(\mu\text{-dppf})]$ was prepared from $[Au_2Cl_2(\mu\text{-dppf})]$ with two equivalents of $PhSeSiMe_3$ (Scheme 14).

$[Au_2(SePh)_2(\mu\text{-dppf})]$ reacts with one equivalent of $[Ag(OTf)]$ in dichloromethane giving the salt $[Au_2(\mu\text{-SePh})(\mu\text{-dppf})]OTf$ which contains a bridging selenolato ligand between two gold(I) atoms. In the crystal structure (Fig. 9) the asymmetric unit consists of a dimer of two molecules rotated by 98° with respect to each other and held together by intermolecular Au···Au interactions of 2.9238(7) Å. In addition, there are also intramolecular Au···Au interactions of *ca.* 3 Å. Thus, the four gold centres built a tetranuclear array [Au–Au–Au = 139.18(2)°; 137.01(2)°] with distorted linear geometries. Au–Se bond distances (2.44–2.47 Å) are in the usual range for compounds with bridging selenolato ligands.

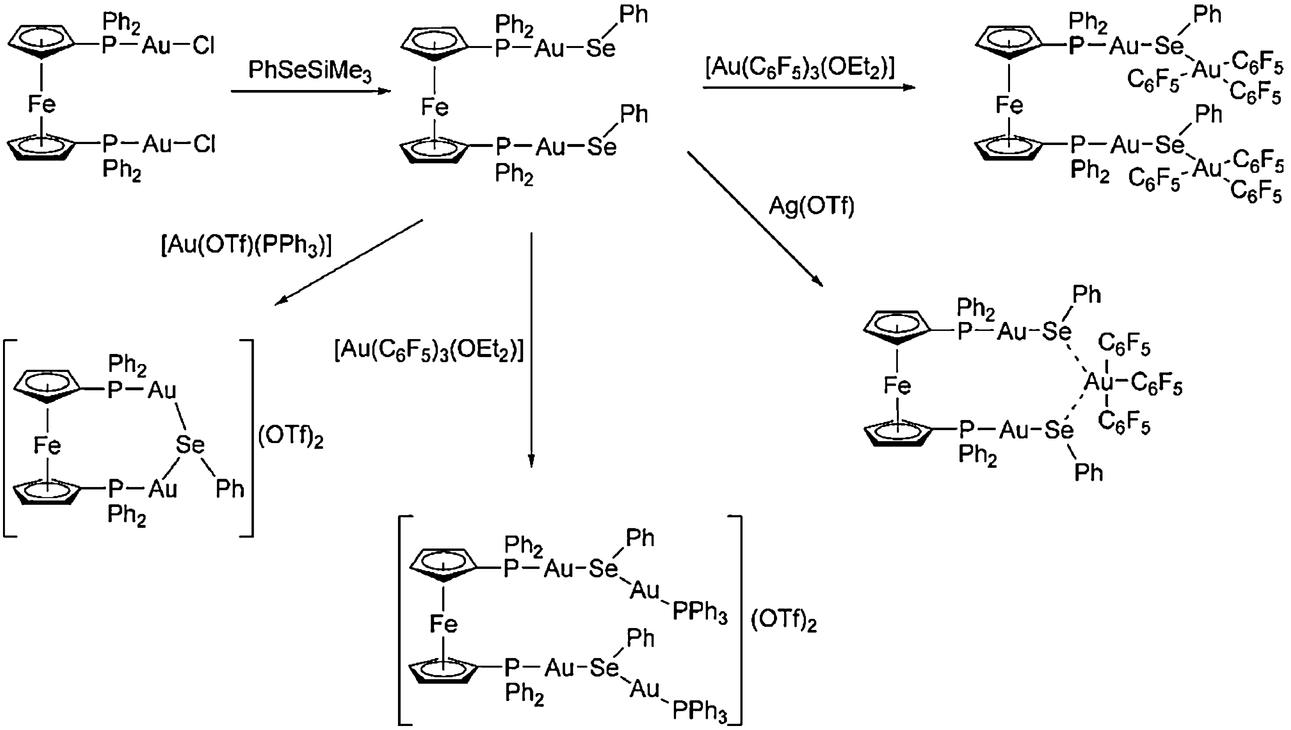
The tetranuclear gold(I) salt $[(\mu\text{-dppf})\{Au^I(\mu\text{-SePh})Au^I(PPh_3)\}_2](OTf)_2$ was obtained by addition of $[Au(OTf)(PPh_3)]$ to $[Au_2(SePh)_2(\mu\text{-dppf})]$. The complex shows two singlet resonances due to the two different phosphorus atoms in its ^{31}P NMR spectrum. The mixed gold(I)–gold(III) complexes $[(\mu\text{-dppf})\{Au^I(\mu\text{-SePh})\}_2Au^{III}(C_6F_5)_3]$ and $[(\mu\text{-dppf})\{Au^I(\mu\text{-SePh})Au^{III}(C_6F_5)_3\}_2]$ were both prepared by the reaction of one or two equivalents of $[Au(C_6F_5)_3(OEt_2)]$ with $[Au_2(SePh)_2(\mu\text{-dppf})]$, respectively (Scheme 15) [41]. In $[(\mu\text{-dppf})\{Au^I(\mu\text{-SePh})\}_2Au^{III}(C_6F_5)_3]$, a rapid exchange of the $Au(C_6F_5)_3$ fragment between both selenium



Scheme 12.



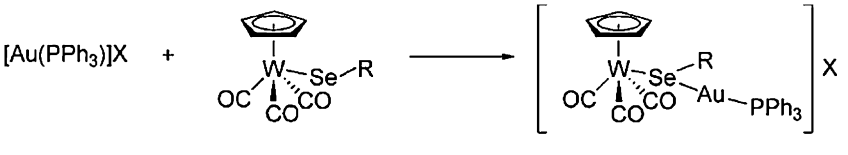
Scheme 13.



Scheme 14.

coordination sites is proposed. The alternative possibility, namely pentacoordinate gold(III), is rare in gold chemistry. The tetranuclear complex $[(\mu\text{-dppf})\{Au^{I}(\mu\text{-SePh})Au^{III}(C_6F_5)_3\}_2]$ contains two gold(I) and two gold(III) centres bridged *via* a phenylselenolato ligand. Its ^{19}F NMR spectrum displays the typical pattern for equivalent pentafluorophenyl groups and its crystal structure (Fig. 10) reveals gold(I)–gold(III) distances of *ca.* 3.6 Å, which suggests the presence of a weak aurophilic interaction [42].

The gold(III) unit is square planar; the gold atom being coplanar with one selenium and each of the three carbon atoms, as is the case in the dinuclear gold(III) complex $[\{Au(C_6F_5)_3\}_2\{\mu\text{-Fe}(\eta^5\text{-}C_5H_4SePh)_2\}]$ [39] described above. The Au(III)–C bond distances



X = SbF_6, ClO_4; R = CH_2Ph, CH_2SiMe_3

Scheme 15.

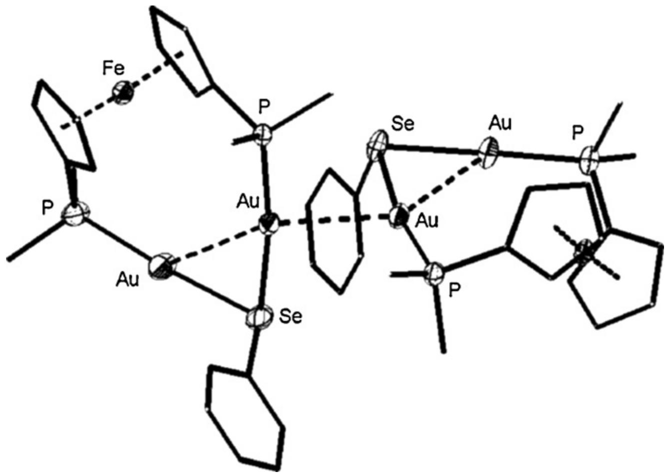


Fig. 9. Molecular structure of $[Au_2(\mu\text{-}SePh)(\mu\text{-}dppf)]_2$ adapted from [41]. Only the *ipso*-C atoms of the PPh_2 groups are shown. Hydrogen atoms as well as the OTf anion have been omitted for clarity.

cis to selenium [2.051(4) Å] are slightly longer than those *trans* to selenium [2.036(3) Å], probably due to the lower *trans* influence of the $PhSe^-$ ligand. However, the difference between the two is barely significant.

2.3. Alkylselenolato derivatives

Alkylselenolatogold derivatives are of both academic interest and are also used in photographic materials. There is a significant amount of patent literature detailing this application, however little (if any) preparative and characterisation details of the disclosed substances are available. In 1993, Eastman Kodak patented photographic material containing macrocyclic polyselenoether gold(I) compounds to improve the chemical sensitisation in silver halide photography [43]. A second patent, describing selenoethers bound to gold thiosulfonato complexes followed soon after [44]. The Fuji Film Company patented several cationic dinuclear gold benzylselenolato compounds of the type $[Au_2(\mu\text{-}SeCH_2R)(PPh_3)_2]^+$ [45]. Patents covering a whole class of mononuclear derivatives [Au(SeR)L] containing anionic selenolato ligands, as well as neutral selenoether derivatives were filed [45–51]. These substances serve as heat-developable materials in photography, exhibiting high sensitivity with a maximum density and little printout fogging after image formation [52]. In addition, incorporation of gold–selenium compounds into silver halide photographic materials was found to shorten the development process and improve image quality [48,49].

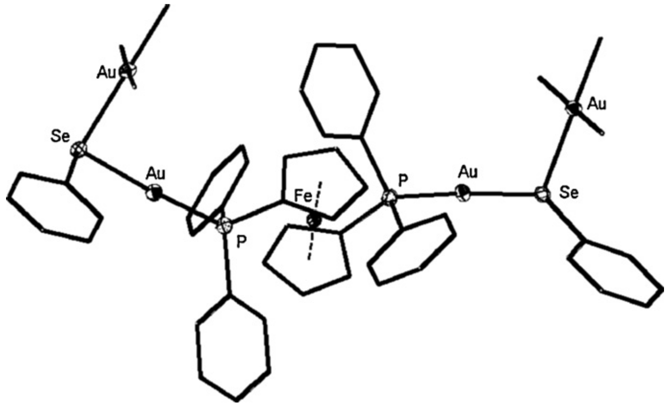


Fig. 10. Molecular structure of $[(\mu\text{-}dppf)\{Au^I(\mu\text{-}SePh)Au^{III}(C_6F_5)_3\}_2]$ adapted from [41]. Only the *ipso*-C atoms of the C_6F_5 groups are shown and hydrogen atoms have been omitted for clarity.

In 1994, the preparation and crystal structure of $[Au_2(\mu\text{-}SeCH_2Ph)(PPh_3)_2]SbF_6$ was reported [28]. The complex was obtained by the reaction of dibenzyldiselenide with $[AuCl(PPh_3)]$ in the presence of $[AgSbF_6]$. The crystal structure resembles that of the corresponding phenylselenolato complex shown in the previous section. Three years later, the same group published studies of cationic heteronuclear complexes with benzylselenolato or (trimethylsilyl)methylselenolato ligands which bridge a Ph_3PAu and a $CpW(CO)_3$ unit [53] (Scheme 15).

The heteronuclear complexes $[(\eta^5\text{-}Cp)(CO)_3W(\mu\text{-}SeR)Au(PPh_3)]X$ ($R = CH_2Ph$, CH_2SiMe_3; $X = SbF_6$, ClO_4) were prepared by addition of $[Au(PPh_3)]X$ to $[W(SeR)(CO)_3(\eta^5\text{-}Cp)]$ ($R = CH_2Ph$ or CH_2SiMe_3) as yellow air-stable crystals.

The ^{77}Se NMR spectra of the complexes reveal strong downfield shifts of the resonances (*ca.* 90 ppm for $R = CH_2Ph$, *ca.* 280 ppm for $R = CH_2SiMe_3$) when compared to the starting materials. The salt $[(\eta^5\text{-}Cp)(CO)_3W(\mu\text{-}SeCH_2SiMe_3)AuPPh_3]SbF_6$ was characterised by X-ray diffraction (Fig. 11). It crystallises with two independent cations and one molecule of dichloromethane in the unit cell. The selenium atom is trigonal pyramidally coordinated, the Au–Se bond lengths [2.4381(13) Å, 2.4415(13) Å] resemble those of other cationic selenolato gold complexes. No W–Au interaction is present since the W–Au distance of 3.86 Å is larger than the sum of the van der Waals radii. The Au–Se–W angle of *ca.* 97° is almost 20° larger than the Au–Se–Au angle in the benzylselenolato complex $[\{(Ph_3P)Au\}_2Se(CH_2Ph)]^+$ mentioned in the previous section. This is likely due to the aurophilic interactions, which force the gold centres into close proximity and thus reduce the Au–Se–Au angle.

Naumann et al. [54] synthesised the anionic trifluoromethylselenolato gold(I) complexes $[Q][Au(SeCF_3)_2]$ ($[Q]^+ = [NMe_4]^+$, $[Cs(15\text{-}Crown\text{-}5)_2]^+$, $[PPN]^+$) by ligand substitution of AuCl with two equivalents of $[Q][SeCF_3]$. The resulting complexes were characterised in solution by ^{19}F, ^{77}Se and ^{13}C NMR spectroscopy and, in the case of the PPN derivative, by X-ray diffraction (Fig. 12). In the solid-state this complex consists of the virtually linear [Au–Se–Au = 172.7(1)°] $[Au(SeCF_3)_2]^-$ anion and the PPN cation.

In solution the ^{19}F, ^{77}Se and ^{13}C NMR spectra give the same sets of signals for the anions, independent of the cation present.

Bonasia et al. [55] prepared the air- and moisture-stable colourless gold(I) chalcogenolates $[Au\{EC(SiMe_3)_3\}]$ (E = S, Se, Te) by

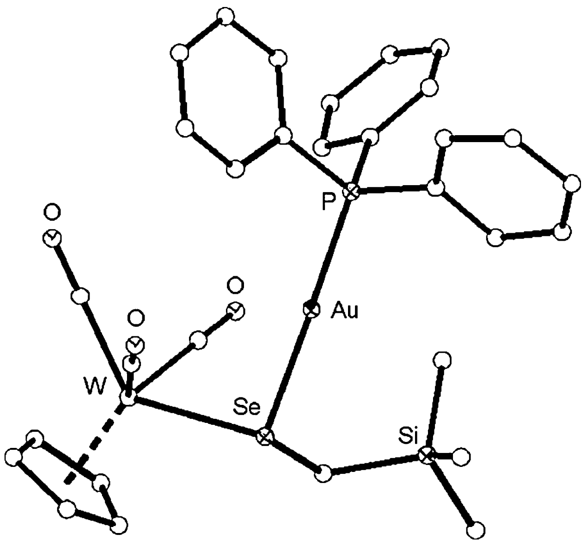
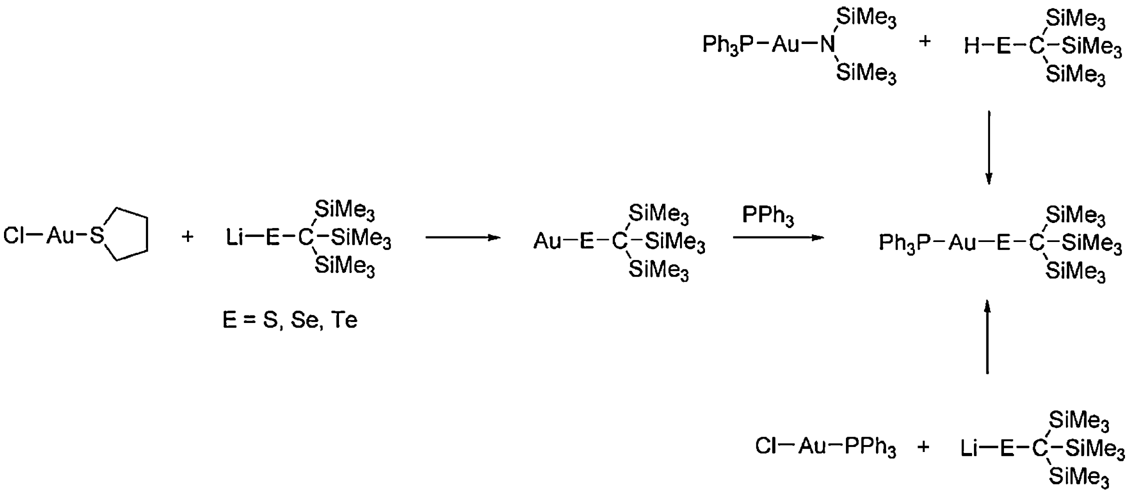
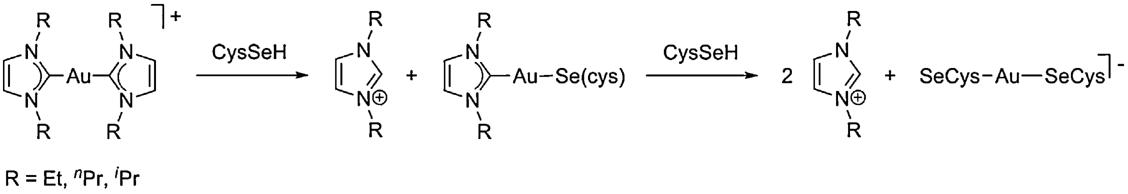


Fig. 11. Molecular structure of the cation $[(\eta^5\text{-}Cp)(CO)_3W(\mu\text{-}SeCH_2SiMe_3)AuPPh_3]^+$ adapted from [53]. Hydrogen atoms have been omitted for clarity.



Scheme 16.



Scheme 17.

a metathesis reaction of the lithium salt [Li{EC(SiMe$_3$)$_3$}] and [AuCl(tht)]. The sulfur and tellurium derivatives were found to exist in the solid-state as tetramers [Au$_4${EC(SiMe$_3$)$_3$}$_4$] (see Section 3 for a detailed discussion of the Te derivative), it was therefore assumed that this also the case for the selenium analogue. The triphenylphosphine adduct [Au{SeC(SiMe$_3$)$_3$}(PPh$_3$)] is formed either by a metathesis reaction between [Li{SeC(SiMe$_3$)$_3$}] and [AuCl(PPh$_3$)] or by substitution of [Au{N(SiMe$_3$)$_2$}(PPh$_3$)] with HSeC(SiMe$_3$)$_3$ or by ring opening of [Au$_4${SeC(SiMe$_3$)$_3$}$_4$] with triphenylphosphine in about 70% yield (Scheme 16).

Investigations involving cationic bis(*N*-heterocyclic carbene) gold(I) complexes and their reactions with selenocysteine were reported by the group of Berners-Price and coworkers [56]. Addition of these complexes to selenocysteine in a buffered solution resulted in successive substitution of the carbene ligands giving the [Au(SeCys)$_2$]$^-$ anion as final product (Scheme 17).

As in the case of the phosphine complexes, the selenium ligands can easily replace both carbene ligands. The bulkier the substituent on the carbene ligand, the better is the steric shielding of the gold atom and the slower the substitution reaction.

The reaction rates of acetonitrile gold(I) halo complexes [AuX(MeCN)] (X = Br, Cl) with dimethylselenide were studied by potentiometric titration at −20 °C [57]. Substitution of coordinated acetonitrile was observed accompanied by formation of neutral chlorodimethylselenide gold(I) [AuCl(SeMe$_2$)] and bromodimethylselenide [AuBr(SeMe$_2$)] complexes, respectively. According to this study the stability constants of the [AuX(L)] (L = SMe$_2$, SeMe$_2$, TeMe$_2$) compounds increase in the order S < Se < Te, in agreement with other studies.

In 1972, Schmidbaur and Dash obtained the chloro(dimethyl)(dimethylselenide)gold(III) complex [AuClMe$_2$(SeMe$_2$)], a colourless liquid, by reaction of the dinuclear gold(III) complex [AuCl(Me)$_2$]$_2$ with two equivalents of SeMe$_2$ (Scheme 18) [58]. The analogous bridge cleavage reaction with the iodo derivative [AuI(Me)$_2$]$_2$ was unsuccessful. By ^{1}H NMR spectroscopy the *cis*-geometry of the complex was confirmed due to the presence of ^{77}Se satellites on the signal corresponding to the methyl group *trans* to the selenoether. Variable temperature NMR studies also showed that in these complexes the dimethylselenide is bound stronger to gold than Me$_2$S.

The trinuclear gold(I) complex [Au$_3$Cl$_3${μ^3-(MeSeCH$_2$)$_3$CMe}] was synthesised in 1996 [59] by reacting the tripodal selenoether MeC(CH$_2$SeMe)$_3$ with three equivalents of [AuCl(tht)] in dichloromethane (Scheme 19). The colourless solid (85% yield) was characterised by ^{1}H NMR and IR spectroscopy; ^{77}Se NMR spectra could not be recorded because of poor solubility.

The tetrahydroselenophenegold(I) iodide complex [AuI(SeC$_4$H$_8$)] was obtained from a mixture of tetrahydroselenophene, iodine and elemental gold after a period of 3 weeks at room temperature [60]. In this redox reaction gold is slowly oxidised by the iodine and dissolved. Light yellow crystals were obtained which darken

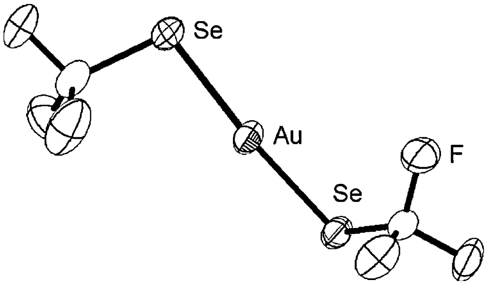
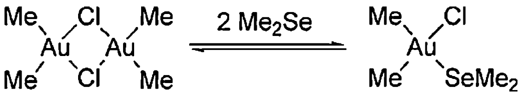
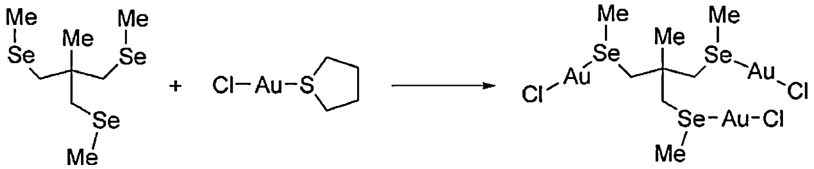


Fig. 12. Molecular structure of the [Au(SeCF$_3$)$_2$]$^-$ anion adapted from [54].



Scheme 18.



Scheme 19.

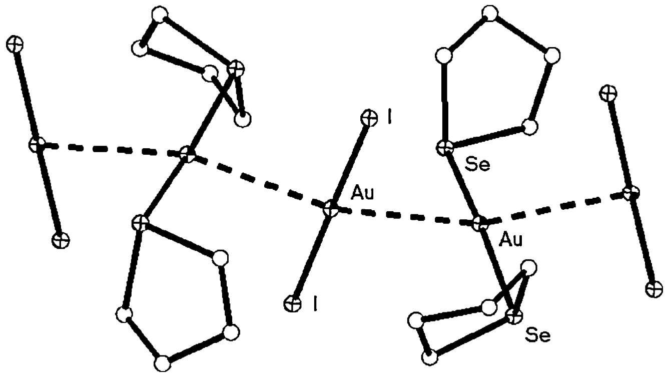


Fig. 13. Molecular structure of $[Au(C_4H_8Se)_2]^+[AuI_2]^-$ adapted from [60]. Hydrogen atoms have been omitted for clarity.

after 1 h, but are still more stable than their thio-analogues. X-ray diffraction studies showed its structure to be isostructural to bis(tetrahydrothiophene) gold(I) diiodoaurate. Both are composed of infinite zigzag chains consisting of $[Au(C_4H_8Se)_2]^+$ and $[AuI_2]^-$ units joined by relatively short intermolecular gold–gold distances [2.987(2) Å, 3.001(2) Å] (Fig. 13). The two components of the polymer chain are rotated by 90° with respect to each other.

The reaction of tetrahydrothiophene gold(I) chloride with the diselenoethers 1,5-diselenacyclooctane and 3*H*-1,4,5,7-tetrahydro-2,6-benzodiselenonine gave colourless solids in low yields (about 30%) which were formulated as $[Au_2Cl_2(\mu\text{-}L)]$ (L = selenoether) based on NMR spectroscopy and microanalysis [61]. It is presumed that in these compounds each AuCl fragment is bound linearly to the selenium atoms of the heterocycle (Scheme 20).

2.4. Selenourea derivatives

Curiously, although selenourea derivatives of silver have been known for more than a hundred years, gold selenourea derivatives have only been studied in the past decades. In 1958, a Russian analytical group studied the behaviour of heavy metal salts with selenourea [62] and observed that selenourea added to aqueous gold(III) solutions gives a yellow coloured compound, which was not characterised at all. The ambidentate selenourea $Se{=}C(NH_2)_2$ is highly nucleophilic since the amino groups have a strong electron-donating effect; its nucleophilicity is comparable to that of the phenylselenide ion. In gold complexes selenourea binds exclusively to gold *via* selenium in contrast to urea and thiourea, which may also bind to gold *via* the nitrogen [63].

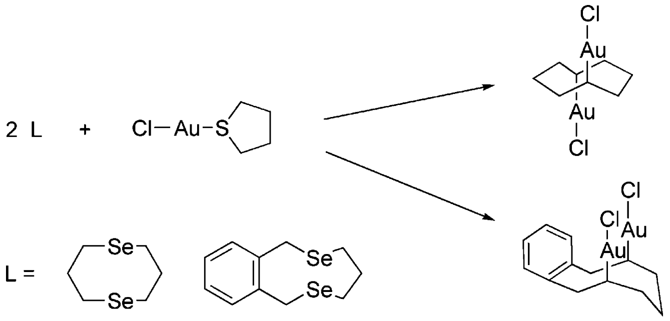
Cationic selenourea(phosphine)gold(I) complexes of the type $[Au(P)\{SeC(NH_2)_2\}]Cl$ (P = phosphine) are generally prepared by reaction of the phosphine gold(I) chloride with selenourea (Scheme 21). The compounds are colourless air-stable solids, which are sensitive to moisture. In the following section a detailed discussion of their chemistry and structures will be presented.

In 1991, Jones and Thöne [63] published the structure of the chloride salt of the triphenylphosphine(selenourea)gold(I) cation $[Au\{SeC(NH_2)_2\}(PPh_3)]^+$ as well as the corresponding dppm complex $[Au_2\{SeC(NH_2)_2\}_2(\mu\text{-dppm})]Cl_2$. Characterisation included ^1H, ^{31}P and ^{77}Se NMR spectroscopy as well as X-ray diffraction (see below). $[Au\{SeC(NH_2)_2\}(PPh_3)]Cl$ is converted into the neutral selenido-bridged complex $[\{(Ph_3P)Au\}_2Se]$ in an aqueous sodium carbonate solution. The mechanism of this transformation is unclear; formation of free selenourea and elemental red selenium are observed as byproducts.

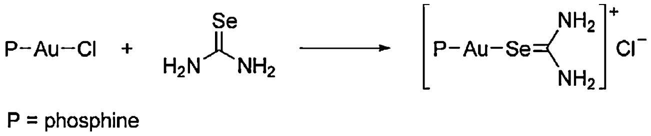
The methyldiphenylphosphine and dimethylphenylphosphine derivatives $[Au\{SeC(NH_2)_2\}(PPh_2Me)]Cl$ and $[Au\{SeC(NH_2)_2\}(PPhMe_2)]Cl$, respectively, have also been reported [64]. In 2003, a whole series of selenoureagold(I) salts of the type $[Au\{Se(NH_2)_2\}(P)]Cl$ containing a variety of different phosphines including trimethyl, triethyl, tricyclohexyl, cylohexyldiphenyl, tri(*p*-tolyl), and tri(*o*-tolyl) was published [65]. The trimethylphosphine derivative has been studied in great detail, including X-ray diffraction (see below), ^{77}Se, ^{31}P, and ^{13}C solid-state NMR spectroscopy [66] and solution NMR spectroscopy [65,67].

Within this series some general trends were found which apply to all selenourea gold compounds. Compared to free selenourea, the C═Se stretch is shifted to lower wave numbers upon coordination to gold, in addition strong absorptions are found for the CN bonds [ν(C–N) = *ca.* 1500 cm^{-1}] and the amine bonds [ν(N–H) = *ca.* 3200 cm^{-1}] in the IR spectra.

The ^{31}P NMR spectra showed a downfield shift for the singlet resonance of the bound phosphine in comparison to that of the free ligands. This is caused by the deshielding effect generated from the higher electron density at the phosphorus atom due to a strengthened π-bonding character towards gold. In turn, this effect weakens the selenium–gold(I) bond which is visible in the upfield shift of the selenourea–carbon resonances in the ^{13}C NMR spectra. In this series of compounds, the strongest Au–Se bond (and weakest Au–P bond) is found in the PPh_3 derivative, the weakest Au–Se bond (and strongest Au–P bond) in the PCy_3 complex. In the ^{77}Se NMR spectra signals from free selenourea are also downfield shifted compared to those of the bound selenourea in $[Au\{SeC(NH_2)_2\}(PMe_3)]_2Cl_2$ (200.50 ppm) [67] or $[Au\{SeC(NH_2)_2\}(PPh_3)]Cl$ (206.31 ppm) [67].



Scheme 20.



Scheme 21.

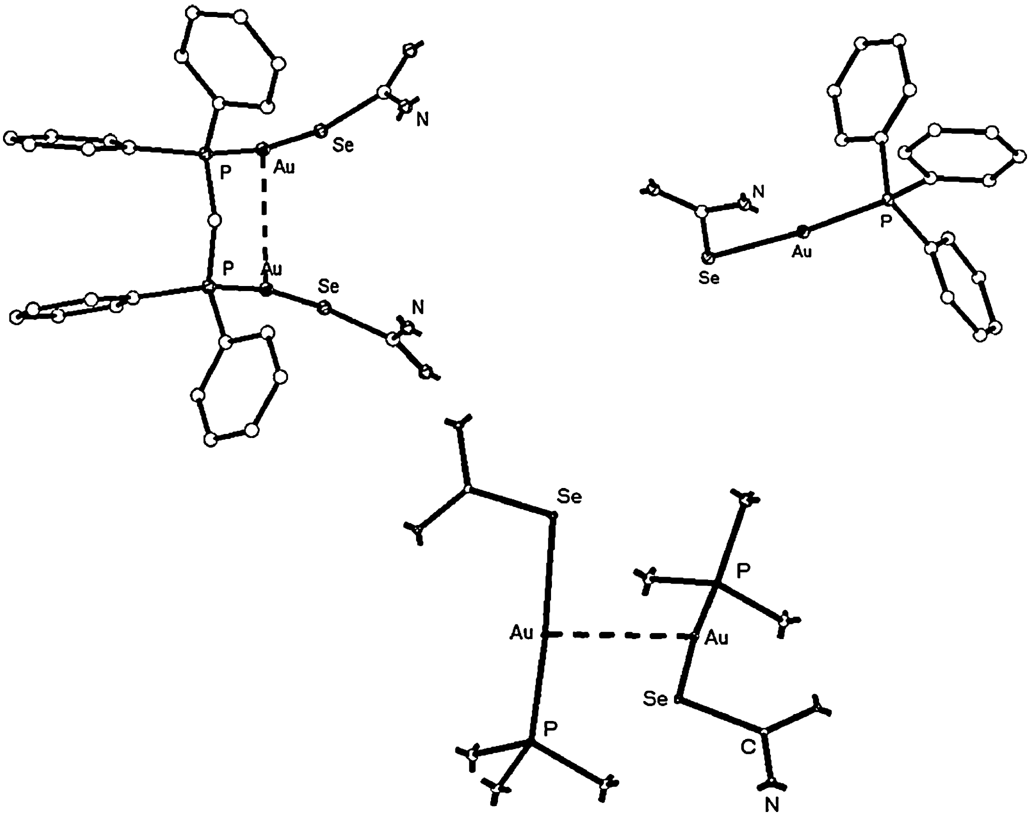
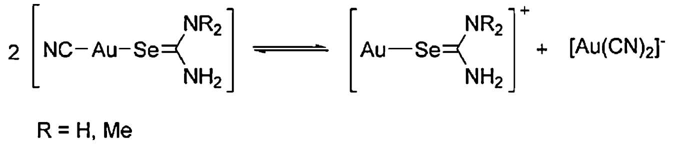


Fig. 14. Molecular structures of the cations $[Au_2\{SeC(NH_2)_2\}_2(\mu\text{-dppm})]^{2+}$ (top left) adapted from [63], $[Au(Ph_3P)\{SeC(NH_2)_2\}]^+$ (top right) adapted from [63] and $[Au\{SeC(NH_2)_2\}(PMe_3)]^+$ (bottom) adapted from [66]. Hydrogen atoms have been omitted for clarity.

An X-ray diffraction study of $[Au\{SeC(NH_2)_2\}(PMe_3)]Cl$ (Fig. 14 right) revealed that the compound consists of a dimeric unit of $[Au(Me_3P)\{SeC(NH_2)_2\}]^+$ cations which are connected by weak gold(I)–gold(I) interactions of 3.0386(5) Å [66]. In contrast, the triphenylphosphine analogue $[Au(Ph_3P)\{SeC(NH_2)_2\}]Cl$ is monomeric in the solid-state (Fig. 14 centre) [63]. Each cation features a nearly linearly coordinated gold centre [P–Au–Se angle, *ca.* 175°] with Au–Se distances [Au–Se, *ca.* 2.4 Å] in the expected range [63]. The dinuclear bis(diphenylphosphinomethane) cation $[Au_2\{SeC(NH_2)_2\}_2(\mu\text{-dppm})]^{2+}$ [63] crystallises in *cis*-orientation (Fig. 14 left) due to intramolecular gold(I)-gold(I) interactions of 3.236(1) Å. In this complex, coordination about gold deviates significantly from its linearity with a P–Au–Se angle of 171°.

N,*N*-Dimethylselenourea and selenourea react with AuCN giving the cyano(selenourea)gold(I) complexes $[Au\{SeC(NH_2)_2\}(CN)]$ and $[Au\{SeC(NH_2)(NMe_2)\}(CN)]$, respectively, which were characterised by ^1H, ^{13}C, and ^{15}N NMR spectroscopy [68]. These complexes undergo a scrambling reaction in solution where an equilibrium mixture of $[Au\{SeC(NH_2)(NR_2)\}(CN)]$ and $[Au\{SeC(NH_2)(NR_2)\}_2]^+$ (R = H, Me) and $[Au(CN)_2]^-$ is observed (Scheme 22). The equilibrium constant of this scrambling reaction was measured using ^{13}C NMR spectroscopy.

The reaction of *N*,*N*-dimethyl selenourea with $[AuCl(PPh_3)]$ gives the corresponding triphenylphosphine salt $[Au\{SeC(NH_2)(NMe_2)\}(PPh_3)]Cl$ [69]. Similarly, the trimethylphosphine and triethylphosphine derivatives were also synthesised. Their spectral behaviour mimics that of the selenourea derivatives described above.



Scheme 22.

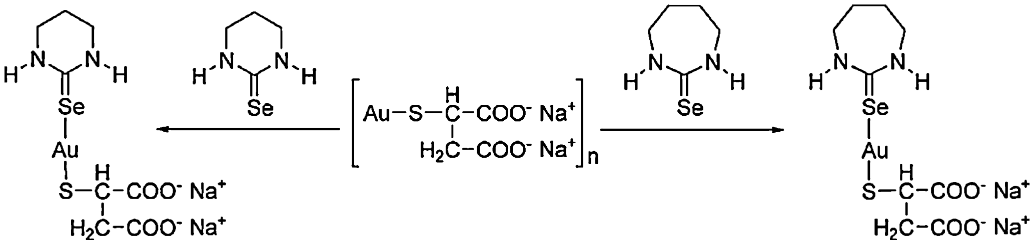
In recent years, the application of various selenourea gold(I) derivatives in photography has been patented by the Fuji Film Company [46,48,49,70].

2.5. Gold selenium complexes in biological systems

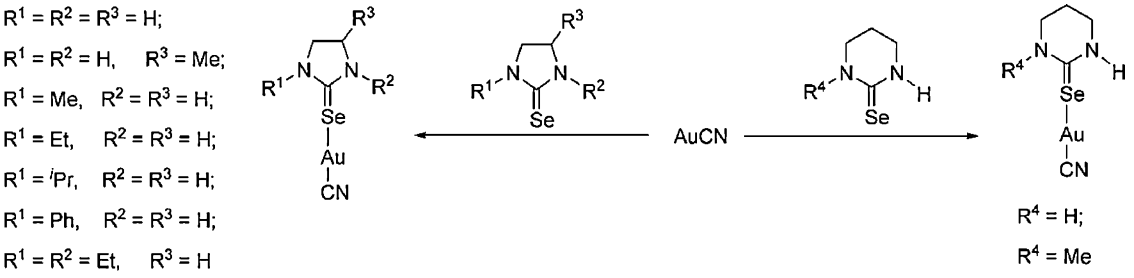
Thioredoxin reductases (TRR) are a class of enzymes responsible for catalytic reduction of thioredoxins. The molecular structure of human TRR shows the presence of a selenocystein containing fragment, which is essential for the catalytic activity. Binding of Au(I) to this active site promotes cell death because accumulated peroxide can no longer be reduced. To gain some further understanding of how gold(I) complexes interact with this enzyme, DFT calculations using some model compounds were carried out [71]. It was shown that binding of gold at the selenium active site model was stronger than that at the sulfur site.

Glutathione peroxidase (GPx) is one of the most intensively studied mammalian selenoproteins involved in the catalysis of biological redox reactions. It is a member of the selenoprotein class possessing in its active site selenocysteine located in the N-terminal part of the enzyme. GPx plays a major role in human antioxidant defense by reducing hydrogen peroxide to water or organic hydroperoxides to alcohols; one GPx is specific for the direct reduction of phospholipids and cholesterol hydroperoxides [72].

Gold drugs which enter a cell bind competitively to the active site of GPx, thus inhibiting its catalytic function. In consequence, there is an imbalance of the cellular redox system because of accumulation of peroxides, leading to oxidative damage of the cell [73,74]. The catalytic cycle of GPx involves oxidation by a peroxide forming a selenenic acid derivative GPx-OH, the OH moiety of



Scheme 23.



Scheme 24.

which is subsequently substituted by glutathione, forming a mixed selenium–sulfur intermediate. This compound is reduced by a further molecule of glutathione, thus regenerating the active site. The oxidised glutathione is recovered by the reducing agent NADPH (nicotinamide adenine dinucleotide phosphate) and glutathione reductase (GR) (Fig. 15). Therefore, studies of interactions of GPx with gold derivatives should help to understand the mechanism of action of gold drugs.

Recently, Bhabak and Mugesh reported the design of a synthetic model for the inhibition of the GPx system by various gold compounds [75]. Their system is based on the organoselenium species $[SeC_6H_4(2\text{-}CH_2NMe_2)]_2$ and $Se\{C_6H_4(2\text{-}CH_2NMe_2)\}$ as active site models. The reduction of peroxides by these compounds in the presence of several gold compounds $[AuCl(PR_3)]$ (R = Me, Et, Ph) and PhSH (as thiol cofactor) was examined by various spectroscopic methods including ^{77}Se NMR spectroscopy. During the reaction the formation of selenolato gold compounds of the type $[Au\{SeC_6H_4(2\text{-}CH_2NMe_2)\}(PR_3)]$ (R = Me, Et, Ph) was detected. Furthermore, it was observed, that inhibition was competitive with respect to peroxide, suggesting that also in the biological system gold compounds inhibit GPx by forming a gold selenolato complex at the active site.

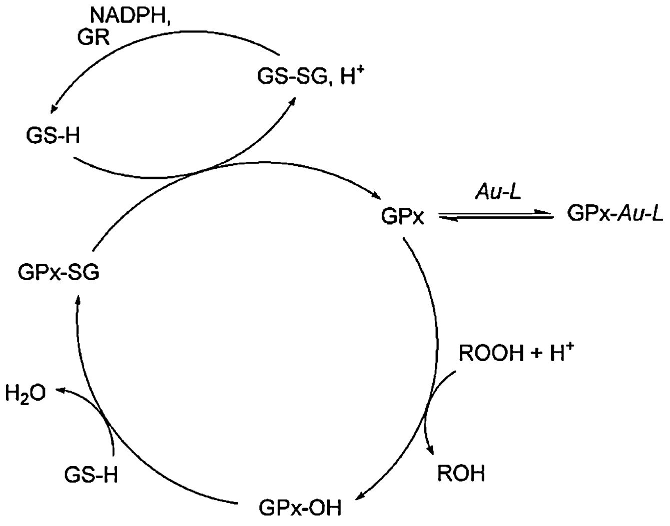


Fig. 15. Redox cycle of the catalytic reduction of a peroxide by GPx (GPx-OH = selenenic acid, GS-H = glutathione, GR = glutathione reductase) adapted from [72,73].

Selenones bound to gold(I) were extensively studied by Isab and coworkers to learn more about their formation, reaction and possible metabolism in organisms. To investigate the competitive binding between a gold drug and the selenocysteine active site of GPx, the model reaction between selenones and gold thiolate drugs was studied in aqueous solution [74].

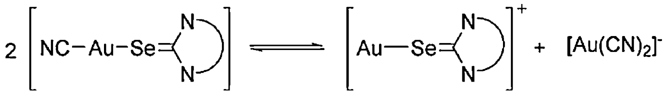
The interaction between 1,3-diazipinane-2-selenone (DiazSe) or 1,3-diazipine-2-selenone (DiapSe) with Myochrisin was monitored by NMR spectroscopy in D_2O. It was found that the selenone(thiomalate)gold(I) complexes [Au(tm)DiazSe] and [Au(tm)DiapSe] are formed (Scheme 23) and, in addition, some thiomalate was released and oxidised to thiomalic disulfide [74].

Cyano selenone gold(I) complexes of the type [Au(CN)(selenone)] were synthesised by reaction of the appropriate selenone and gold(I) cyanide (Scheme 24) [68,76].

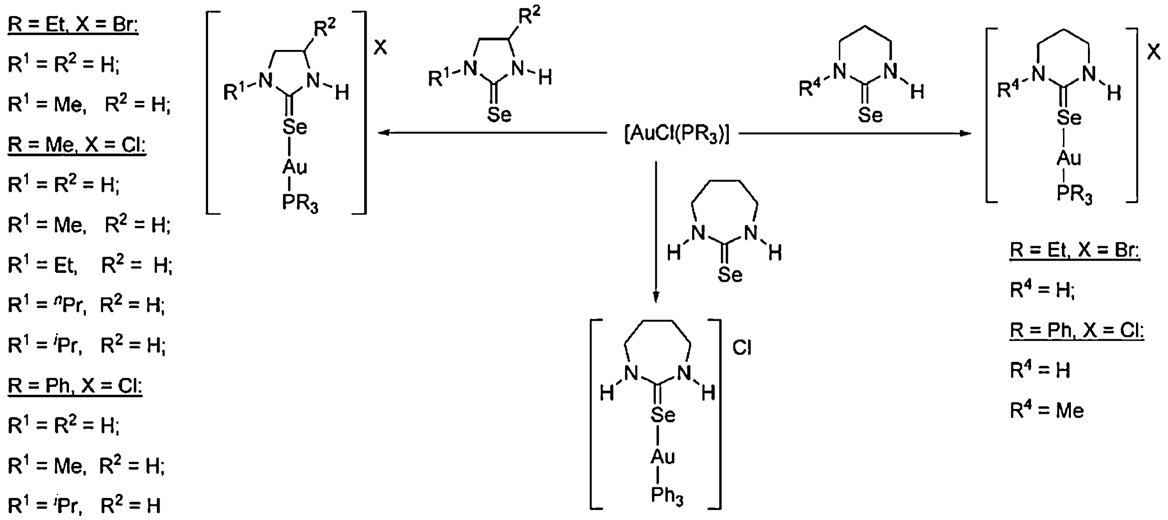
These cyano selenium compounds undergo ligand scrambling reactions like their sulfur counterparts, which were observed by ^{13}C and ^{15}N NMR spectroscopy (Scheme 25) [68,76].

Such ligand scrambling reactions are important because cyanides react with gold drugs in the body. The resulting $[Au(CN)_2]^-$ anion migrates into the erythrocytes, a location of glutathione peroxidase, and influences the metabolism of the gold drug [76]. Compared to analogous sulfur species, the equilibrium constants for the scrambling reactions of the cyano(selenone)gold(I) complexes are higher, consistent with the increased basicity of selenones.

The ^1H NMR spectra of the complexes illustrated in Schemes 23 and 24 show that complexation induces a downfield shift of all resonances as well as broadening of the N–H signals [76]. IR spectroscopy illustrates that complexation of the free selenones leads to lower frequencies of the C=Se vibrational bands [76]. The NH vibration can be seen at *ca.* 3200 cm^{-1} in both



Scheme 25.



Scheme 26.

free selenones and the complexes, indicating that the selenone form is conserved in the solid-state.

Further investigations focused on the phosphine(selenone) gold(I) cations $[Au(P)(selenone)]^+$ (P = PMe_3, PEt_3, PPh_3) (Scheme 26) [67,69,77]. These compounds were prepared from the reaction between the phosphine gold(I) halides and the selenones.

Some general trends for this class of compounds can be observed: in the IR spectra, the C=Se and C–N stretching frequencies of the coordinated selenones shift to lower and higher wavenumbers, respectively, compared to those of the free selenones [69]. In the ^1H NMR spectra, the NH signals broaden and shift downfield because of the deshielding effect induced by an increase in π-electron density in the C–N bond upon coordination to the gold atom [77]. At the same time, the C=Se double bond character is weakened whilst that of the C–N single bond increases. These factors cause an upfield shift of the C=Se carbon signals in the ^{13}C NMR spectra [69,77]. Compared to the phosphine gold halide starting materials, the ^{31}P NMR spectra of the selenone complexes show downfield shifted singlet resonances due to the π-accepting ability of the phosphines with the deshielding effect at the phosphorus atoms [69,77]. The smallest shift differences between selenone complex and precursor are observed for weakly basic selenones [77]. Both the cone angle and the basicity of the phosphine influence the ^{31}P NMR chemical shift differences, illustrated by the fact that the trimethylphosphine gold(I) complexes exhibit greater shift differences than the analogous triethylphosphine or triphenylphosphine complexes [67].

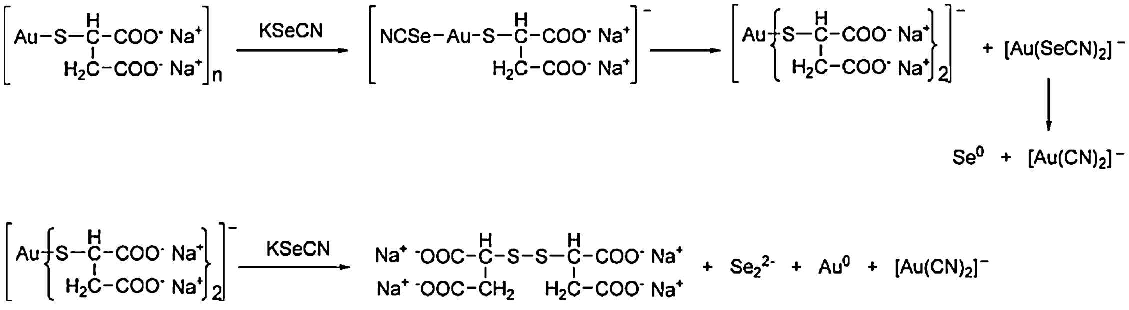
Given the fact that tobacco smoking patients, which are administered gold drugs, accumulate gold in their red blood cells, requires knowledge of the fate of gold drugs in the presence of pseudohalogens [7]. Therefore, Isab and coworkers studied the behaviour of gold selenocyanates in an aqueous medium to rudimentarily mimic the interaction of seleno-compounds with gold drugs in a biological system [7,78].

Addition of selenocyanate to Myochrysine, polymeric aurothiomalate $[Au\{SCH(CO_2Na)CH_2CO_2Na\}]_n$, leads to the monomeric complex $[Au(SeCN)\{SCH(CO_2Na)CH_2CO_2Na\}]^-$ which rearranges to $[Au\{SCH(CO_2Na)CH_2CO_2Na\}_2]^-$ and $[Au(SeCN)_2]^-$. The latter is unstable and readily decomposes to elemental selenium and $[Au(CN)_2]^-$ (Scheme 27) [7].

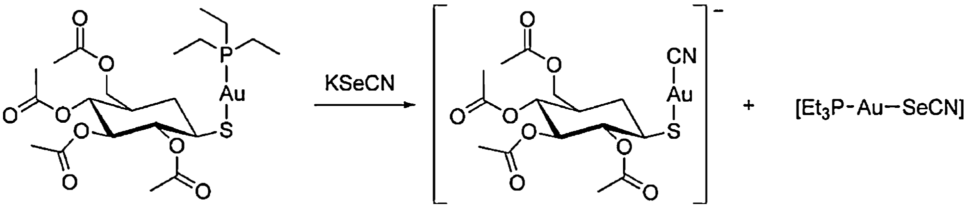
In contrast, addition of selenocyanate to $[Au\{SCH(CO_2Na)CH_2CO_2Na\}_2]^-$ induces its decomposition to Se_2^{2-}, thiomalic disulfide (by oxidation of liberated thiomalic acid) and $[Au(CN)_2]^-$ accompanied by deposition of gold metal (Scheme 27).

Later, these studies were extended to Auranofin [78]. Its reaction with potassium selenocyanate was monitored by ^{31}P and ^{13}C NMR spectroscopy. The sugar moiety is substituted in a methanol/water (20:1) solution by selenocyanate giving the triethylphosphine(selenocyanato)gold(I) complex $[Au(SeCN)(Et_3P)]$ and the tetra-2,3,4,6-O-acetyl-thio-β-D-glucopyranosato cyanoaurate anion $[(C_{14}H_2O_9S)AuCN]^-$ (Scheme 28). These products undergo further decomposition reactions finally yielding $[(Et_3P)_2Au]^+$, $Et_3P{=}O$, $[Au(CN)_2]^-$, and elemental selenium. This study shows that both gold–sulfur and gold–phosphorus bonds can be cleaved by selenocyanate. A labelling experiment using $Se^{13}CN^-$ and $[Au(CN)_2]^-$ proved that the cyanide was exchanged without any formation of elemental selenium [79].

The same group examined reactions of triethylphosphine and trimethylphosphine gold(I) cations with selenocystamine and selenocystine in D_2O using ^{31}P NMR spectroscopy [80]. The results show that a complex sequence of reactions occurs, which ultimately leads to the observation of signals due to the phosphine



Scheme 27.



Scheme 28.

oxide and precipitation of a solid material. During the reaction, signals corresponding to the gold cations $[Au(Et_3P)_2]^+$ as well as $[Au(SeR)(Et_3P)_2]^+$ can be seen. The rate of cleavage of the diselenide selenocystamine was observed to slow down when triethylphosphine was used instead of trimethylphosphine. Using selenocystamine instead of selenocystine also decelerates the reaction rate.

Addition of selenocysteamine, selenocystine as well as selenoacetic acid to gold(I) thiomalate gave $[Au(SeR)_2]^-$ complexes (Scheme 29) as was shown by NMR spectroscopy [79].

2.6. Selenosugars

Inspired by the efficiency of Auranofin and Myochrisin as anti-arthritis drugs, several selenium derivatives were prepared and patented with the aim to reduce side-effects and increase efficiency [81].

Pill et al. [82] published the preparation and characterisation of some gold phosphine complexes including the selenium analogue of Auranofin (2,3,4,6-tetra-O-acetyl-1-seleno-β-D-glucopyranosato-Se)(trimethylphosphine)gold(I) (Scheme 30).

The synthesis was carried out by addition of a methanol solution of the selenouronium bromide derivative of the acetyl-protected selenoglucose to a suspension of the phosphine gold(I) chloride at 0 °C in the presence of sodium methoxide. The products were characterised by IR, ^1H, ^{31}P, and ^{13}C NMR spectroscopy and elemental analysis. The anti-inflammatory effect of the triphenylphosphine complex was tested but showed only minor toxicity. Mirabelli et al. reported the dinuclear dppe gold(I) derivatives of acetyl-protected selenoglucose and selenoglucose itself [83]. The former was prepared by K_2CO_3 promoted hydrolysis of the selenouronium hydrobromide derivative of tetraacetylglucose and subsequent reaction with $[Au_2Cl_2(\mu\text{-dppe})]$. The glucopyranose derivative was obtained in low yield from hydrolysis of the tetraacetate with NaOMe in methanol. Characterisation was limited to melting point measurements, optical rotation as well as NMR and IR spectroscopy. The *in vivo* anti-tumor activity against P388 leukemia cells was examined, however, these selenium derivatives showed negligible activity. Although this study demonstrated the inactivity of these species, a patent with selenosugargold(I) derivatives as anti-tumor drugs has been filed [84]. The Fuji Film Company patented these types of compounds as intermediates for drugs, pharmaceuticals, agricultural chemistry and photographic materials [45–47,49–51,85].

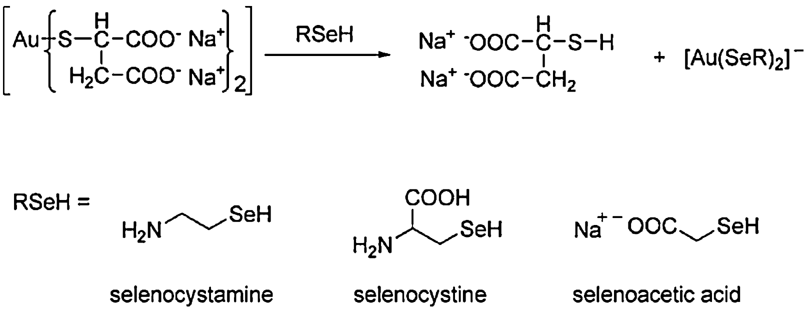
2.7. Selenocarbamate and maleonitrile selenolate derivatives

Monoselenocarbamato gold(I) complexes were first prepared over 30 years ago *via* the reaction of (triphenylphosphine) gold(I) chloride with the ammonium salts of the *N*,*N*-dimethyl derivative $[NH_4][SeC(O)NMe_2]$ or the piperidine derivative $[NH_4][SeC(O)NC_5H_{10}]$ giving the triphenylphosphine(selenocarbamato) gold(I) complexes $[Au\{SeC(O)NMe_2\}(Ph_3P)]$ and $[Au\{SeC(O)NC_5H_{10}\}(Ph_3P)]$, respectively (Scheme 31) [86].

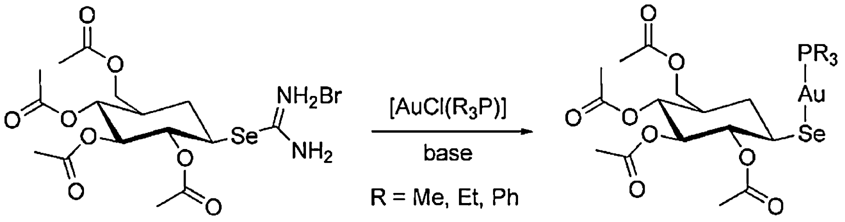
Both products are unstable towards oxygen and decompose easily both in the solid-state and in solution. Characterisation was limited to IR and ^1H NMR spectroscopy as well as elemental analysis. From the IR spectra it was deduced that the carbamato ligands bind to gold solely *via* selenium. ^1H NMR spectra measured at different temperatures showed the splitting and broadening of the NCH_x peaks into two signals at lower temperatures, explained by different ^1H–^{77}Se coupling between the protons *trans* and *cis* to selenium relative to the CN bond in the planar monoselenocarbamate. The more upfield shifted peak is broader but less intense, as it shows stronger coupling with the ^{77}Se isotope. Data derived from simulated ^1H NMR spectra gave the thermodynamic constants for the hindered rotation around the CN bond with partial double bond character.

Recently, the proton of the selenocarbamate ester PhN(H)C(Se)OMe was abstracted with a base and subsequently, this deprotonated intermediate was reacted with a series of phosphine gold(I) chloride complexes to give mono- and dinuclear phosphine gold(I) complexes of the type $[Au\{SeC(OMe)NPh\}P]$ [P = PTA, PPh_3, $P(o\text{-tolyl})_3$, $P(p\text{-MeOC}_6H_4)_3$] and $[Au_2\{SeC(OMe)NPh\}_2(\mu\text{-P-P})]$ (P-P = dppm, dppe, *trans*-dppee, dppp, dppf) (Scheme 32) [87,88]. The products were obtained in moderate to good yields as colourless or pale-yellow air-stable solids. Characterisation included ^1H and ^{31}P NMR spectroscopy showing shifts in the typical ranges of phosphine gold(I) complexes, ^{77}Se NMR spectra could not be measured because of their poor solubility and stability in solution and the low sensitivity of the ^{77}Se nucleus.

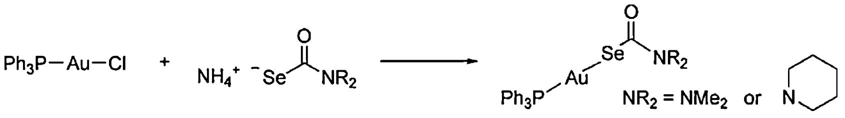
Molecular structures of the dppp and dppf derivatives were obtained (Fig. 16), which allowed some comparisons between the free and the deprotonated selenocarbamate to be made. The C–Se



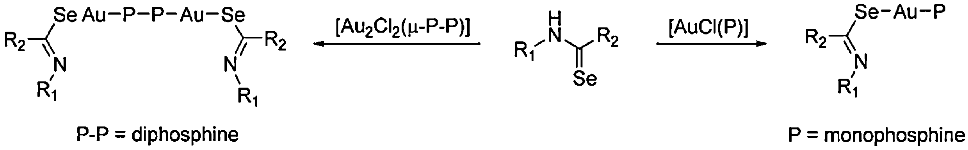
Scheme 29.



Scheme 30.



Scheme 31.



Scheme 32.

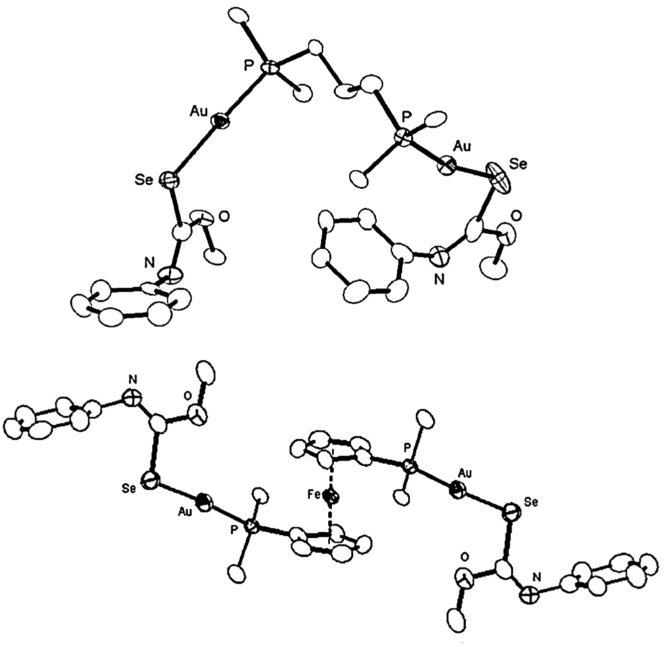


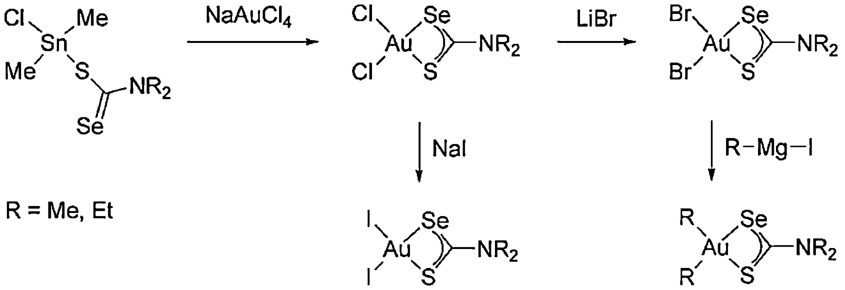
Fig. 16. Molecular structures of [$Au_2\{SeC(OMe)NPh\}_2(\mu$-dppp)] (top) and [$Au_2\{SeC(OMe)NPh\}_2(\mu$-dppf)] (bottom) adapted from [88]. Hydrogen atoms have been omitted for clarity and only the *ipso*-C atoms of the Ph_2P groups are shown.

bond distances increase upon coordination to gold, whilst the C–N bonds shorten due to the formation of a partial double bond. The Se–C–N angles open up by more than 10°, forcing the other angles around this C atom to contract by about 5°.

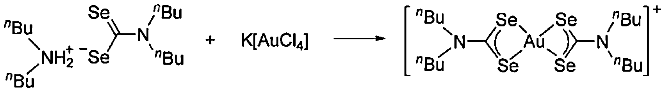
Similar gold(I) complexes containing other selenoamide derivatives such as PyC(Me)NN(H)C(Se)NR and $ArC(O)NHC(Se)NR_2$ have also been prepared and structurally characterised including ^{77}Se NMR spectroscopy [89].

Sonoda and Tanaka synthesised the (selenothiocarbamato)gold(III) complexes [$AuL_2(SSeCNR_2)$] (L = Cl, Br, I, Me, or Et; R = Me, Et) (Scheme 33) [90]. The red dichlorogold(III) complexes [$AuCl_2(SSeCNR_2)$] (R = Me, Et) were prepared by addition of a solution of Na[$AuCl_4$] to a solution of the organotin(IV) compounds [$SnClMe_2(SSeCNR_2)$] (R = Me, Et). The red bromo and the violet iodo derivatives were obtained by halide metathesis using LiBr and NaI, respectively. The chloro-*N*,*N*-dimethyl complex proved to be a mixture of [$AuCl_2(SSeCNMe_2)$] and [$AuCl_4$][$Au(SSeCNMe_2)_2$] as was shown by IR spectroscopy.

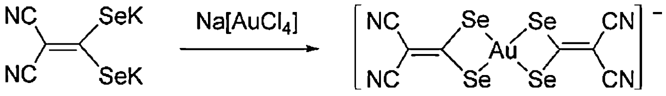
The far-IR spectrum of the [$AuCl_4$]$^-$ anion shows a characteristic Au–Cl band at 355 cm^{-1} which was observed in the mixture, the other two bands at 331 and 318 cm^{-1} were assigned to the Au–Cl vibration of [$AuCl_2(SSeCNMe_2)$], consistent with data of the *N*,*N*-diethylselenothiocarbamato derivative [$AuCl_2(SSeCNEt_2)$]. Heating induced the rearrangement of the ionic complex [$AuCl_4$][$Au(SSeCNMe_2)_2$] to the neutral, mononuclear complex [$AuCl_2(SSeCNEt_2)$], evidenced by the disappearance of the [$AuCl_4$]$^-$ signal in the IR spectrum.



Scheme 33.



Scheme 34.



Scheme 37.

The dialkyl *N*,*N*-dialkylselenothiocarbamato gold(III) complexes $[AuMe_2(SSeCNMe_2)]$, $[AuMe_2(SSeCNEt_2)]$, and $[AuEt_2(SSeCNMe_2)]$ were obtained by reaction of the corresponding dibromo gold(III) complexes $[AuBr_2(SSeCNR_2)]$ (R = Me, Et) with methyl or ethyl magnesium iodide in Et_2O at −70 °C. All these compounds are light-sensitive but stable towards air and moisture. A marked double bond character was suggested for the central C–N bond in the bidentate, chelating selenothiocarbamato ligands coordinated to gold(III), based on IR spectroscopy. The ^1H NMR spectra of the *N*,*N*-dialkylselenothiocarbamato derivatives exhibit doubling of the expected proton signals because these groups are located in different environments. An unambiguous assignment of these alkyl proton signals was not possible. In conclusion, the spectroscopic data was consistent with the presence of a square planar coordinated gold(III) centre and a planar selenothiocarbamato unit.

The *N*,*N*-di(*n*-butyl)diselenocarbamate salt $[(^nBu)_2H_2N][Se_2CN(^nBu)_2]$ was reacted with $K[AuCl_4]$ in methanol to give yellow, diamagnetic prisms of the gold(III) tris-chelate complex $[Au\{Se_2CN(^nBu)_2\}_3]$, which decomposes slowly at room temperature (Scheme 34) [91].

Kirmse et al. attempted to prepare a gold(II) bis(diethyl diselenocarbamato) complex by adding $[Et_2H_2N][Se_2CNEt_2]$ in aqueous solution to a $K[AuCl_4]$ solution [92]. However, this reaction led to a red mixture containing $[Au(Se_2CNEt_2)]$, $[Au(Se_2CNEt_2)_2]$, and elemental gold (Scheme 35). According to the authors, a chloroform solution of $[Au(Se_2CNEt_2)]$ disproportionates within several hours to give elemental gold and the stable tris(diethyl diselenocarbamato) complex $[Au\{Se_2CN(Et)_2\}_3]$. During the oxidation reaction of gold(I) to gold(III) the authors claim to observe an intermediate gold(II) complex by ESR spectroscopy.

Van der Linden and Nijssen [93] added the (selenocarbamato)zinc salt $[Zn(Se_2CEt_2)_2]$ to a solution of $K[AuBr_4]$ reduced with sodium sulfite giving the *N*,*N*-diethyl(diselenocarbamate)gold(I) complex $[Au(Se_2CNEt_2)]$, which is unstable in solution and disproportionates easily to elemental gold, the selenocarbamate and the cationic (diselenocarbamato)gold(III) salt $[Au(Se_2CNEt_2)_2]Br$ as orange-red needles. Addition of Br_2 to this salt results in the substitution of one diselenocarbamate by two bromide ions giving red needles of $[AuBr_2(Se_2CNEt_2)]$ (Scheme 36).

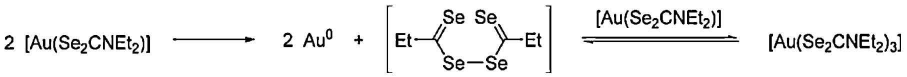
When the analogous butyl derivative $[Zn(Se_2CNBu_2)_2]$ is reacted with an excess of the gold precursor, yellow crystals of the mixed valent gold(I)/gold(III) salt $[Au(Se_2CNBu_2)_2][AuBr_2]$ were obtained (Scheme 36). The compounds were characterised by UV and IR spectroscopy, elemental analysis, and conductivity measurements. $[Au(Se_2CNEt_2)_2]Br$ behaves in nitrobenzene as a 1:1 electrolyte as does the thio-analogue. Both, sulfur and selenium complexes, can be electrochemically reduced, however only reduction of the selenocarbamato complex is reversible.

The tris(*N*,*N*-dibutyl diselenocarbamato) gold(III) complex $[Au\{Se_2CN(^nBu_2)\}_3]$ as well as the bis(isomaleonitrile diselenolato) gold(III) salt $[^nBu_4N][AuSe_2C_2(CN)_2]$ were patented as additives for photographic silver halide emulsions [94,95].

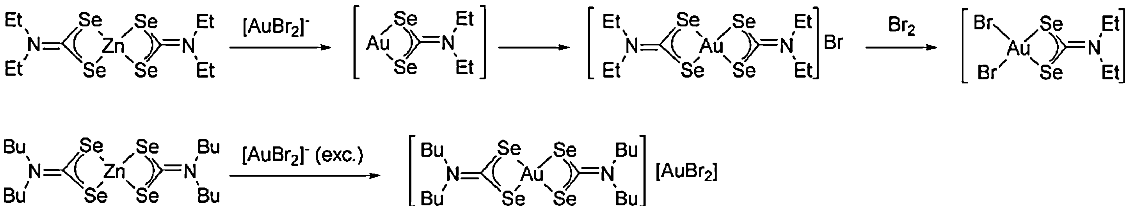
The structurally related salt $[Au\{(Se_2)C{=}C(CN)_2\}_2]PPh_4$ was prepared by heating a mixture of $Na[AuCl_4]$ and two equivalents of the potassium salt $(NC)_2C{=}C(SeK)_2$ in an aqueous solution in the presence of Ph_4PCl [96]. The alkali metal salts of this complex were very soluble and difficult to isolate. Conductivity measurements in dry acetone identified the gold complex as a 1:1 electrolyte. Comparison of the IR bands of the gold complex and the free ligand showed no changes of the C–N bands but a significant shift of 105 cm^{-1} for the C–Se bands, probably due to the high positive charge of the central atom resulting in a strong drift of electrons towards the selenium atom (Scheme 37) [97].

Dietzsch et al. [98] reacted aqueous solutions of $K[AuCl_4]$ with iso-maleonitrile thioselenolate in a 1:2 ratio, forming the brown gold(III) bis-chelate salt $[^nBu_4N][Au\{SeSC{=}C(CN)_2\}_2]$. Using excess ligand in methanol resulted in the formation of the beige gold(I) chelate complex $[^nBu_4N][Au\{SeSC{=}C(CN)_2\}]$. When an acetone solution of this complex is diluted with water, a purple colour forms, which disappears upon addition of acetone. A reversible redox dissociation was proposed for this observation by the authors.

In 1992, Dietzsch et al. reported the preparation and crystal structures of the dichalkogenato gold(I) dimers $[^nBu_4N]_2[Au_2\{\mu\text{-}SeEC{=}C(CN)_2\}_2]$ (E = S, Se) [99]. These were obtained by addition of an ethanolic solution of sulfite-reduced $[AuCl_4]^-$ under inert conditions to $(NC)_2C{=}C(SeK)_2$ or $(NC)_2C{=}C(SeK)(SK)$, respectively, in the presence of $[^nBu_4N]Br$. X-ray diffraction (Fig. 17) revealed identical lattice parameters for each compound, in which two gold atoms are bridged by two dianionic dichalkogenato ligands giving a nearly planar centrosymmetric dimer with a short Au···Au distance of 2.810(1) Å for the thioselenato derivative. The analogous thio-complex has an even shorter gold–gold distance [2.796(1) Å] due to the smaller radius of the sulfur atoms compared to that of Se. For the isostructural diselenolato complex only the unit cell parameters of crystals were determined, but no full structure solution



Scheme 35.



Scheme 36.

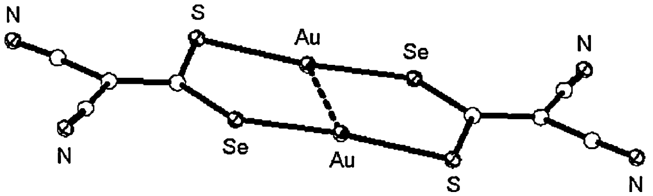


Fig. 17. Molecular structure of the dianion $[Au_2\{\mu\text{-SSeC=C(CN)}_2\}_2]^{2-}$ adapted from [99].

was carried out. The weak intramolecular gold–gold interactions in these complexes were studied by *ab initio* calculations at the Hartree–Fock level of theory.

Further characterisation was carried out by IR and ^{77}Se NMR spectroscopy. The ^{77}Se NMR spectra in CD_3CN show one signal for the diselenolato dianion $[Au_2\{\mu\text{-Se}_2C{=}C(CN)_2\}_2]^{2-}$ (666.0 ppm) and two signals for the selenolatothio derivative (639.0 ppm, 625.1 ppm) due to the presence of *cis* and *trans* isomers [99].

2.8. Selenium heterocycles

8-Selenoquinoline has been proposed as chelating agent for the separation of metal salts by thin layer chromatography [100]. Amongst the metals examined, gold(I) was found to give a brown material which precipitates out of solution under acidic conditions and was extractable with chloroform. No attempt was made to characterise this substance, as the focus was solely directed towards chromatographic metal separation. 20 years later, Russian researchers employed the same reaction in order to determine gold concentrations in aqueous solutions by UV–vis spectroscopy [101,102].

For the investigation of super- or semi-conducting materials based on gold, a series of compounds containing gold(III) complexes with chelating organoselenium ligands co-crystallised with various counterions have been reported (Fig. 18). In the subsequent section, these will be discussed in detail.

In an aqueous solution two equivalents of pyrazine-2,3-diselenolate (pds) react with $[AuCl_4]^-$ to give the bis(pyrazine-2,3-diselenolato)aurate(III) anion which was isolated as the tetrabutyl ammonium salt [103,104]. Electrocrystallisation or diffusion crystallisation of the salt in the presence of tetrathiafulvalene (ttf) gave black crystals of $(ttf)_3[Au(pds)_2]_2{\cdot}2.8\ CH_2Cl_2$ and $(ttf)[Au(pds)_2]$. The former was characterised by X-ray diffraction, whilst only the cell parameters of the latter were determined [103]. The same group also studied the structures, electronic and magnetic properties of other complexes containing $[Au(pds)_2]^-$ with different cation:anion ratios including $(ttf)_2[Au(pds)_2]_2$, $(ttf)_3[Au(pds)_2]_3$, $(dt\text{-}ttf)_4[Au(pds)_2]_3$ (dt-ttf = $\Delta^{2,2'}$-bithieno[3,4-d]-1,3-dithiol), and $[Fe(qsal)_2][Au(pds)_2]$ (Hqsal = N-(8-quinolyl)salicyl-aldimine) [103–107]. Some of these complexes were found to exhibit semi-conducting behaviour at room temperature.

The gold(III) charge-transfer complexes $[Q][Au(dssds)_2]^-$ ($[Q] = [^nBu_4N]^+$, $[Ph_4As]^+$) were obtained in low yields from the reaction of 1,3-diselenole-2-selenone-4,5-diselenolate (prepared *in situ* by saponification of 4,5-dibenzoylseleno-1,3-diselenol-2-selone with base) with $K[AuCl_4]$ under dinitrogen in methanol (Scheme 38) [108–110]. These complexes show typical C=Se absorption bands in the range of 890–900 cm^{-1} and their ^{77}Se NMR spectra display three resonances, one of which is shifted upfield in comparison to that of free 4,5-dibenzoylseleno-1,3-diselenol-2-selone [109–111]. $[^nBu_4N][Au(dssds)_2]$ is transformed into the neutral, semi-conducting complex $[Au(dssds)_2]$ by oxidation of the ligand with iodine. Interestingly, addition of $[Fe(Cp)_2]PF_6$ to $[^nBu_4N][Au(dssds)_2]$ leads to the formation of $[Fe(Cp)_2]_{0.2}[Au(dssds)_2]$, a complex of especially high conductivity, whilst the addition of $[ttf]_3[BF_4]_2$ gives $[ttf]_{0.3}[Au(dssds)_2]$, which still shows considerable conductivity due to the presence of ttf radical cations [112].

As an extension of this chemistry, various groups examined structurally similar ligands in which two or more selenium atoms were replaced by sulfur. In 1991, Olk et al. synthesised the gold(III) complexes $[^nBu_4N][Au(dtsds)_2]$ and $[^nBu_4N][Au(dttds)_2]$ containing 1,3-dithiol-2-selenone-4,5-diselenolate (dtsds) and 1,3-dithiol-2-thione-4,5-diselenolate (dtsds) by the same method described above (Scheme 38) [113,114]. Characterisation of these compounds was carried out using ^{77}Se, ^{13}C, NMR and IR spectroscopy [113,114] as well as cyclic voltammetry [115]. The chemical shifts of the ^{13}C resonances in the NMR spectra of $[^nBu_4N][Au(dtsds)_2]$ and $[^nBu_4N][Au(dttds)_2]$ fall in between those of the analogous thione and carbonyl (E1 = S, O) compounds [113].

Laguna and coworkers used the zinc salt $[^nBu_4N][Zn(dttds)_2]$ or the organotin reagent $[Sn(dttds)Me_2]$ to transfer the dttds dianion to gold(I) and gold(III) centres under mild conditions (Scheme 39) [116,117]. Thus, $[^nBu_4N][Au(dttds)_2]$ was prepared in good yield by mixing acetone solutions of $[^nBu_4N][Zn(dttds)_2]$ and $[^nBu_4N][AuBr_4]$ at room temperature [117].

Electrochemical oxidation of $[^nBu_4N][Au(dttds)_2]$ in the presence of $[^nBu_4N]ClO_4$ gave a small amount of black crystals of the stoichiometry $[^nBu_4N]_{0.4}[Au(dttds)_2]$ as determined by elemental analysis and conductivity. Cation exchange of $[^nBu_4N][Au(dttds)_2]$ with $[ttf]_3[^nBu_4N]_2$ lead to the red gold(III) complex $[ttf][Au(dttds)_2]$ which was characterised by conductivity measurements as well as IR and Raman spectroscopy. Based on these data, the compound was formulated as an ionic salt without any apparent oxidation of the ligand.

The two insoluble gold(III) complexes $[Au(dttds)(S_2CNR_2)]$ [R = Me (90%), CH_2Ph (72%)] were obtained from the reaction of

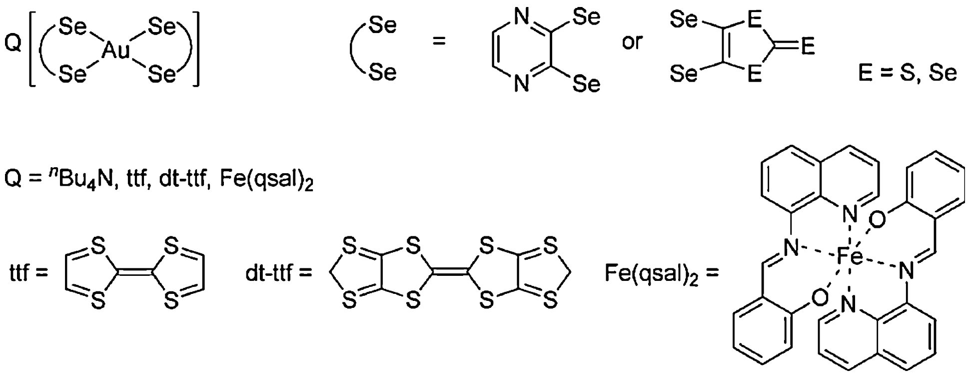
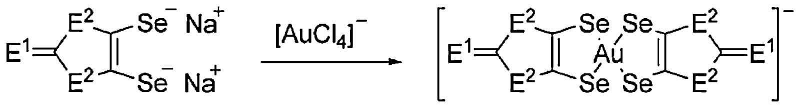
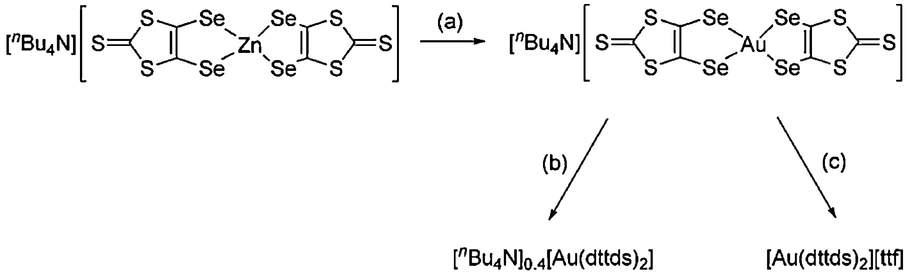


Fig. 18. Gold(III) compounds studied for their superconducting properties.



$E^1 = E^2 = Se$: dssds (1,3-diselenole-2-selenone-4,5-diselenolate)
$E^1 = Se$, $E^2 = S$: dtsds (1,3-dithiole-2-selenone-4,5-diselenolate)
$E^1 = E^2 = S$: dttds (1,3-dithiole-2-thione-4,5-diselenolate)

Scheme 38.



(a) [^{n}Bu$_4$N][AuBr$_4$], (b) electrocrystallisation, (c) (ttf)$_3$(BF$_4$)$_2$

Scheme 39.

[Sn(dttds)Me$_2$] with [AuBr$_2$(S$_2$CNR$_2$)$_2$] (Scheme 40) [117]. The byproduct, SnCl$_2$Me$_2$, could easily be separated by washing with acetone. The dinuclear C$_6$F$_5$ salt (PPN)$_2$[(C$_6$F$_5$Au)$_2$(μ-dttds)] was obtained by addition of two equivalents of (PPN)[Au(C$_6$F$_5$)Cl] to [Sn(dttds)Me$_2$]. ^{19}F NMR spectroscopy showed signals due to two equivalent C$_6$F$_5$ groups; the LSIMS(−) mass spectrum provided additional evidence for the proposed structure.

The dinuclear gold(I) complexes [(Ph$_3$PAu)$_2$(μ-dttds)] and [(MePh$_2$PAu)$_2$(μ-dttds)] as well as [Au$_2$(μ-dttds)$_2$(μ-dppm)] and [Au$_2$(μ-dttds)$_2$(μ-dppe)] were all obtained from the zinc salt [^{n}Bu$_4$N][Zn(dttds)$_2$] and the corresponding chloro(phosphine)gold(I) complexes [117]. The complexes [(Ph$_3$PAu)$_2$(μ-dttds)] and [(MePh$_2$PAu)$_2$(μ-dttds)] may be also be prepared using [Sn(dttds)Me$_2$] (Scheme 41) [116]. Although [Au$_2$(μ-dttds)$_2$(μ-dppe)] is monomeric, the dppm derivative is spectroscopically quite different: in the ^{31}P NMR spectrum of the former, a singlet is observed, whilst the other displays an AA'XX' system. Unfortunately, the FAB+ mass spectra of both only show signals due to fragmentation. Based on comparison of spectral data of the sulfur analogue, which exists both in solution and solid-state as a tetranuclear complex [118], a similar structure has been proposed for [Au$_2$(μ-dttds)$_2$(μ-dppm)].

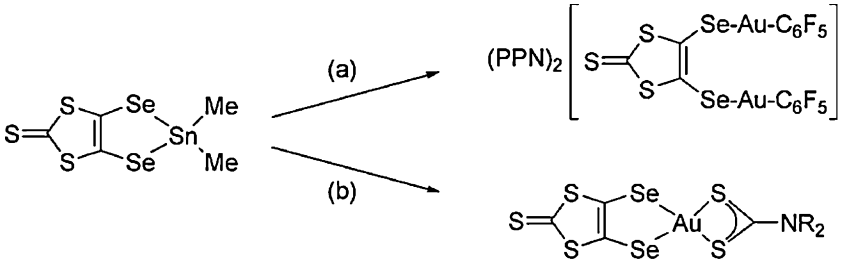
The trinuclear gold(I) complex [(MePh$_2$PAu)$_3$(dttds)]ClO$_4$ [117] is formed by the reaction of [(MePh$_2$PAu)$_2$(μ-dttds)] with [Au(PPh$_2$Me)]ClO$_4$, the corresponding PPh$_3$ derivative could however not be isolated. The ^{31}P NMR spectrum of [(MePh$_2$PAu)$_3$(dttds)]ClO$_4$ displays one broad resonance due to rapid exchange of the phosphines at room temperature; at low temperature two distinct sharp signals are observed [117].

Heuer et al. obtained the green bis(diselenolene)gold(III) complex [^{n}Bu$_4$N][Au{κ-*Se*-SeC(CF$_3$)C(CF$_3$)Se}] by oxidative addition of the heterocyclic diselenide bis(trifluoromethyl)diselenete to [AuCl(PPh$_3$)] in benzene (Scheme 42) [119].

The tendency for oxidation of the phosphine is thought to be the driving force of the reaction. At least three to four equivalents of the heterocycle are required for the reaction to occur; significant amounts of triphenylphosphine selenide and other organic byproducts are formed.

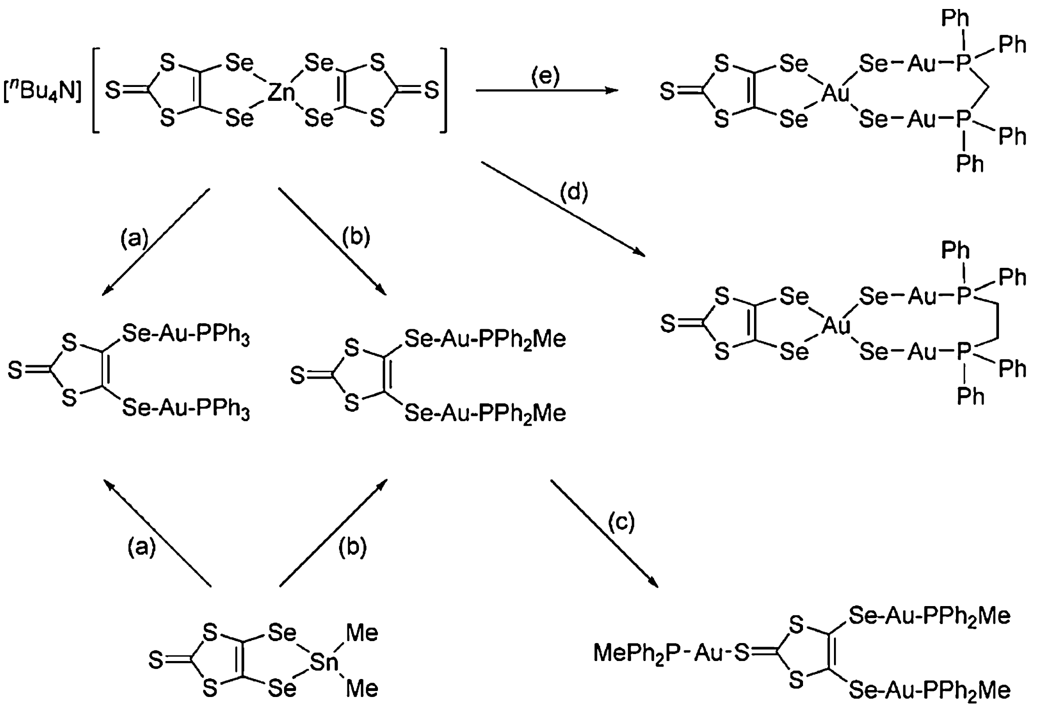
2.9. Carborane derivatives

Carboranes are of current interest due to their unique structures and their pseudo-aromatic character similar to benzene. A series of gold compounds containing selenium derivatives of 1,2-dicarba-*closo*-dodecaboranes were published in 2003. Canales et al. reacted [(C$_2$B$_{10}$H$_{11}$)SeH], obtained *via* lithiation of the parent carborane, with mono- and dinuclear chlorogold derivatives including [AuCl(PPh$_3$)], [Au$_2$Cl$_2$(μ-dppe)], [Au$_2$Cl$_2$(μ-dppf)], PPN[AuCl$_2$], and [AuCl(AsPh$_3$)] in the presence of sodium carbonate (Scheme 43) [120]. The dinuclear salt [(Ph$_3$PAu)$_2$(μ-SeC$_2$B$_{10}$H$_{11}$)]ClO$_4$ was



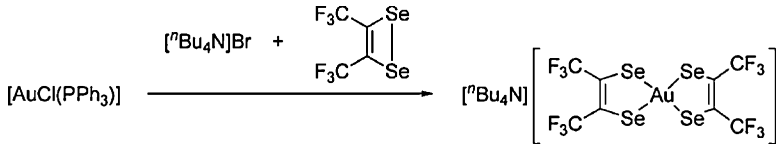
(a) 2 (PPN)[Au(C$_6$F$_5$)Cl], (b) [AuBr$_2$(S$_2$CR$_2$)] (R = Me, CH$_2$Ph)

Scheme 40.



(a) [AuCl(PPh$_3$)], (b) [AuCl(PPh$_2$Me)], (c) [Au(OClO$_3$)(PPh$_2$Me)], (d) [Au$_2$Cl$_2$(μ-dppe)], (e) [Au$_2$Cl$_2$(μ-dppm)]

Scheme 41.



Scheme 42.

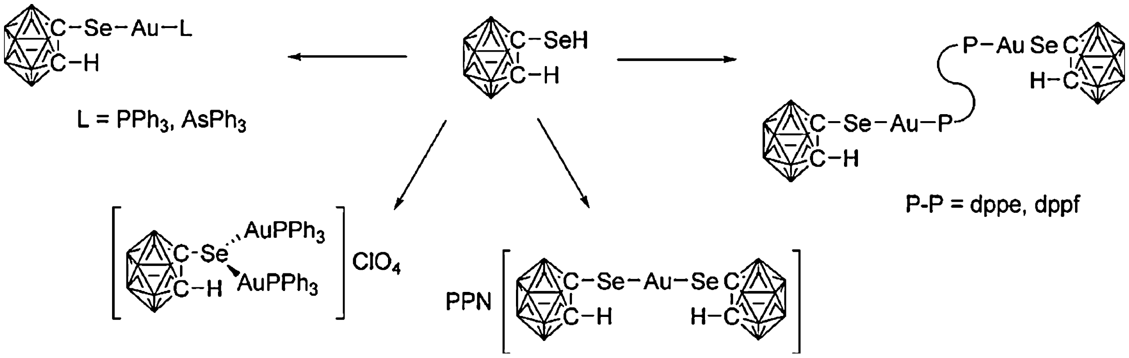
synthesised using the oxonium salt [O{Au(PPh$_3$)}$_3$]ClO$_4$. These complexes were isolated in good yields as colourless solids which were characterised by IR, ^{1}H and ^{31}P NMR spectroscopy, LSIMS(+) spectrometry, elemental analysis, and conductivity measurements. The crystal structure of [Au(SeC$_2$B$_{10}$H$_{11}$)(PPh$_3$)] is discussed below.

The methyl-substituted derivative [Au(1-Se-2-Me-1,2-*closo*-C$_2$B$_{10}$H$_{10}$)(PPh$_3$)] was subsequently reported in 2006 [121]. In this case, the selenol was unstable so that the *in situ* formed lithium salt was reacted with [AuCl(PPh$_3$)] (Scheme 44).

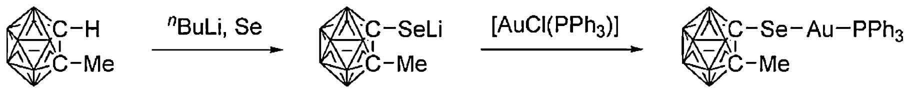
Molecular structures of the two (triphenylphosphine) gold(I) complexes [Au(SeC$_2$B$_{10}$H$_{11}$)(PPh$_3$)] [120] and [Au(SeMeC$_2$B$_{10}$H$_{11}$)(PPh$_3$)] [121] are shown in Fig. 19.

In both complexes the P–Au–Se bond is almost linear (*ca.* 175°); the angles about selenium in the compounds are approximately 97° for the unsubstituted cage and 100° for the Me-substituted carborane. In the solid-state [Au(SeC$_2$B$_{10}$H$_{11}$)(PPh$_3$)] forms head-to-tail dimers with rather long aurophilic interactions of 3.3035(4) Å [120]. The methyl-substituted carborane derivative also crystallises as a centrosymmetric dimer joined by Au···Se interactions of 3.4783(6) Å; here the gold atoms are more than 4 Å apart [121].

The ^{11}B NMR signals of the methyl-substituted derivative appear at −5.96 and −9.12 ppm, typical for this type of *closo* cluster [121]. The proton-substituted carborane complex was analysed by ^{77}Se NMR spectroscopy showing a singlet at 453 ppm [120].



Scheme 43.



Scheme 44.

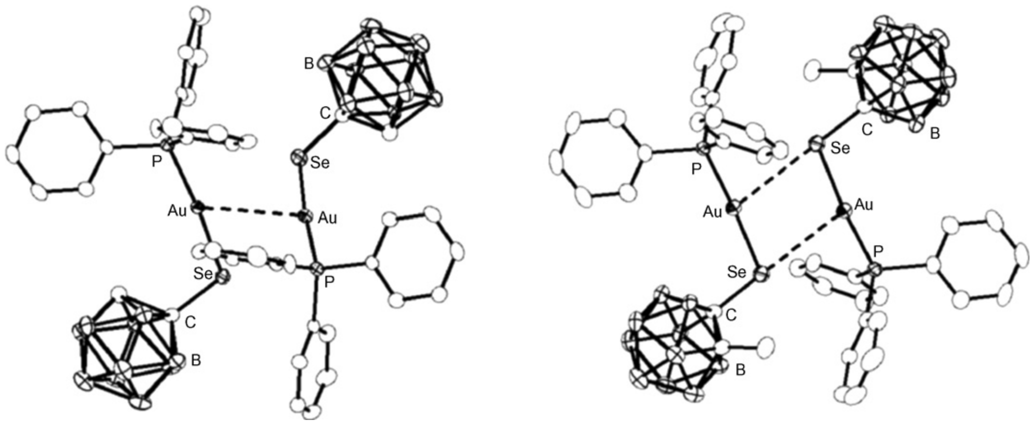


Fig. 19. Molecular structures of [Au($SeC_2B_{10}H_{11}$)(PPh_3)] (left) adapted from [120] and [Au($SeMeC_2B_{10}H_{11}$)(PPh_3)] (right) adapted from [121]. Hydrogen atoms have been omitted for clarity.

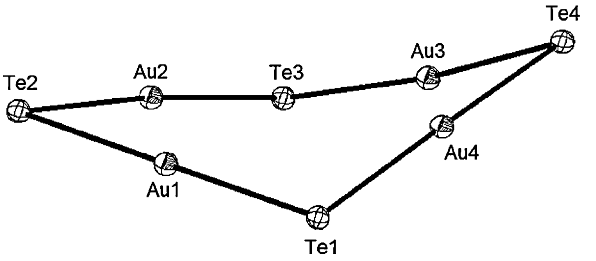


Fig. 20. Butterfly-shaped Au_4Te_4 core of the tetramer [$Au_4\{TeC(SiMe_3)_3\}_4$] adapted from [55].

This signal is quite close to that of its triphenylarsine analogue [Au($SeC_2B_{10}H_{11}$)($AsPh_3$)] at 440 ppm. Both resonances are shifted upfield by about 300 ppm compared to that of the free carborane.

Qiu et al. carried out a DFT/FF (finite field) study of some carborane(phosphino)gold selenium compounds to learn more about their non-linear optical properties [122]. The results show that the second order NLO coefficients of these model complexes are of practical value, warranting further experimental studies of these systems.

3. Gold complexes with organotellurium ligands

The known chemistry of gold compounds containing organotellurium ligands is considerably less developed than that of selenium: only four papers have been published, which describe complexes containing monoanionic organotellurolate ligands.

In a comparative structural study the group of Arnold reported the preparation and structures of a series of gold(I) chalcogenato complexes containing $^-EC(SiMe_3)_3$ (E = S, Se, Te) as well as the Si

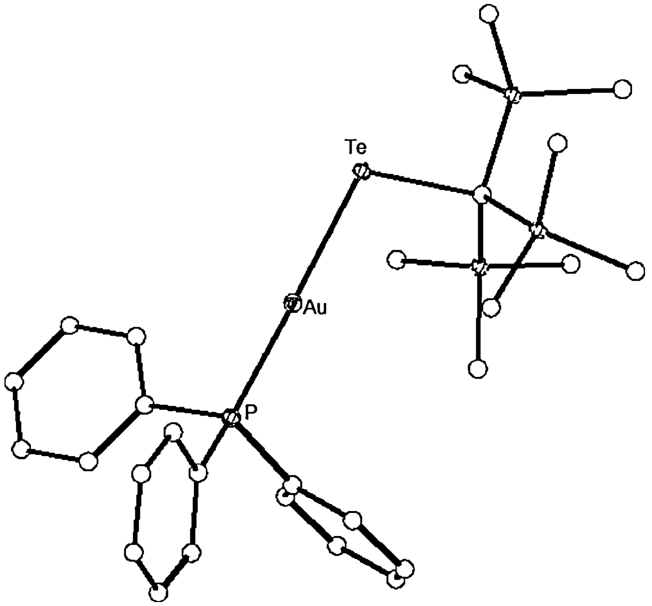


Fig. 21. Molecular structure of [Au{$TeC(SiMe_3)_3$}(PPh_3)] adapted from [55]. Hydrogen atoms have been omitted for clarity.

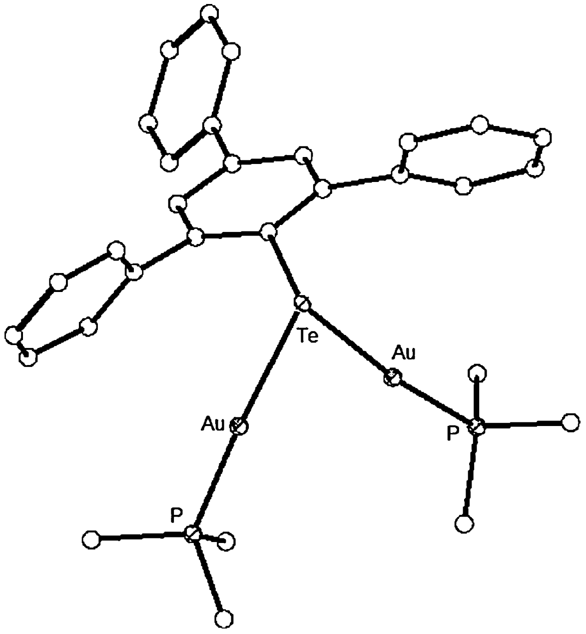


Fig. 22. Molecular structure of the cation [μ-{($Ph_3C_6H_2$)Te}$Au_2(PPh_3)_2$]$^+$ adapted from [123]. Hydrogen atoms have been omitted for clarity and only the *ipso*-C atoms of the PPh_3 groups are shown.

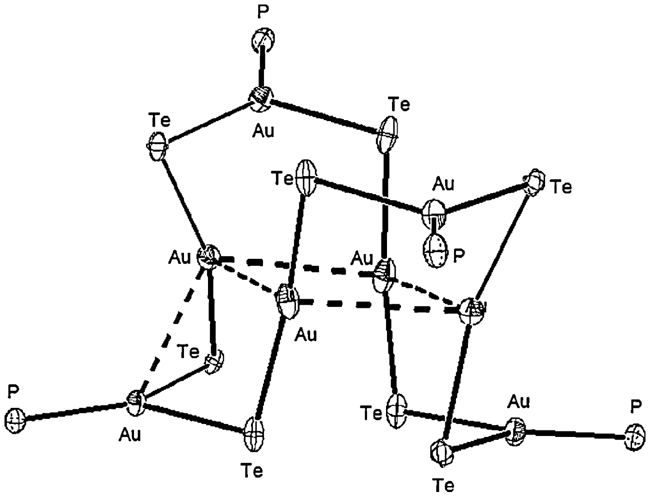


Fig. 23. $Au_8Te_8P_4$ core of the cluster $[Au_8(\mu\text{-}TePh)_8(PPh_3)_4]$ adapted from [125].

and Ge derivatives thereof [55]. The compounds were prepared by reaction of the appropriate lithium salts with [AuCl(tht)]. The tellurolato complex exists (just like the sulfur and selenium congeners) in the solid-state as a tetramer $[Au_4\{TeC(SiMe_3)_3\}_4]$, which consists of a bent, butterflied Au_4Te_4 core (Fig. 20).

The reaction of $LiTeC(SiMe_3)_3$ with $[AuCl(PPh_3)]$ gave yellow prisms of $[Au\{TeC(SiMe_3)_3\}(PPh_3)]$, which are thermally stable up to 130 °C. The complex forms a dimer *via* intermolecular Au–Te interactions of 2.566(1) Å in the solid-state (Fig. 21).

Strähle and coworkers reported that the attempted reaction of the bulky tellurolate $(2,4,6\text{-}Ph_3C_6H_2)Te^-$ with $[Au(PPh_3)]^+$ resulted in reduction of the gold salt and simultaneous oxidation of the tellurolate to the corresponding ditelluride [123]. However, the ditelluride itself reacts with $[Au(PPh_3)]BF_4$ to give the salt $[\mu\text{-}\{(Ph_3C_6H_2)Te\}Au_2(PPh_3)_2]BF_4$, which was characterised by X-ray diffraction (Fig. 22). The tellurolato ligand bridges two gold atoms, resulting in a gold–gold separation of 2.9529(7) Å.

Addition of iodine oxidises the gold(I) salt to the neutral, dimeric gold(III) complex $[Au_2I_2\{(Ph_3C_6H_2)Te\}_2]$. Here, the two tellurolate ligands bridge a pair of square planar coordinated AuI_2 units. This is so far the only known example of a gold(III) complex containing an organotellurium ligand.

The reaction of $Me_4N[TeCF_3]$ with AuCl in a 2:1 molar ratio leads to the formation of the aurate anion $[Au(TeCF_3)_2]^-$, which was isolated as the PPN salt. The ^{19}F and ^{125}Te NMR spectra of the salt show sharp singlet resonances with the appropriate satellites ($^2J_{Te\text{–}F}$ = 165 Hz). In the solid-state, the salt consists of discrete cations and anions. The aurate anions are virtually linear (Te–Au–Te = 177.4°) with the tellurolate ligands adopting an angle of around 100° [124].

Recently, the group of Laguna reported that the reaction of [AuCl(P)] (P = PPh_3, PPh_2py) with tellurolates derived from Ph_2Te_2 or *p*-tolyl$_2$Te$_2$ leads to the formation of orange, luminescent clusters of the type $[Au_8(\mu\text{-}TeR)_8(P)_4]$ (R = Ph, *p*-tolyl; P = PPh_3, PPh_2py) [125]. This contrasts with analogous reactions of selenolates, which give mononuclear [Au(SeR)(P)] type species. The clusters seem to remain intact in solution, as was shown by ^{31}P NMR spectroscopy; one sharp singlet is observed both at room temperature and at −90 °C. The structure of the clusters is made up of three stacked layers of gold and tellurium atoms (Fig. 23). The top and bottom layers consist of four Te atoms and two AuP units, whilst the middle layer is a planar, diamond-shaped array of four gold atoms. There are short Au–Au interactions ranging from *ca.* 2.9 to 3.3 Å between the gold atoms of the cluster.

Appendix A.

Au–E (E = Se, Te) distances and Au–E–C bond angles in all known molecular structures of this class of compounds.

Compound	Au–E distance (Å)	Au–E–C angle (°)	Ref.
$[Ph_4As][Au(SeCN)_4]$	2.457(1) 2.467(1)	103.0(3) 103.5(3)	[13]
$[Au(SeCN)(o\text{-}tolyl)_3P]$	2.4259(3)	96.73(11)	[18]
$[Au(^tBu_2Im)(SeCN)]$	2.4142(8)	97.0(3)	[23]
$[Au(SePh)(PPh_3)]$	2.422(1) 2.415(1)	105.7(2) 105.3(2)	[27]
$[Au_2(SePh)_2(\mu\text{-}dppe)]$	2.412(1) 2.417(1)	97.1(2) 94.9(3)	[28]
$[Au_2Cl(SePh)\{(CH_2)_2PPh_2\}_2]$	2.469(2)	108.9(5)	[31]
$[AuCl(Ph_2Se)]$	2.378(1)	100.3(2) 103.6(2)	[33]
$[AuCl_3(Ph_2Se)]$	2.445(1)	107.8(3) 97.7(2)	[33]
$[Au_2(\mu\text{-}SePh)(Ph_3P)_2]SbF_6$	2.446(2) 2.447(2)	97.8(4) 101.8(3)	[27]
$[Au_2(\mu\text{-}4\text{-}ClC_6H_4Se)(Ph_3P)_2]SbF_6$	2.444(1) 2.452(1)	101.3(4) 102.5(4)	[34]
$[(AuPPh_3)_2(SeC_{10}H_7)]SbF_6[Au(PPh_3)(SeC_{10}H_7)]$	2.456(2) 2.430(2) 2.413(2)	101.7(3) 106.4(3) 96.5(4)	[28]
$[(PPh_3)AuSe(C_6H_4)SeAu(PPh_3)]$	2.408(1) 2.401(2)	103.2(4) 103.5(4)	[38]
$[(PEtPh_2)AuSe(C_6H_4)_2SeAu(PEtPh_2)]$	2.409(1) 2.409(1)	105.5(3) 105.5(3)	[38]
$[(P^iPr_3)AuSe(C_6H_4)_2SeAu(P^iPr_3)]$	2.407(1) 2.407(2)	102.1(4) 105.2(4)	[38]

Appendix A (*Continued*)

Compound	Au–E distance (Å)	Au–E–C angle (°)	Ref.
$[Au_2\{SeC_6H_4(2\text{-}CH_2NMe_2)\}_2(\mu\text{-dppe})]$	2.404(1)	98.2(2)	[29]
$[Au_2\{SeC_6H_4(2\text{-}CH_2NMe_2)\}_2(\mu\text{-dppf})]$	2.4245(5)	101.08(9)	[29]
	2.4250(8)	101.73(9)	
$[Au_2(\mu\text{-SePh})(\mu\text{-dppf})]OTf$	2.4454(12)	108.3(6)	[41]
	2.4621(13)	94.8(6)	
	2.4706(11)	103.2(3)	
	2.4523(12)	101.7(3)	
$[(\mu\text{-dppf})\{Au^{I}(\mu\text{-SePh})Au^{III}(C_6F_5)_3\}_2]$	Au(I):	108.3(6)	[41]
	2.4408(5)	94.9(6)	
	2.4392(5)	103.2(3)	
	Au(III):	101.7(3)	
	2.4896(4)		
	2.4878(4)		
$[Au_2(\mu\text{-SeCH}_2Ph)(PPh_3)_2]SbF_6$	2.444(3)	80.3(1)	[28]
	2.443(3)	82.1(1)	
$[(\eta^5\text{-Cp})(CO)_3W(\mu\text{-SeCH}_2SiMe_3)AuPPh_3]SbF_6$	2.4381(13)	104.9(4)	[53]
	2.4415(13)		
$[PPN][Au(SeCF_3)_2]$	2.388(1)	101.3(1)	[54]
	2.393(1)	102.7(2)	
$[AuI(SeC_4H_8)]$	2.430(3)	106(1)	[60]
	2.436(3)	107(1)	
		108.1(8)	
		104(1)	
$[Au\{SeC(NH_2)_2\}(PPh_3)]Cl$	2.412(2)	95.0(5)	[63]
	2.427(2)	97.1(5)	
$[Au\{SeC(NH_2)_2\}_2(\mu\text{-dppm})]Cl_2$	2.430(1)	101.0(3)	[63]
	2.426(1)	99.9(3)	
$[Au\{SeC(NH_2)_2\}(PMe_3)]Cl$	2.4360(6)	100.34(17)	[66]
$[Au_2\{SeC(OMe)NPh\}_2(\mu\text{-dppe})]$	2.4172(13)	104.5(4)	[88]
	2.4162(13)	103.6(5)	
$[Au_2\{SeC(OMe)NPh\}_2(\mu\text{-dppp})]$	2.4072(12)	98.6(3)	[88]
	2.3991(14)	109.3(3)	
$[Au_2\{SeC(OMe)NPh\}_2(\mu\text{-dppf})]$	2.4048(12)	98.8(3)	[88]
$[^{n}Bu_4N][Au\{SeSC{=}C(CN)_2\}]_2$	2.345(3)	109.36	[99]
$(ttf)_3[Au(pds)_2]_2\cdot 2.8CH_2Cl_2$	2.429(1)	100.8(3)	[103]
	2.431(1)	102.4(4)	
$(ttf)_2[Au(pds)_2]_2$	2.420(2)	103.6(6)	[104]
	2.423(2)	102.2(7)	
	2.434(3)	100.6(7)	
	2.416(2)	101.4(8)	
$(ttf)_3[Au(pds)_2]_2$	2.431(2)	102.1(8)	[104]
	2.427(2)	100.8(6)	
$(ttf)_3[Au(pds)_2]_3$	2.430(2)	102.1(6)	[104]
	2.426(2)	100.8(6)	
$(dt\text{-}ttf)_4[Au(pds)_2]_3$	2.4157(19)	101.0(6)	[105,106]
	2.4213(19)	100.0(5)	
	2.425(2)	101.3(5)	
	2.4353(19)	101.4(5)	
	2.426(3)		
	2.431(2)		
$[Fe(qsal)_2][Au(pds)_2]$	2.4245(8)	101.3(2)	[107]
	2.4261(8)	101.4(2)	
	2.4199(8)	101.3(2)	
	2.4340(8)	100.5(2)	
$[Au(SeC_2B_{10}H_{11})(PPh_3)]$	2.4167(4)	100.37(12)	[120]
$[Au(SeMeC_2B_{10}H_{11})(PPh_3)]$	2.4254(6)	97.40(15)	[121]
$[Au_4\{TeC(SiMe_3)_3\}_4]$	2.566(3)	105.5(9)	[55]
	2.560(3)	109.2(8)	
	2.559(3)	105.2(9)	
	2.568(3)	106.7(7)	
$[Au\{TeC(SiMe_3)_3\}(PPh_3)]$	2.566(1)	104.1(4)	[55]
$[\mu\text{-}\{(Ph_3C_6H_2)Te\}Au_2(PPh_3)_2]BF_4$	2.592(1)	97.1(3)	[123]
	2.578(2)	91.4(3)	

Appendix A (*Continued*)

Compound	Au–E distance (Å)	Au–E–C angle (°)	Ref.
$[Au_2I_2\{(Ph_3C_6H_2)Te\}_2]$	2.595(1) 2.606(1) 2.598(1) 2.602(1)	109.2(4) 100.7(4) 106.5(5) 100.8(5)	[123]
$[PPN][Au(TeCF_3)_2]$	2.549(1) 2.533(1)	98.6(3) 101.9(3)	[124]
$[Au_8(\mu\text{-}TePh)_8(PPh_3)_4]$	2.7111(9) 2.7369(9) 2.6952(9) 2.7063(9) 2.5982(9) 2.5994(9) 2.5862(10) 2.5877(9) 2.5745(10) 2.5863(10) 2.6092(8) 2.6116(8) 2.6785(9) 2.7157(9) 2.6991(8) 2.7358(9)	67.96(2)[a] 68.98(2) 98.29(3) 100.90(3) 89.06(3) 96.11(3) 68.67(2) 67.37(2)	[125]
$[Au_8(\mu\text{-}TePh)_8(PPh_2py)_4]$	2.7126(16) 2.7211(14) 2.6071(13) 2.584(2) 2.587(2) 2.6045(14) 2.7080(14) 2.7257(16)	95.22(6)[a] 66.16(3) 96.22(6) 66.69(4)	[125]

[a] Au–Te–Au angles.

Appendix B.

Compilation of ^{77}Se and ^{125}Te NMR data of gold complexes containing organoselenium and organotellurium ligands.

Compound	Frequency (MHz) Solvent reference standard[a]	Chemical shift (ppm) Multiplicity[b] Coupling constant (Hz)	Ref.
$[Au_2(SePh)_2(\mu\text{-}dppe)]$	38.2 $CDCl_3$	−181.5	[28]
$[AuCl_3(SePh_2)]$	–[c] $CDCl_3$	534.7	[33]
$[Au(2,4,6\text{-}{}^tBu_3C_6H_2Se)(PPh_3)]$	57.24 C_6D_6	170.6 d, $^2J_{Se-P} = 41$	[35,36]
$[(PPh_3)AuSe(C_6H_4)SeAu(PPh_3)]$	76.217 $CDCl_3$	148.2	[38]
$[(PPh_3)AuSe(C_6H_4)_2SeAu(PPh_3)]$	76.217 $CDCl_3$	156.6	[38]
$[(PEtPh_2)AuSe(C_6H_4)SeAu(PEtPh_2)]$	76.217 $CDCl_3$	148.6	[38]
$[(PEtPh_2)AuSe(C_6H_4)_2SeAu(PEtPh_2)]$	76.217 $CDCl_3$	157.0	[38]
$[(P^iPr_3)AuSe(C_6H_4)_2SeAu(P^iPr_3)]$	76.217 $CDCl_3$	143.7	[38]
$[Au\{SeC_6H_4(2\text{-}CH_2NMe_2)\}(PPh_3)]$	76.4 $CDCl_3$	118.5	[29]
$[Au\{SeC_6H_4(2\text{-}CH_2NMe_2)\}(PPh_2py)]$	76.4 $CDCl_3$	120.3	[29]
$[Au_2\{SeC_6H_4(2\text{-}CH_2NMe_2)\}_2(\mu\text{-}dppm)]$	76.4 $CDCl_3$	161.3	[29]
$[Au_2\{SeC_6H_4(2\text{-}CH_2NMe_2)\}_2(\mu\text{-}dppe)]$	76.4 $CDCl_3$	125.2	[29]
$[Au_2\{SeC_6H_4(2\text{-}CH_2NMe_2)\}_2(\mu\text{-}dppf)]$	76.4 $CDCl_3$	424.2	[29]
$[{}^nBu_4N][Au(C_6F_5)_3\{SeC_6H_4(2\text{-}CH_2NMe_2)\}]$	76.4 $CDCl_3$	205.9	[29]

Appendix B (*Continued*)

Compound	Frequency (MHz) Solvent reference standard[a]	Chemical shift (ppm) Multiplicity[b] Coupling constant (Hz)	Ref.
$[(\eta^5\text{-Cp})(CO)_3W(\mu\text{-}SeCH_2Ph)Au(PPh_3)]SbF_6$	38.2 Acetone-d6	−250.6	[53]
$[(\eta^5\text{-Cp})(CO)_3W(\mu\text{-}SeCH_2SiMe_3)Au(PPh_3)]SbF_6$	38.2 Acetone-d6	−351.4	[53]
$[(\eta^5\text{-Cp})(CO)_3W(\mu\text{-}SeCH_2SiMe_3)Au(PPh_3)]ClO_4$	38.2 Acetone-d6	−244.1	[53]
$[Au(SeCF_3)_2]^-$	–[c] CD_3CN	237 q, $^2J_{Se-F} = 44$ Hz	[54]
$[Au\{SeC(NH_2)_2\}(PPh_3)]Cl$	–[c] $CDCl_3/CD_3OD$	217 d, $^2J_{Se-P} = -13$ Hz	[63]
$[Au_2\{SeC(NH_2)_2\}_2(\mu\text{-dppm})]Cl_2$	–[c] DMSO-d6	214 d, $^2J_{Se-P} = -13$ Hz	[63]
$[Au\{SeC(NH_2)_2\}(PMe_3)]Cl$	95.35 DMSO-d6 SeO_2	200.50	[67]
$[Au\{SeC(NH_2)_2\}(PPh_3)]Cl$	95.35 DMSO-d6 SeO_2	206.31	[67]
$[Au\{SeC(NH_2)(NMe_2)\}(Me_3P)]Cl$	95.35 DMSO-d6 SeO_2	221.33	[67]
$[Au\{SeC_6H_4(2\text{-}CH_2NMe_2)\}(PMe_3)]$	67.3 $CDCl_3$	87	[75]
$[Au\{SeC_6H_4(2\text{-}CH_2NMe_2)\}(PEt_3)]$	67.3 $CDCl_3$	76	[75]
$[Au\{SeC_6H_4(2\text{-}CH_2NMe_2)\}(PPh_3)]$	67.3 $CDCl_3$	74	[75]
$[Au\{SeC_6H_4(2\text{-}CH_2NMe_2)\}_2]$	67.3 $CDCl_3$	57	[75]
$[Au(ImSe)(PMe_3)]Cl$	95.35 DMSO-d6 SeO_2	90.94	[67]
$[Au(MeImSe)(PMe_3)]Cl$	95.35 DMSO-d6 SeO_2	89.77	[67]
$[Au(EtImSe)(PMe_3)]Cl$	95.35 DMSO-d6 SeO_2	82.19	[67]
$[Au(^nPrImSe)(PMe_3)]Cl$	95.35 DMSO-d6 SeO_2	81.20	[67]
$[Au(^iPrImSe)(PMe_3)]Cl$	95.35 DMSO-d6 SeO_2	80.95	[67]
$[Au(ImSe)(Et_3P)]Br$	95.35 DMSO-d6 SeO_2 in D_2O	90.94	[77]
$[Au(MeImSe)(Et_3P)]Br$	95.35 DMSO-d6 SeO_2 in D_2O	89.77	[77]
$[Au(DiazSe)(Et_3P)]Br$	95.35 DMSO-d6 SeO_2 in D_2O	212.65	[77]
$[^nBu_4N]_2[Au\{Se_2C{=}C(CN)_2\}]_2$	47.75 CD_3CN	666.0	[99]
$[^nBu_4N]_2[Au\{SeSC{=}C(CN)_2\}]_2$	47.75 CD_3CN	639.0 625.1 (mixture of isomers)	[99]
$[Ph_4As][Au(dssds)_2]$	47.75 DMSO-d6 Ph_3PSe in $CDCl_3$	988.1	[111]

Appendix B (*Continued*)

Compound	Frequency (MHz) Solvent reference standard[a]	Chemical shift (ppm) Multiplicity[b] Coupling constant (Hz)	Ref.
$[Bu_4N][Au(dssds)_2]$	47.77 DMSO-d6	1317.2 (C=Se), 1110.6 (SeC_2), 718.2 (Se–Au)	[114]
	76.01 DMSO-d6	1330.1 (C=Se), 1120.9 (SeC_2), 729.0 (Se–Au)	[110]
$[Bu_4N][Au(dtsds)_2]$	47.77 DMSO-d6	997.3 (C=Se), 686.7 (Se–Au)	[114]
$[Bu_4N][(dttds)_2Au]$	47.77 DMSO-d6	693.1 (Se–Au)	[114]
	47.77 DMSO-d6 H_2SeO_3	−606.7 (Se–Au)	[126]
$[Au(SeC_2B_{10}H_{11})(PPh_3)]$	–[c] $CDCl_3$ Se_2Me_2	453	[120]
$[Au(SeC_2B_{10}H_{11})(AsPh_3)]$	–[c] $CDCl_3$ Se_2Me_2	440	[120]
$[Au_4\{TeC(SiMe_3)_3\}_4]$	–[c] C_6D_6 –[c]	−302	[55]
$[Au\{TeC(SiMe_3)_3\}(PPh_3)]$	–[c] C_6D_6 –[c]	−148	[55]
$[Me_4N][Au(TeCF_3)_2]$	126.4 CD_3CN Me_2Te	356 q, $^2J_{Te-F}$ = 165 Hz	[124]

[a] If nothing is specified, $SeMe_2$ was used as external reference.

[b] If no multiplicity is given, a singlet resonance is implied; d, doublet; q, quartet.

[c] Data not given.

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