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Polymeric and macrocyclic gold(I) complexes with bridging dithiolate and diphosphine ligands

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Dedicated to Professor D.M.P. Mingos.

Abstract

The reaction of digold(I) diphosphine complexes $[Au_2(O_2CCF_3)_2(\mu\text{-}Ph_2P\text{–}X\text{–}PPh_2)]$ with dithiols HS–Y–SH can give either macrocyclic complexes $[Au_2(\mu\text{-}S\text{–}Y\text{–}S)(\mu\text{-}Ph_2P\text{–}X\text{–}PPh_2)]$ or polymeric complexes $[Au_2(\mu\text{-}S\text{–}Y\text{–}S)(\mu\text{-}Ph_2P\text{–}X\text{–}PPh_2)]_n$. The structures of the macrocyclic complex $[Au_2\{\mu\text{-}(S\text{-}4\text{-}C_6H_4)_2S\}\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}]$, and the polymeric complexes $[Au_n\{\mu\text{-}(S\text{–}CH_2CO_2CH_2CH_2O)_2\text{-}1,4\text{-}C_6H_4\}_n(\mu\text{-}trans\text{-}Ph_2PCH{=}CHPPh_2)_n]$ and $[Au_n\{\mu\text{-}(S\text{–}CH_2CO_2CH_2CH_2O)_2\text{-}1,5\text{-}C_{10}H_6\}_n(\mu\text{-}trans\text{-}Ph_2PCH{=}CHPPh_2)_n]$ have been determined. Evidence is presented that the complexes exist primarily as macrocycles in solution and that, in favorable cases, ring-opening polymerization occurs during crystallization.

Keywords: Gold; Dithiolate; Diphosphine; Macrocycle; Polymer; Ring-opening polymerization

1. Introduction

Metal containing polymers have been studied intensely since the incorporation of metal centers into polymer chains can lead to useful catalytic, electrical, optical, or magnetic materials, which are not possible with the purely organic analogs [1]. The thiolate derivatives are the most useful of all gold complexes in present and potential industrial applications, with uses in gold pastes, self-assembled monolayers, chemical vapor deposition, luminescent materials and pharmacology [2–4], and so there is intense interest in the synthesis and properties of these compounds [3–15]. In gold(I) complexes, intermolecular aurophilic gold···gold bonding can be used in the formation of supramolecular architectures, for example in the cross-linking of polymer chains or in the induction of chain folding [3–15].

Several simple gold(I) complexes are polymeric in nature, including the simple halogen or thiolate bridged gold(I) complexes (**A**, Chart 1) [3]. Gold polymers involving diacetylides with diphosphine or di-isonitrile ligands have also been described, although the inherent skeletal rigidity of these linear materials, and their correspondingly low solubilities, hindered structural characterization [16,17]. Examples of structurally characterized gold(I) polymers are limited. They can incorporate linear P–Au–P (**B**, Chart 1), P–Au–N (**C**, Chart 1) or P–Au–O linkages, or tricoordinate P_2AuCl (**D**, Chart 1) or P_3Au groups [16–23]. An important example is the thiolate bridged antiarthritic drug gold(I) thiomalate, which contains linear S–Au–S groups (**A**, Chart 1) [14].

The isolation of crystalline polymers can be accomplished as a result of the lability of many gold(I)–ligand bonds, and it is typical that solutions contain low molecular weight oligomers or macrocycles which associate during crystallization to form the polymers [16–23]. The interconversion between macrocycles and polymers was first demonstrated in cationic

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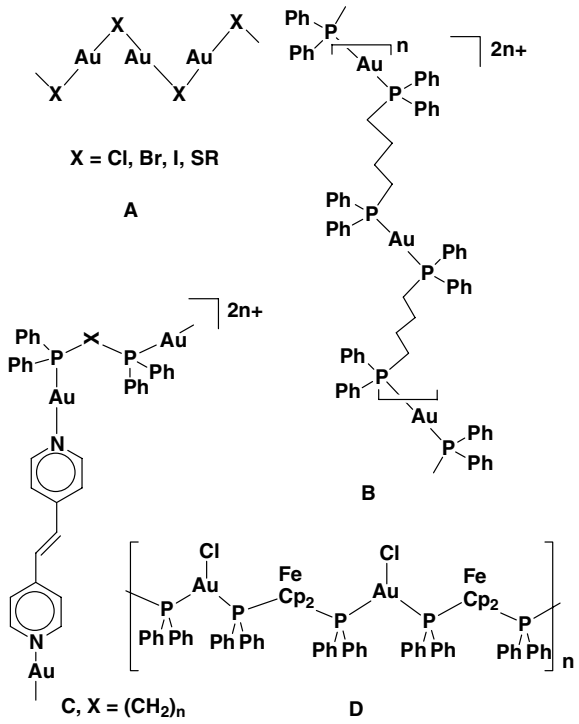


Chart 1. Some polymeric gold(I) complexes.

complexes of gold(I) with a combination of the bridging ligands *trans*-1,4-bis(pyridyl)ethene gold(I) complexes with diphosphines $Ph_2P(CH_2)_nPPh_2$. The structure changed from a ring when $n = 2$, to a sinusoidal polymer when $n = 3$, to a stretched linear polymer when $n = 4$, as the Au···Au separation increased (Scheme 1). The aim of the present work was to find a system in which dithiolate ligands would be used in place of *trans*-1,4-bis(pyridyl)ethane, and so give neutral macrocycles or polymers, and to gain further insight into ring-opening polymerization of coordination compounds.

Numerous eight-membered macrocyclic gold(I) complexes have been prepared by using dithiocarbamate or dithiophosphate ligands [3,24]. Larger rings (10–14 atoms) have been prepared, for example by combining gold(I) with 1,3-propanedithiol and the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 2$–5) as shown in Scheme 1 [25–30]. Insoluble side products, thought to have polymeric structures, were obtained in several cases and the similar reactions with 1,4-butanedithiol gave only the insoluble, polymeric material [25]. We anticipated that incorporation of more flexible aliphatic and ester groups in the backbone of the dithiol would increase the solubility of the gold(I) complexes, and that diphosphine ligands which favor either the *syn* or *anti* conformation could be used to influence the equilibrium between macrocyclic and ring-opened isomeric forms of the products [16,17,20]. The synthesis and structural characterization of gold(I) thiolate macrocycles of formula $[R(OCH_2CH_2O_2CCH_2SAu)_2$- $(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$ ($n = 1$–6), and the first examples of linear P–Au–S coordinated neutral gold-polymers using the rigid diphosphine *trans*-1,2-bis(diphenylphosphino)ethylene, are described below. A preliminary account of a part of this work has been published [30].

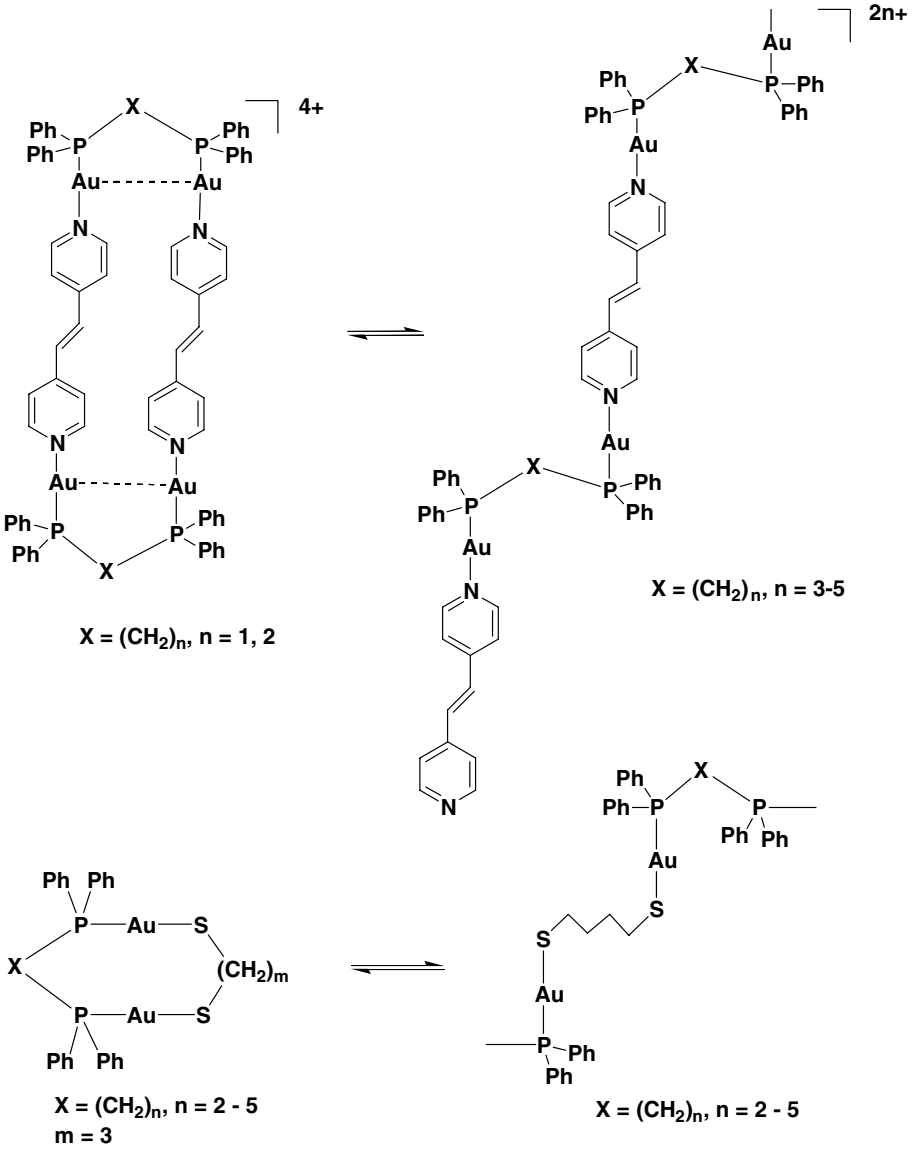
2. Results and discussion

2.1. Synthesis of gold(I) dithiolate complexes

The new dithiol ligands were prepared by the alkylation of aromatic diphenols with chloroethanol in base [31,32], followed by condensation of the product alcohol with mercaptoacetic acid [33]. For example, the reaction 2-chloroethanol with 1,4-dihydroxybenzene gave 1,4-C_6H_4-$(OCH_2CH_2OH)_2$, which reacted with mercaptoacetic acid to give the dithiol 1,4-$C_6H_4(OCH_2CH_2O_2CCH_2SH)_2$ (**1**) (Scheme 2). The dithiols $R(OCH_2CH_2O_2CCH_2SH)_2$ with R = 1,5-$C_{10}H_6$ (**2**), 4,4′-$C_6H_4C_6H_4$ (**3**), 4,4′-$CMe_2(C_6H_4)_2$ (**4**), were prepared similarly (Scheme 3). The more rigid dithiol 4,4′-$S(C_6H_4SH)_2$ (**5**), the dithiol without a central aromatic group ($-CH_2O_2CCH_2SH)_2$ (**6**), and the dithiol with additional ether units 4,4′-$C_6H_4C_6H_4(OCH_2CH_2$-$OCH_2CH_2OCH_2CH_2O_2CCH_2SH)_2$ (**7**), were prepared for comparison (Schemes 4–6). The dithiols **1**–**7** were characterized by their NMR and IR spectra and by MS.

The gold(I) diphosphine dithiolate complexes were readily prepared by reaction of two equivalents of $[AuCl(SMe_2)]$ with the corresponding diphosphine ligand, PP, to give $[Au_2Cl_2(\mu\text{-P–X–P})]$, followed by reaction with silver trifluoroacetate to give $[Au_2(O_2CCF_3)_2(\mu\text{-PP})]$, and then by reaction of the gold(I) trifluoroacetate complex with a dithiol ligand (HS–Y–SH), with displacement of the weakly bonded trifluoroacetate ligands with loss of trifluoroacetic acid [34], to give the product $[Au_2(\mu\text{-S–Y–S})(\mu\text{-P–X–P})]$. The syntheses are illustrated in Schemes 2–6. These gold(I) dithiolate complexes were isolated as colourless air-stable solids, most of which were soluble in nitrobenzene or dichloromethane, or in a mixture of these solvents. For example, the dithiol **1** and diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ gave the macrocyclic complexes **8** [**8a**, $n = 1$; **8b**, $n = 2$; **8c**, $n = 3$; **8d**, $n = 4$; **8e**, $n = 5$; **8f**, $n = 6$] while the diphosphine ligand *trans*-$Ph_2PCH{=}CHPPh_2$ gave a macrocycle **8g** in solution but a polymer **8g*** in the solid state (Scheme 2). The dithiols **2**–**7** gave similar complexes **9**–**14**, respectively.

The complexes **8** gave simple NMR spectra as expected for a macrocyclic structure. For example, complex **8a** gave single resonances in the ^{1}H NMR spectrum for the phenylene group at $\delta = 6.70$ and for each methylene group at $\delta = 4.30$ [CO_2CH_2], 3.95 [$ArOCH_2$], and 3.75 [CH_2S] and a single resonance in the ^{31}P NMR spectrum at $\delta = 30.4$. The ESI-MS gave a peak at $m/z = 1123$ corresponding to $[\mathbf{8a}{+}H]^+$ and no higher mass peaks. The complex with the diphosphine ligand *trans*-$Ph_2PCH{=}CHPPh_2$ was shown to have the polymeric structure **8g*** in the solid state, as described below, but it appears to have the macrocyclic structure **8g** in solution (Scheme 2). Thus, the ^{1}H NMR parameters for **8g** are similar to those for **8a**, and the ^{31}P NMR spectrum contained a single resonance, whereas a polymer **8g*** is expected to give broader, more complex spectra. In support, the ESI-MS gave a peak at $m/z = 1135$ corresponding to $[\mathbf{8g}{+}H]^+$ and no higher mass



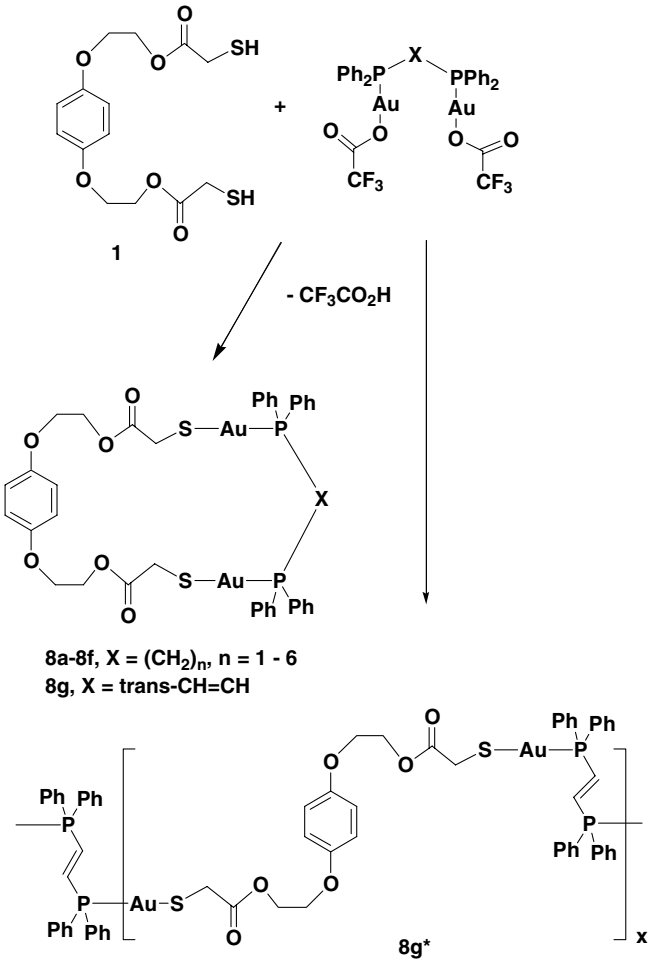
Scheme 1. Equilibrium between macrocycles and ring-opened polymers.

peaks, and an accurate mass determination was in good agreement with the expected value.

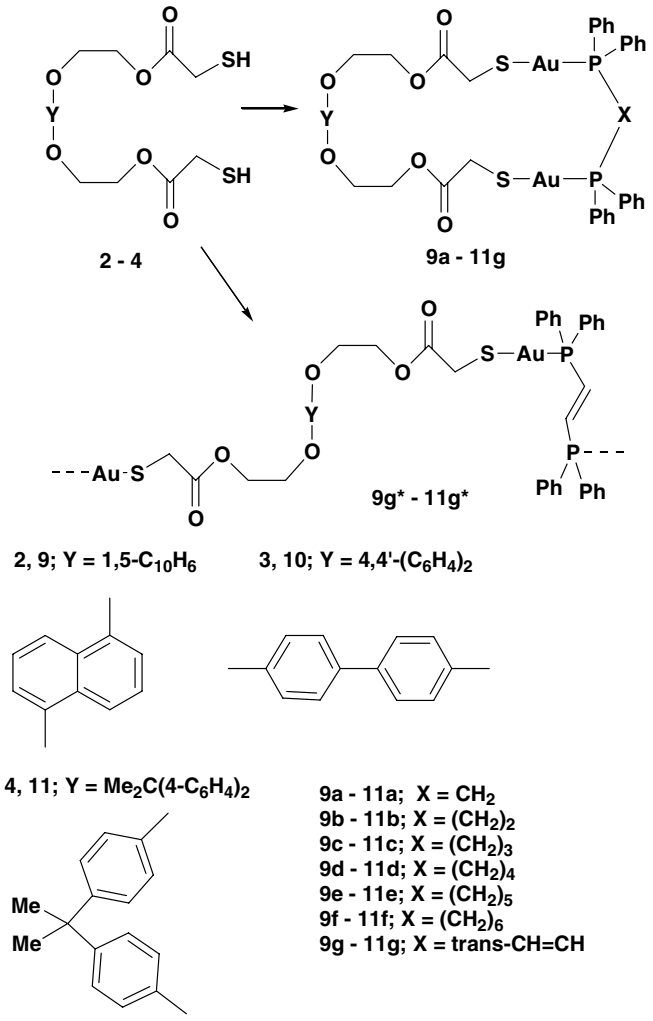
In complex **9a**, [1,5-$C_{10}H_6$($OCH_2CH_2O_2CCH_2SAu$)$_2$(μ-dppm)], Scheme 3, the CH_2SAu group gives a singlet resonances at $\delta = 3.85$ in the ^{1}H NMR, shifted downfield from the free ligand by 0.54 ppm. A single phosphorus resonance was observed at $\delta = 30.8$, indicating formation of a macrocyclic complex. For complex **9g**, [1,5-$C_{10}H_6$($OCH_2CH_2O_2$-CCH_2SAu)$_2$(μ-*trans*-$Ph_2PCH{=}CHPPh_2$)], the CH_2SAu protons gave a resonance at $\delta = 3.53$ in the ^{1}H NMR, and a single resonance in the ^{31}P NMR at $\delta = 35.0$. The freshly prepared complex **9g** was freely soluble in the reaction solution but, following crystallization, it was sparingly soluble in dichloromethane or nitrobenzene. These data suggest a macrocyclic structure **9g** in solution but a polymeric structure **9g*** of the solid complex, and this interpretation is supported by ESI-MS data for the solution and by X-ray structure determination of the crystalline complex. Complete NMR data for the gold thiolate complexes **9**–**11** are listed in Section 4. Complex **10a** was insoluble and so is likely to have a polymeric structure in the solid state.

The gold(I) thiolates obtained from the ligands $S(C_6H_4SH)_2$ (Scheme 4) and ($–CH_2O_2CCH_2SH)_2$ (Scheme 5) were characterized similarly. However, the complexes **12g** and **13g** were insoluble, and so the equilibrium between macrocycle and polymer is presumed to be displaced towards the polymeric form when compared to the other dithiolates studied. The polymeric complexes **12g** and **13g** were thermally stable up to 280 °C, whereupon they gave sharp decomposition to elemental gold.

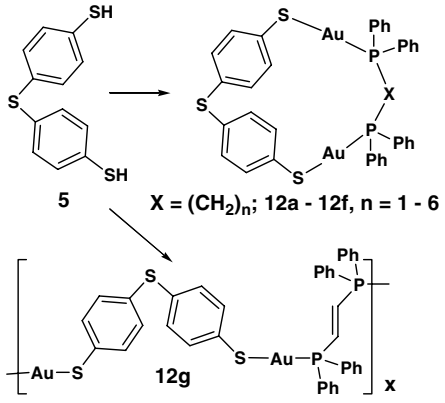
Complexes containing chains of polyether units have been widely used throughout supramolecular chemistry, and are often used to bind alkali and alkaline earth metal cations [35], or in the self-assembly of catenanes and rotaxanes [36–38]. The organization of oligo(ethylene glycol) terminated alkanethiolates chemisorbed onto gold



Scheme 2. Dithiolate complexes obtained from the dithiol **1**.



Scheme 3. The dithiolate complexes **9**–**11**.



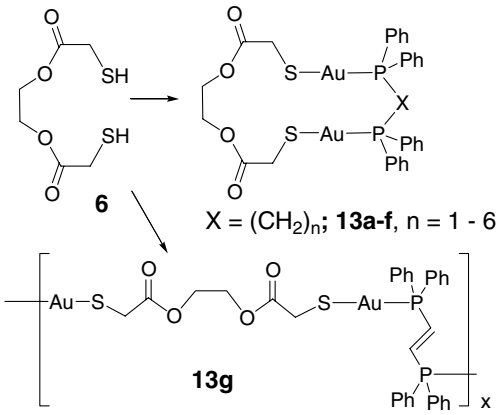
Scheme 4. The dithiolate complexes **12**.

surfaces has shown to be aided by intermolecular interactions among the chains [39]. In the present work, the dithiol ligand $[4,4'\text{-}C_6H_4C_6H_4\{(OCH_2CH_2)_3OCOCH_2SH\}_2]$ was prepared and converted to the macrocyclic complexes **14a**–**14g** (Scheme 6). The ^1H NMR spectra of these complexes gave well-resolved resonances for the dithiol and diphosphine protons, and the ^{31}P NMR spectra each contained a single resonance. The structures in solution are therefore proposed to be the macrocycles.

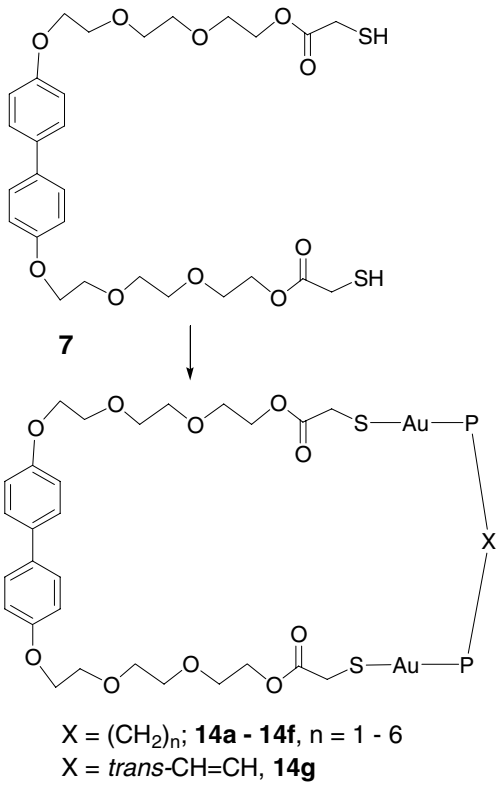
The spectroscopic data for the complexes suggested formation of gold(I) diphosphine dithiolate macrocycles in each case in solution. However, the solution and solid state structures might differ, and the structures of the complexes **8g**, **9g**, and **12d** were determined crystallographically, in order to provide a benchmark.

2.2. Structures of the complexes

The molecular structure of the 19-atom ring complex **12d** is shown in Fig. 1. The ring structure is slightly twisted, with a dihedral angle P(1)–Au(1)–Au(2)–P(2) = 29.5°, resulting from the displacement of the S–Au groups on opposite sides of the S(2)–S(1)–S(3) plane [C(61)–S(3)–Au(1) = 103.3(2)°]. The bond lengths Au(1)–S(3) = 2.303(1), Au(1)–P(1) = 2.262(1), and C(61)–S(3) = 1.77(1) Å are typical for linear phosphine gold-thiolate complexes [3–10,40–44], and the gold atoms have approximately linear stereochemistry, with P(1)–Au(1)–S(3) = 176.2(1)°. The hinge angle C(54)–S(1)–C(64) = 102.2°, with



Scheme 5. The dithiolate complexes **13**.



Scheme 6. The polyether dithiolate complexes **14**.

aryl rings twisted by 37.1° and 128.1° about the plane defined by the sulfur bridge and the two *ipso* carbon atoms. These angles are similar to those in the acetylide complex $[S(4\text{-}C_6H_4OCH_2CCAu)_2(Ph_2P(CH_2)_4PPh_2)]$, which has the hinge angle C–S–C = 104.3(3)° and aryl twist angles of 1.1° and 97.2° [45]. The closest intramolecular approach of gold atoms in complex **12d** is 8.33 Å, giving a slightly wider ring than in the diacetylide derivatives. The shortest intermolecular Au···Au distance is 6.05 Å, indicating that no aurophilic interactions are present in the solid state structure of complex **12d**.

Complexes **8g*** and **9g*** have similar polymeric structures. In complex **8g***, Fig. 2, each gold atom is linearly

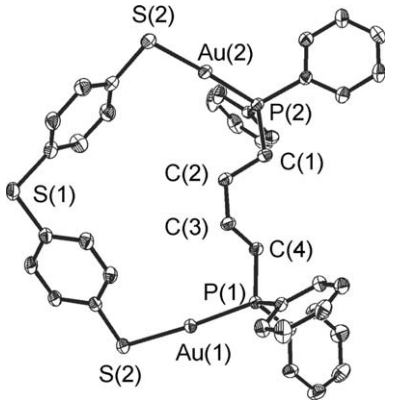


Fig. 1. A view of the structure of complex **12d**. Selected bond lengths (Å) and angles (°): Au(1)–P(1), 2.262(1); Au(1)–S(3), 2.303(1); Au(2)–P(2), 2.263(1); Au(2)–S(2), 2.298(1); S(3)–C(61), 1.770(5); S(2)–C(51), 1.775(5); S(1)–C(54), 1.761(5); S(1)–C(64), 1.779(5); P(1)–Au(1)–S(3), 176.21(5); P(2)–Au(2)–S(2), 176.02(5); C(61)–S(3)–Au(1), 103.3(2); C(51)–S(2)–Au(2), 103.0(2); C(54)–S(1)–C(64), 102.2(2).

coordinated to a phosphine and thiolate ligand with angle P–Au–S = 178.1(1)°, and the pitch of the polymer is 20.99 Å. There is an inversion center in the middle of the hydroquinone ring, resulting in equivalency of the thioglycol chains on either side. The diphosphine has the symmetry-imposed *anti* conformation, with dihedral angle Au–P(1)–P(1A)–Au(A) = 180°. The plane of the hydroquinone ring is oriented orthogonal to the P···P axis, resulting in a spiraling chain structure. The association between neighboring polymer chains occurs through π-stacking between phenyl groups and through weak intermolecular Au···S (3.70 Å) and S···S (3.60 Å) interactions. The diphosphine P···P bite distances of 4.49 Å is too long to

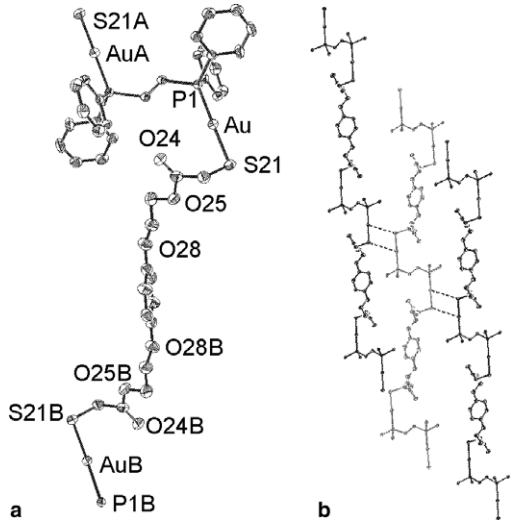


Fig. 2. Views of the structure of complex **8g***: (a) part of a single polymer chain and (b) the association with neighboring chains. Selected bond lengths (Å) and angles (°): Au–P(1), 2.256(2); Au–S(21), 2.296(3); S(21)–C(22), 1.80(1); C(23)–O(24), 1.17(1); C(23)–O(25), 1.39(2); P(1)–Au–S(21), 178.1(1); C(22)–S(21)–Au, 103.6(4); O(24)–C(23)–O(25), 122(1).

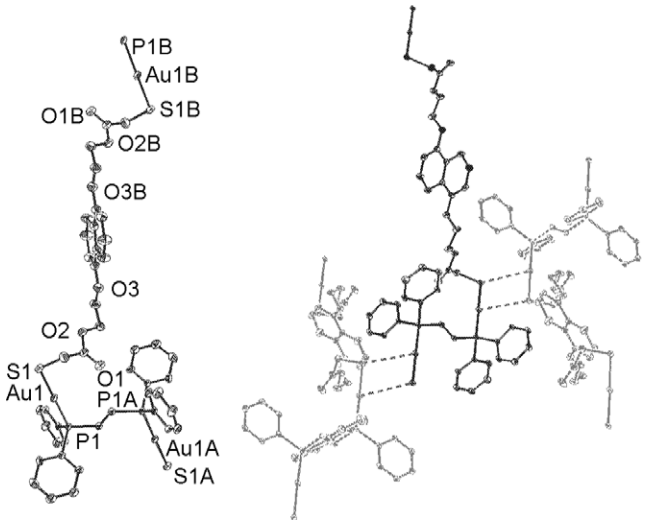


Fig. 3. Views of the structure of complex **9g***, showing a single polymer chain and the association between polymer chains. Selected bond distances and angles: Au(1)–P(1), 2.257(3); Au(1)–S(1), 2.300(3); S(1)–C(1), 1.80(1); O(2)–C(2), 1.34(2); C(3)–C(4), 1.45(2); O(2)–C(3), 1.47(1); O(3)–C(5), 1.37(1); C(2)–O(1), 1.22(1); O(3)–C(4), 1.47(2); P(1)–Au(1)–S(1), 178.9(1), C(1)–S(1)–Au(1), 104.4(5).

allow aurophilic interactions between the coordinated gold atoms (intrachain Au···Au = 4.95 Å). Alternating chains align in a criss-cross pattern in the lattice (Fig. 2b).

Complex **9g*** forms a similar stretched one-dimensional polymer, with a pitch of 21.74 Å, as shown in Fig. 3. The chains connecting the thiolate donor to the naphthalene bridge are helical, with each pair having opposite helicity. The packing of the polymers is similar to **8g***, with individual chains linked through Au···S, S···S, and π–π intermolecular interactions, with interchain distances Au···S = 3.53 Å and S···S = 3.61 Å. The interchain gold···gold distance of 4.72 Å is much too long to represent an aurophilic interaction.

3. Conclusions

The dithiolate bridged gold macrocycles of composition $[Ar(OCH_2CH_2O_2CCH_2SAu)_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$ and $[(-CH_2O_2CCH_2SAu)_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$ with $n = 1$–6 have been prepared. The ring sizes range from 15-membered in **13a** to 44-membered in **14f**. The structure of one example in the solid state, **12d**, has been determined but the less rigid complexes incorporating ester and ether groups did not crystallize well. Nevertheless, they can be assigned macrocyclic structures in solution based on the NMR data and, in some cases, support from ESI-MS data. It is not certain if the macrocyclic structures are maintained in the solid state.

Polymeric gold(I) thiolate complexes are often insufficiently soluble to allow crystallization, but the presence of the flexible ether and ester units in the organic backbone has proved to be useful in allowing crystalline polymers of gold(I) with diphosphine and dithiolate ligands to be obtained. The novel coordination polymers **8g*** and **9g*** (Figs. 2 and 3) were prepared using the diphosphine ligand *trans*-bis(diphenylphosphino)ethylene, in combination with dithiols $[Ar(OCH_2CH_2O_2CCH_2SH)_2]$, with $Ar = C_6H_4$ or $C_{10}H_6$. The ligand *trans*-$Ph_2PCH{=}CHPPh_2$ has a natural tendency to adopt the *anti* conformation of the two PPh_2 units, and this favors the polymer over the macrocycle, even in combination with the highly flexible dithiolate ligands used in this work. These polymeric complexes have high thermal stability, and decompose only on heating to about 280 °C, leaving a residue of metallic gold.

4. Experimental

The reagents 1,5-$C_{10}H_6(OCH_2CH_2OH)_2$, 1,4-$C_6H_4(OCH_2CH_2OH)_2$, 4,4′-$C_6H_4C_6H_4(OCH_2CH_2OH)_2$, $CMe_2(C_6H_4OCH_2CH_2OH)_2$ and 4,4′-$C_6H_4C_6H_4\{(OCH_2CH_2)_3OH\}_2$ were prepared according to the literature methods [31,32,46]. Subsequent preparation of the new dithiolate ligands followed the known general procedure [33]. The gold(I) diphosphine complexes were prepared following standard protocols [13,20].

NMR spectra were recorded using a Varian Mercury 400 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts are reported relative to TMS, while ^{31}P chemical shifts are reported relative to an 85% H_3PO_4 external standard. All reactions involving gold reagents were performed in darkened flasks.

$[1,5\text{-}C_{10}H_6(OCH_2CH_2O_2CCH_2SH)_2]$ (**2**). 1,5-$C_{10}H_6(OCH_2CH_2OH)_2$ (2.50 g, 10.07 mmol) and TsOH (0.639 g, 3.37 mmol) were dissolved in toluene (100 mL). Excess $MgSO_4$ (~2 g) and mercaptoacetic acid (2.10 mL, 30.21 mmol) were added and the dark brown mixture refluxed for 4 h. The mixture was filtered, and the filtrate was washed sequentially with saturated aqueous $NaHCO_3$ and H_2O. The organic fraction was dried with $MgSO_4$, filtered, and the solvent removed. The residue was washed with ether and collected by filtration. Yield: 2.50 g, 63%. mp 97–98 °C. NMR in $CDCl_3$: $\delta(^1H) = 7.87$, 6.84 [d, 2H, $^3J(HH) = 8$ Hz, *o*,*p*-ArH], 7.39 [t, 2H, $^3J(HH) = 8$ Hz, *m*-ArH], 4.64 [t, 4H, $^3J(HH) = 5$ Hz, CH_2CO_2], 4.35 [t, 4H, $^3J(HH) = 5$ Hz, $ArOCH_2$], 3.31 [d, 4H, $^3J(HH) = 8$ Hz, CH_2S], 2.02 [t, 2H, $^3J(HH) = 8$ Hz, SH]; $\delta(^{13}C)$ 171.19 (C═O), 154.18 (*ipso* C–O), 126.90 (*ipso* C–C), 125.49 (*m*-ArH), 115.14, 106.04 (*o*,*p*-ArH), 66.34 ($ArOCH_2$), 64.13 (CH_2CO_2), 26.71 (CH_2SH). *Anal*. Calc. for $C_{18}H_{20}O_6S_2$: C, 54.53; H, 5.08. Found: C, 55.01; H, 5.18%. EI-MS, $m/z = 396.070$; calcd for $C_{18}H_{20}O_6S_2$: 396.070.

Similarly prepared were the following: [1,4-$C_6H_4(OCH_2CH_2O_2CCH_2SH)_2$] (**1**). Yield: 88%. mp 78–79 °C. NMR in $CDCl_3$: $\delta(^1H) = 6.84$ [s, 4H, ArH], 4.45 [t, 4H, $^3J(HH) = 4$ Hz, CH_2CO_2], 4.13 [t, 4H, $^3J(HH) = 4$ Hz, $ArOCH_2$], 3.29 [d, 4H, $^3J(HH) = 8$ Hz, CH_2S], 2.01 [t, 2H, $^3J(HH) = 8$ Hz, SH]; $\delta(^{13}C) = 171.13$ (C═O), 153.16 (*ipso* C), 115.94 (ArH), 66.63 ($ArOCH_2$), 64.27 (CH_2CO_2), 26.67 (CH_2SH). *Anal*. Calc. for $C_{14}H_{18}O_6S_2$: C, 48.54; H,

5.24. Found: C, 49.05; H, 5.52%. EI-MS, $m/z = 346.054$; calcd for $C_{14}H_{18}O_6S_2$: 346.054. [4,4′-$C_6H_4C_6H_4$($OCH_2CH_2O_2CCH_2SH)_2$] (**3**). Yield: 75%. mp 102–103 °C. NMR in $CDCl_3$: $\delta(^1H) = 7.41$ [d, $^3J(HH) = 9$ Hz, 4H, *m*-Ar], 6.90 [d, $^3J(HH) = 9$ Hz, 4H, *o*-Ar], 4.45 [t, $^3J(HH) = 5$ Hz, 4H, CH_2O], 4.16 [t, $^3J(HH) = 5$ Hz, 4H, $ArOCH_2$], 3.25 [d, $^3J(HH) = 8$ Hz, CH_2S], 1.96 [t, $^3J(HH) = 8$ Hz, 2H, SH]; $\delta(^{13}C)$ 171.16 (C=O), 157.76 (*ipso* C–O), 134.11 (*ipso* C–C), 128.06 (*m*-Ar) 115.12 (*o*-Ar), 66.02 ($ArOCH_2$), 64.22 (CH_2O), 26.68 (CH_2SH). *Anal*. Calc. for $C_{20}H_{22}O_6S_2$: C, 56.85; H, 5.25. Found: C, 56.43; H, 5.05%. EI-MS, $m/z = 422.085$; calcd for $C_{20}H_{22}O_6S_2$: 422.085. [CMe_2{4-C_6H_4($OCH_2CH_2O_2CCH_2SH$)}$_2$] (**4**). Yield: 82%. NMR in $CDCl_3$: $\delta(^1H)$ 7.14 [d, $^3J(HH) = 9$ Hz, 4H, *m*-Ar], 6.81 [d, $^3J(HH) = 9$ Hz, 4H, *o*-Ar], 4.48 [t, $^3J(HH) = 5$ Hz, 4H, CH_2O], 4.17 [t, $^3J(HH) = 5$ Hz, 4H, $ArOCH_2$], 3.29 [d, $^3J(HH) = 8$ Hz, CH_2S], 2.01 [t, $^3J(HH) = 8$ Hz, 2H, SH], 1.63 [s, 6H, CMe_2]. [4,4′-$C_6H_4C_6H_4${$(OCH_2CH_2)_3OCOCH_2SH$}$_2$] (**7**). Yield: 48%. mp 79–80 °C. NMR in $CDCl_3$: $\delta(^1H) = 7.46$ [d, $^3J(HH) = 8$ Hz, 4H, *m*-Ar], 6.96 [d, $^3J(HH) = 8$ Hz, 4H, *o*-Ar], 4.30 [t, $^3J(HH) = 5$ Hz, 4H, CH_2O], 4.16 [t, $^3J(HH) = 5$ Hz, 4H, CH_2O], 3.87 [t, $^3J(HH) = 5$ Hz, 4H, CH_2O], 3.74 [t, $^3J(HH) = 5$ Hz, 8H, CH_2O], 3.70 [t, $^3J(HH) = 5$ Hz, 4H, $ArOCH_2$], 3.28 [d, $^3J(HH) = 8$ Hz, CH_2S], 2.01 [t, $^3J(HH) = 8$ Hz, 2H, SH]; $\delta(^{13}C) = 171.16$ (C=O), 158.08 (*ipso* C–O), 133.80 (*ipso* C–C), 127.92 (*m*-Ar) 115.08 (*o*-Ar), 71.06 ($ArOCH_2$), 70.90, 70.06, 69.20, 67.71, 64.97 (CH_2O), 26.71 (CH_2SH). EI-MS, *m*/*z*: 598.189; calcd for $C_{20}H_{22}O_6S_2$: 598.189.

[1,4-C_6H_4($OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2PCH_2PPh_2$)] (**8a**). To a solution of [Au_2Cl_2(μ-$Ph_2PCH_2PPh_2$)] (0.300 g, 0.35 mmol) in CH_2Cl_2 (10 mL), a solution of silver trifluoroacetate (0.161 g, 0.70 mmol) was added in MeOH (2 mL). The reaction mixture was stirred for 30 min, then filtered through celite to remove AgCl. Dithiol **1** (0.122 g, 0.35 mmol) in CH_2Cl_2 (2 mL) was added. The solution was stirred for 3 h, then the product was precipitated by addition of pentane (100 mL). The resulting colorless powder was collected by filtration and washed with acetone and ether. Yield: 0.234 g, 59%. NMR in CD_2Cl_2: $\delta(^1H) = 6.8$–7.3 [m, 20H, Ph], 6.70 [s, 4H, ArH], 4.30 [s, 4H, CH_2CO_2], 3.95 [s, 4H, $ArOCH_2$], 3.75 [s, 4H, CH_2S]; 3.65 [s, 2H, CH_2P]. $\delta(^{31}P) = 30.40$ (s). *Anal*. Calc. for $C_{39}H_{38}Au_2O_6P_2S_2$: C, 41.72; H, 3.41. Found: C, 41.38; H, 3.41%.

Similarly, by use of the appropriate diphosphine ligand, the following were prepared: [1,4-C_6H_4($OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2PCH_2CH_2PPh_2$)] (**8b**). Yield: 35%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40$–7.70 [m, 20H, Ph], 6.50 [s, 4H, ArH], 4.35 [s, 4H, CH_2CO_2], 3.94 [s, 4H, $ArOCH_2$], 3.53 [s, 4H, CH_2S]; 2.74 [m, 4H, CH_2P]. $\delta(^{31}P) = 34.55$ (s). *Anal*. Calc. for $C_{40}H_{40}Au_2O_6P_2S_2$: C, 42.26; H, 3.55. Found: C, 41.84; H, 3.23%. [1,4-C_6H_4($OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$)] (**8c**). Yield: 84%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40$–7.70 [m, 20H, Ph], 6.68 [s, 4H, ArH], 4.31 [t, 4H, $^3J(HH) = 4$ Hz, CH_2CO_2], 4.01 [t, 4H, $^3J(HH) = 4$ Hz, $ArOCH_2$], 3.54 [s, 4H, CH_2S], 2.82 [m, 4H, CH_2P], 1.88 [m, 2H, CH_2]; $\delta(^{31}P) = 29.78$ (s). *Anal*. Calc. for $C_{41}H_{42}Au_2O_6P_2S_2$: C, 42.79; H, 3.68. Found: C, 42.19; H, 3.39%. [1,4-C_6H_4($OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] (**8d**). Yield: 73%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40$–7.61 [m, 20H, Ph], 6.59 [s, 4H, ArH], 4.32 [t, 4H, $^3J(HH) = 5$ Hz, CH_2CO_2], 3.96 [t, 4H, $^3J(HH) = 5$ Hz, $ArOCH_2$], 3.64 [s, 4H, CH_2S], 2.41 [m, 4H, CH_2P], 1.77 [m, 4H, CH_2]. $\delta(^{31}P) = 33.44$ (s). *Anal*. Calc. for $C_{42}H_{44}Au_2O_6P_2S_2$: C, 43.31; H, 3.81. Found: C, 42.89; H, 3.47%.

[1,4-C_6H_4($OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_5PPh_2$)] (**8e**). Yield: 90%. NMR in CD_2Cl_2: $\delta(^1H) = 7.45$–7.69 [m, 20H, Ph], 6.67 [s, 4H, ArH], 4.35 [t, 4H, $^3J(HH) = 5$ Hz, CH_2CO_2], 4.04 [t, 4H, $^3J(HH) = 5$ Hz, $ArOCH_2$], 3.62 [s, 4H, CH_2S], 2.45 [m, 4H, CH_2P], 1.83 [m, 2H, CH_2], 1.59 [m, 4H, CH_2]. $\delta(^{31}P) = 32.63$ (s). *Anal*. Calc. for $C_{43}H_{46}Au_2O_6P_2S_2$: C, 43.81; H, 3.91. Found: C, 43.43; H, 3.59%. [1,4-C_6H_4($OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_6PPh_2$)] (**8f**). Yield: 69%. NMR in CD_2Cl_2: $\delta(^1H) = 7.43$–7.69 [m, 20H, Ph], 6.69 [s, 4H, ArH], 4.35 [t, 4H, $^3J(HH) = 5$ Hz, CH_2CO_2], 4.03 [t, 4H, $^3J(HH) = 5$ Hz, $ArOCH_2$], 3.68 [s, 4H, CH_2S], 2.42 [m, 4H, CH_2P], 1.64 [m, 4H, CH_2], 1.48 [m, 4H, CH_2]. $\delta(^{31}P) = 34.90$ (s). *Anal*. Calc. for $C_{40}H_{38}Au_2O_6P_2S_2$: C, 44.30; H, 4.06. Found: C, 43.80; H, 3.70%. [1,4-C_6H_4($OCH_2CH_2O_2CCH_2SAu)_2$(μ-*trans*-$Ph_2PCH{=}CHPPh_2$)]$_n$ (**8g**). Yield: 95%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40$–7.62 [m, 20H, Ph], 7.39 [t, 2H, $^2J(HP) = 18$ Hz, =CHP], 6.53 [s, 4H, ArH], 4.23 [t, 4H, $^3J(HH) = 5$ Hz, CH_2CO_2], 3.93 [t, 4H, $^3J(HH) = 5$ Hz, $ArOCH_2$], 3.58 [s, 4H, CH_2S]. $\delta(^{13}C) = 173.54$ (C=O), 152.71 (*ipso* C), 133.96, 132.42 (=CH, $J(PC) = 155$ Hz), 129.75 (CH_2S), 116.41 (ArH), 66.97 ($ArOCH_2$), 62.95 (CH_2CO_2). $\delta(^{31}P) = 35.68$ (s). *Anal*. Calc. for $C_{40}H_{38}Au_2O_6P_2S_2$: C, 42.34; H, 3.38. Found: C, 41.71; H, 3.15%. Crystals were grown by slow diffusion of petroleum ether into a solution in CH_2Cl_2.

[1,5-$C_{10}H_6$($OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2PCH_2PPh_2$)] (**9a**). To a solution of [Au_2Cl_2(μ-$Ph_2PCH_2PPh_2$)] (0.250 g, 0.29 mmol) in CH_2Cl_2(10 mL), a solution of silver trifluoroacetate (0.136 g, 0.59 mmol) was added in MeOH (2 mL). The reaction mixture was stirred for 30 min, then filtered through celite to remove AgCl. Dithiol **2** (0.117 g, 0.29 mmol) in CH_2Cl_2 (2 mL) was added. The solution was stirred for 3 h, then the product was precipitated by addition of pentane (100 mL). The resulting colorless powder was collected by filtration and washed with acetone and ether. Yield: 0.272 g, 79%. NMR in CD_2Cl_2: $\delta(^1H) = 7.20$–7.45 [m, 20H, Ph], 7.68, 6.55 [m, 2H, ArH], 7.11 [m, 2H, ArH], 4.49 [s, 4H, CH_2CO_2], 4.13 [s, 4H, $ArOCH_2$], 3.85 [s, 4H, CH_2S], 3.65 [m, 2H, CH_2P]; $\delta(^{31}P) = 30.77$ (s). *Anal*. Calc. for $C_{43}H_{42}Au_2O_6P_2S_2$: C, 43.96; H, 3.60. Found: C, 43.26; H, 3.14%.

Similarly prepared, using the appropriate diphosphine derivative, were the following: [1,5-$C_{10}H_6$($OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_2PPh_2$)] (**9b**). Yield: 57%. NMR in CD_2Cl_2: $\delta(^1H) = 7.34$–7.60 [m, 20H, Ph], 7.82, 6.54 [d, 2H, $^3J(HH) = 8$ Hz, ArH], 7.17 [t, 2H,

^3J(HH) = 8 Hz, ArH], 4.41 [s, 4H, CH_2CO_2], 4.09 [s, 4H, $ArOCH_2$], 3.69 [s, 4H, CH_2S], 2.61 [m, 4H, CH_2P]. $\delta(^{31}P) = 35.46$ (s). *Anal*. Calc. for $C_{44}H_{44}Au_2O_6P_2S_2$: C, 44.45; H, 3.73. Found: C, 43.90; H, 3.51%. [1,5-$C_{10}H_6(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$)] (**9c**). Yield: 83%. NMR in CD_2Cl_2: $\delta(^1H) = 7.38$–7.59 [m, 20H, Ph], 7.82, 6.39 [d, 2H, ^3J(HH) = 8 Hz, ArH], 7.08 [t, 2H, ^3J(HH) = 8 Hz, ArH], 4.49 [s, 4H, CH_2CO_2], 4.08 [s, 4H, $ArOCH_2$], 3.56 [s, 4H, CH_2S], 2.29 [m, 4H, CH_2P], 1.53 [m, 2H, CH_2]. $\delta(^{31}P) = 31.27$ (s). *Anal*. Calc. for $C_{45}H_{46}Au_2O_6P_2S_2$: C, 44.93; H, 3.85. Found: C, 44.62, H, 3.77%. [1,5-$C_{10}H_6(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] (**9d**). Yield: 69%. NMR in CD_2Cl_2: $\delta(^1H) = 7.39$–7.59 [m, 20H, Ph], 7.79, 6.35 [d, 2H, ^3J(HH) = 8 Hz, ArH], 7.11 [t, 2H, ^3J(HH) = 8 Hz, ArH], 4.47 [s, 4H, CH_2CO_2], 4.06 [s, 4H, $ArOCH_2$], 3.63 [s, 4H, CH_2S], 2.08 [m, 4H, CH_2P], 1.47 [m, 4H, CH_2]. $\delta(^{31}P) = 34.37$ (s). *Anal*. Calc. for $C_{46}H_{48}Au_2O_6P_2S_2$: C, 45.40; H, 3.98. Found: C, 45.06, H, 3.84%. [1,5-$C_{10}H_6(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_5PPh_2$)] (**9e**). Yield: 84%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40$–7.63 [m, 20H, Ph], 7.85, 6.55 [d, 2H, ^3J(HH) = 8 Hz, ArH], 7.18 [t, 2H, ^3J(HH) = 8 Hz, ArH], 4.48 [s, 4H, CH_2CO_2], 4.13 [s, 4H, $ArOCH_2$], 3.57 [s, 4H, CH_2S], 2.10 [m, 4H, CH_2P], 1.53 [m, 6H, CH_2]. $\delta(^{31}P) = 34.63$ (s). *Anal*. Calc. for $C_{47}H_{50}Au_2O_6P_2S_2$: C, 45.86; H, 4.09. Found: C, 45.37; H, 3.87%. [1,5-$C_{10}H_6(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_6PPh_2$)] (**9f**). Yield: 56%. NMR in CD_2Cl_2: $\delta(^1H)$ 7.45–7.66 [m, 20H, Ph], 7.82, 6.39 [d, 2H, ^3J(HH) = 8 Hz, ArH], 7.15 [t, 2H, ^3J(HH) = 8 Hz, ArH], 4.49 [s, 4H, CH_2CO_2], 4.08 [s, 4H, $ArOCH_2$], 3.61 [s, 4H, CH_2S]; 2.10 [m, 4H, CH_2P], 1.5 [m, 8H, CH_2]. $\delta(^{31}P) = 35.26$ (s). *Anal*. Calc. for $C_{48}H_{52}Au_2O_6P_2S_2$: C, 46.31; H, 4.21. Found: C, 46.05; H, 3.97%. [1,5-$C_{10}H_6$-($OCH_2CH_2O_2$*CCH*$_2$SAu)$_2$(μ-*trans*-$Ph_2PCH{=}CHPPh_2$)]$_n$ (**9g**). Yield: 88%. NMR in $CDCl_3$: $\delta(^1H) = 7.30$–7.50 [m, 20H, Ph], 7.67, 6.45 [d, 2H, ^3J(HH) = 8 Hz, ArH], 7.05 [t, 2H, ^3J(HH) = 8 Hz, ArH], 7.10 [t, ^2J(HP) = 19 Hz, 2H, =CHP], 4.32 [s, 4H, CH_2CO_2], 4.06 [s, 4H, $ArOCH_2$], 3.53 [s, 4H, CH_2S]. $\delta(^{13}C) = 171.20$ (C=O), 154.07 (*ipso* C–O), 133.95, 132.40 (=CHP, J(PC) = 156 Hz), 129.72 (CH_2SAu), 126.83 (*ipso* C–C), 125.38 (*m*-ArH), 115.50, 106.40 (*o*,*p*-ArH), 66.71 ($ArOCH_2$), 63.30 (CH_2CO_2). $\delta(^{31}P) = 34.97$ (s). *Anal*. Calc. for $C_{44}H_{42}Au_2O_6P_2S_2 \cdot CH_2Cl_2$: C, 42.50; H, 3.49. Found: C, 42.01; H, 3.21%. Crystals of [$C_{10}H_6(OCH_2CH_2O_2CCH_2SAu)_2$(μ-dppee)] · CH_2Cl_2 were grown by slow diffusion of ether into a concentrated solution in CH_2Cl_2.

[4,4′-$C_6H_4C_6H_4(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2PCH_2PPh_2$)] (**10a**). To a solution of [Au_2Cl_2(μ-$Ph_2PCH_2PPh_2$)] (0.300 g, 0.35 mmol) in CH_2Cl_2(10 mL), a solution of silver trifluoroacetate (0.161 g, 0.70 mmol) was added in MeOH (2 mL). The reaction mixture was stirred for 30 min, then filtered through celite to remove AgCl. Dithiol **3** (0.134 g, 0.35 mmol) in CH_2Cl_2 (2 mL) was added. The solution was stirred for 3 h, then the product was precipitated by addition of pentane (100 mL). The resulting colorless powder was collected by filtration and washed with acetone and ether. Yield: 0.334 g, 82%. The compound was insoluble in common organic solvents. *Anal*. Calc. for $C_{45}H_{42}Au_2O_6P_2S_2$: C, 45.08; H, 3.53. Found: C, 44.82; H, 3.28%.

Similarly, by use of the appropriate diphosphine ligand, the following were prepared: [4,4′-$C_6H_4C_6H_4(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_2PPh_2$)] (**10b**). Yield: 71%. NMR in nitrobenzene-d_5: $\delta(^1H) = 7.63$–7.80, 8.10 [m, 20H, Ph], 7.44 [m, 4H, Ar], 7.04 [m, 4H, Ar], 4.80 [s, 4H, CH_2O], 4.53 [s, 4H, $ArOCH_2$], 4.37 [s, 4H, CH_2S], 3.41 [m, 4H, CH_2P]. $\delta(^{31}P) = 31.19$ (s). *Anal*. Calc. for $C_{46}H_{44}Au_2O_6P_2S_2$: C, 45.55; H, 3.66. Found: C, 44.78; H, 3.38%. [4,4′-$C_6H_4C_6H_4(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$)] (**10c**). Yield: 84%. NMR in nitrobenzene-d_5: $\delta(^1H) = 7.61$–7.64, 8.04 [m, 20H, Ph], 7.54 [d, ^2J(HH) = 8 Hz, 4H, Ar], 7.06 [d, ^3J(HH) = 8 Hz, 4H, Ar], 4.76 [s, 4H, CH_2O], 4.40 [s, 4H, $ArOCH_2$], 4.15 [s, 4H, CH_2S], 3.20 [m, 4H, CH_2P], 2.23 [m, 2H, CH_2]. $\delta(^{31}P) = 30.22$ (s). *Anal*. Calc. for $C_{47}H_{46}Au_2O_6P_2S_2$: C, 46.01; H, 3.78. Found: C, 45.32; H, 3.67%. [4,4′-$C_6H_4C_6H_4(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] (**10d**). Yield: 76%. NMR in nitrobenzene-d_5: $\delta(^1H) = 7.61$–7.97 [m, 20H, Ph], 7.53 [d, ^2J(HH) = 8 Hz, 4H, Ar], 7.04 [d, ^3J(HH) = 8 Hz, 4H, Ar], 4.79 [s, 4H, CH_2O], 4.43 [s, 4H, $ArOCH_2$], 4.15 [s, 4H, CH_2S], 2.75 [m, 4H, CH_2P], 2.12 [sbr, 4H, CH_2]. $\delta(^{31}P) = 34.21$ (s). *Anal*. Calc. for $C_{48}H_{48}Au_2O_6P_2S_2$: C, 46.46; H, 3.90. Found: C, 45.89; H, 3.62%. [4,4′-$C_6H_4C_6H_4(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_5PPh_2$)] (**10e**). Yield: 84%. NMR in CD_2Cl_2: $\delta(^1H) = 7.67$–7.45 [m, 20H, Ph], 7.36 [d, ^3J(HH) = 8 Hz, 4H, Ar], 6.83 [d, ^3J(HH) = 8 Hz, 4H, Ar], 4.38 [s, 4H, CH_2O], 4.09 [s, 4H, $ArOCH_2$], 3.62 [s, 4H, CH_2S], 2.44 [m, 4H, CH_2P], 1.76 [m, 2H, CH_2], 1.60 [m, 4H, CH_2]. $\delta(^{31}P) = 33.07$ (s). *Anal*. Calc. for $C_{49}H_{50}Au_2O_6P_2S_2$: C, 46.90; H, 4.02. Found: C, 46.63; H, 3.79%. [4,4′-$C_6H_4C_6H_4(OCH_2CH_2O_2CCH_2SAu)_2$(μ-$Ph_2P(CH_2)_6PPh_2$)] (**10f**). Yield: 58%. NMR in CD_2Cl_2: $\delta(^1H) = 7.68$–7.45 [m, 20H, Ph], 7.35 [d, ^3J(HH) = 8 Hz, 4H, Ar], 6.80 [d, ^3J(HH) = 8 Hz, 4H, Ar], 4.39 [s, 4H, CH_2O], 4.08 [s, 4H, $ArOCH_2$], 3.71 [s, 4H, CH_2S], 2.38 [m, 4H, CH_2P], 1.61 [m, 4H, CH_2], 1.43 [m, 4H, CH_2]; $\delta(^{31}P) = 35.02$ (s). *Anal*. Calc. for $C_{50}H_{52}Au_2O_6P_2S_2$: C, 47.33; H, 4.13. Found: C, 47.64; H, 3.72%. [4,4′-$C_6H_4C_6H_4(OCH_2CH_2O_2CCH_2SAu)_2$(μ-*trans*-$Ph_2PCH{=}$*CHPPh*$_2$)]$_n$ (**10g**). Yield: 59%. NMR in nitrobenzene-d_5: $\delta(^1H) = 7.51$–7.98 [m, 20H, Ph], 7.49 [m, 4H, ArH], 7.08 [m, 6H, ArH and =CHP], 4.83 [s, 4H, CH_2O], 4.42 [s, 4H, $ArOCH_2$], 4.30 [s, 4H, CH_2S]; $\delta(^{31}P) = 30.55$ (s). *Anal*. Calc. for $C_{46}H_{42}Au_2O_6P_2S_2$: C, 45.63; H, 3.50. Found: C, 45.10; H, 3.27%.

[CMe_2{4-$C_6H_4(OCH_2CH_2O_2CCH_2SAu)$}$_2$(μ-$Ph_2PCH_2PPh_2$)] (**11a**). To a solution of [Au_2Cl_2(μ-$Ph_2PCH_2PPh_2$)] (0.200 g, 0.24 mmol) in CH_2Cl_2 (10 mL), a solution of silver trifluoroacetate (0.109 g, 0.47 mmol) was added in MeOH (2 mL). The reaction mixture was stirred for 30 min, then filtered through celite to remove AgCl. Dithiol **4** (0.109 g, 0.24 mmol) in CH_2Cl_2 (2 mL) was added. The solution was stirred for 3 h, then the product was precipi-

tated by addition of pentane (100 mL). The resulting colorless powder was collected by filtration and washed with acetone and ether. Yield: 0.224 g, 77%. NMR in CD_2Cl_2: $\delta(^1H)$ 7.61–7.56, 7.36–7.24 [m, 20H, Ph], 7.04 [d, $^3J(HH) = 8$ Hz, 4H, Ar], 6.70 [d, $^3J(HH) = 8$ Hz, 4H, Ar], 4.35 [s, 4H, CH_2O], 4.06 [s, 4H, $ArOCH_2$], 3.74 [s, 4H, CH_2S], 2.13 [m, 2H, CH_2P], 1.58 [s, 6H, CMe_2]. $\delta(^{31}P) = 30.97$ (s). *Anal.* Calc. for $C_{48}H_{48}Au_2O_6P_2S_2$: C, 46.46; H, 3.90. Found: C, 45.96; H, 3.65%. [CMe_2\{4-$C_6H_4(OCH_2CH_2O_2CCH_2SAu)$\}$_2$(μ-$Ph_2P(CH_2)_2PPh_2$)] (**11b**). Yield: 87%. NMR in CD_2Cl_2: $\delta(^1H) = 7.68$–7.63, 7.46–7.36 [m, 20H, Ph], 6.97 [d, $^3J(HH) = 8$ Hz, 4H, Ar], 6.65 [d, $^3J(HH) = 8$ Hz, 4H, Ar], 4.29 [s, 4H, CH_2O], 4.03 [s, 4H, $ArOCH_2$], 3.66 [s, 4H, CH_2S], 2.79 [m, 4H, CH_2P], 1.56 [s, 6H, CMe_2]. $\delta(^{31}P) = 35.35$ (s). *Anal.* Calc. for $C_{49}H_{50}Au_2O_6P_2S_2$: C, 46.90; H, 4.02. Found: C, 46.64; H, 3.99%.

[CMe_2\{4-$C_6H_4(OCH_2CH_2O_2CCH_2SAu)$\}$_2$(μ-$Ph_2P(CH_2)_3PPh_2$)] (**11c**). Yield: 70%. NMR in CD_2Cl_2: $\delta(^1H) = 7.68$–7.63, 7.46–7.41 [m, 20H, Ph], 7.02 [d, $^3J(HH) = 8$ Hz, 4H, Ar], 6.66 [d, $^3J(HH) = 8$ Hz, 4H, Ar], 4.32 [t, $^3J(HH) = 4$ Hz, 4H, CH_2O], 4.03 [t, $^3J(HH) = 4$ Hz, 4H, $ArOCH_2$], 3.50 [s, 4H, CH_2S], 2.77 [m, 4H, CH_2P], 1.83 [m, 2H, CH_2], 1.58 [s, 6H, CMe_2]. $\delta(^{31}P) = 30.39$ (s). *Anal.* Calc. for $C_{50}H_{52}Au_2O_6P_2S_2$: C, 47.33; H, 4.13. Found: C, 47.37; H, 3.98%. [CMe_2-\{4-$C_6H_4(OCH_2CH_2O_2CCH_2SAu)$\}$_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] (**11d**). Yield: 74%. NMR in CD_2Cl_2: $\delta(^1H) = 7.63$–7.58, 7.47–7.38 [m, 20H, Ph], 6.99 [d, $^3J(HH) = 9$ Hz, 4H, *m*-Ar], 6.64 [d, $^3J(HH) = 9$ Hz, 4H, *o*-Ar], 4.33 [t, $^3J(HH) = 5$ Hz, 4H, CH_2O], 4.03 [t, $^3J(HH) = 5$ Hz, 4H, $ArOCH_2$], 3.57 [s, 4H, CH_2S], 2.39 [m, 4H, CH_2P], 1.73 [m, 4H, CH_2], 1.58 [m, 2H, CH_2], 1.58 [s, 6H, CMe_2]. $\delta(^{31}P) = 34.38$ (s). *Anal.* Calc. for $C_{51}H_{54}O_6P_2S_2Au_2$: C, 47.74; H, 4.24. Found: C, 47.22; H, 4.28%. [CMe_2\{4-$C_6H_4(OCH_2CH_2O_2CCH_2SAu)$\}$_2$(μ-$Ph_2P(CH_2)_5PPh_2$)] (**11e**). Yield: 89%. NMR in CD_2Cl_2: $\delta(^1H) = 7.67$–7.62, 7.49–7.42 [m, 20H, Ph], 7.04 [d, $^3J(HH) = 8$ Hz, 4H, *m*-Ar], 6.68 [d, $^3J(HH) = 8$ Hz, 4H, *o*-Ar], 4.35 [s, 4H, CH_2O], 4.06 [s, 4H, $ArOCH_2$], 3.60 [s, 4H, CH_2S], 2.45 [m, 4H, CH_2P], 1.80 [m, 2H, CH_2], 1.57 [m, 4H, CH_2], 1.60 [m, 6H, CMe_2]. $\delta(^{31}P) = 32.87$ (s). *Anal.* Calc. for $C_{52}H_{56}Au_2O_6P_2S_2$: C, 48.15; H, 4.35. Found: C, 48.34; H, 4.31%. [CMe_2\{4-$C_6H_4(OCH_2CH_2O_2CCH_2SAu)$\}$_2$(μ-$Ph_2P(CH_2)_6PPh_2$)] (**11f**). Yield: 75%. NMR in CD_2Cl_2: $\delta(^1H) = 7.68$–7.63, 7.50–7.39 [m, 20H, Ph], 7.04 [d, $^3J(HH) = 8$ Hz, 4H, *m*-Ar], 6.69 [d, $^3J(HH) = 8$ Hz, 4H, *o*-Ar], 4.36 [s, 4H, CH_2O], 4.06 [s, 4H, $ArOCH_2$], 3.62 [s, 4H, CH_2S], 2.77 [m, 4H, CH_2], 2.41 [m, 4H, CH_2], 1.46 [sbr, 4H, CH_2], 1.60 [s, 6H, CMe_2]. $\delta(^{31}P) = 30.80$ (s). *Anal.* Calc. for $C_{53}H_{58}O_6P_2S_2Au_2$: C, 48.15; H, 4.35. Found: C, 47.89; H, 4.31%. [CMe_2\{4-$C_6H_4(OCH_2CH_2O_2CCH_2$-$SAu)$\}$_2$(μ-*trans*-$Ph_2PCH{=}CHPPh_2$)]$_n$ (**11g**). Yield: 77%. NMR in CD_2Cl_2: $\delta(^1H) = 7.57$–7.37 [m, 22H, Ph and =CHP], 6.96 [d, $^3J(HH) = 8$ Hz, 4H, *m*-Ar], 6.62 [d, $^3J(HH) = 8$ Hz, 4H, *o*-Ar], 4.26 [s, 4H, CH_2O], 4.03 [s, 4H, $ArOCH_2$], 3.55 [s, 4H, CH_2S], 1.58 [s, 6H, CMe_2]. $\delta(^{31}P) = 35.51$ (s). *Anal.* Calc. for $C_{49}H_{48}O_6P_2S_2Au_2$: C, 46.97; H, 3.86. Found: C, 46.20; H, 3.75%.

[S(4-$C_6H_4SAu)_2$(μ-$Ph_2PCH_2PPh_2$)] (**12a**). To a solution of [Au_2Cl_2(μ-$Ph_2PCH_2PPh_2$)] (0.250 g, 0.29 mmol) in CH_2Cl_2(20 mL), a solution of silver trifluoroacetate (0.136 g, 0.59 mmol) was added in MeOH (2 mL). The reaction mixture was stirred for 30 min, then filtered through celite to remove AgCl. Dithiol **5** (0.074 g, 0.29 mmol) in CH_2Cl_2 (5 mL) was added. The solution was stirred for 3 h, then the product was precipitated by addition of pentane (100 mL). The resulting colorless powder was collected by filtration and washed with acetone and ether. Yield: 0.200 g, 66%. NMR in CD_2Cl_2: $\delta(^1H) = 7.05$–7.65 [m, 24H, Ph, Ar], 6.95 [m, 4H, Ar], 4.46 [m, 2H, CH_2P]. $\delta(^{31}P) = 36.62$ (s). *Anal.* Calc. for $C_{37}H_{30}Au_2P_2S_3$: C, 43.28; H, 2.95. Found: C, 42.77; H, 2.64%.

Similarly, by use of the appropriate diphosphine ligand, the following were prepared: [S(4-$C_6H_4SAu)_2$(μ-$Ph_2P(CH_2)_2$-PPh_2)](**12b**). Yield: 58%. NMR in CD_2Cl_2: $\delta(^1H) = 7.30$–7.50 [m, 24H, Ph, Ar], 6.90 [m, 4H, Ar], 2.80 [m, 4H, CH_2P]; $\delta(^{31}P) = 35.90$ (s). *Anal.* Calc. for $C_{38}H_{32}Au_2P_2S_3$: C, 43.85; H, 3.10. Found: C, 43.52; H, 2.84%. [S(4-$C_6H_4SAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$)] (**12c**). Yield: 36%. NMR in CD_2Cl_2: $\delta(^1H) = 7.31$–7.58 [m, 24H, Ph, Ar], 6.92 [d, 4H, $^3J(HH) = 8$ Hz, Ar], 2.78 [m, 4H, CH_2P], 1.08 [m, 2H, CH_2]; $\delta(^{31}P) = 32.22$ (s). *Anal.* Calc. for $C_{39}H_{34}Au_2P_2S_3$: C, 44.41; H, 3.25. Found: C, 43.50; H, 3.34%.

[S(4-$C_6H_4SAu)_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] (**12d**). Yield: 47%. NMR in CD_2Cl_2: $\delta(^1H) = 7.36$–7.59 [m, 24H, Ph, Ar], 6.93 [d, 4H, $^3J(HH) = 8$ Hz, Ar], 2.36 [m, 4H, CH_2P], 1.71 [m, 4H, CH_2]; $\delta(^{31}P) = 35.29$ (s). *Anal.* Calc. for $C_{40}H_{36}Au_2P_2S_3$: C,44.95; H,3.39. Found: C, 44.43; H, 3.30%. Crystals of [$S(C_6H_4SAu)_2$(μ-dppb)]·$C_6H_5NO_2$ were grown from a solution of nitrobenzene and ether. [S(4-$C_6H_4SAu)_2$(μ-$Ph_2P(CH_2)_5PPh_2$)] (**12e**). Yield: 45%. NMR in CD_2Cl_2: $\delta(^1H) = 7.31$–7.63 [m, 24H, Ph, Ar], 6.97 [d, 4H, $^3J(HH) = 8$ Hz, Ar], 2.40 [m, 4H, CH_2P], 1.63 [m, 4H, CH_2] 1.51 [m, 2H, CH_2]; $\delta(^{31}P) = 33.44$ (s). *Anal.* Calc. for $C_{41}H_{38}Au_2P_2S_3$: C, 45.48; H, 3.54. Found: C, 44.93; H, 3.18%. [S(4-$C_6H_4SAu)_2$(μ-$Ph_2P(CH_2)_6PPh_2$)] (**12f**). Yield: 53%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40$–7.66 [m, 24H, Ph, Ar], 6.99 [d, 4H, $^3J(HH) = 8$ Hz, Ar], 2.39 [m, 4H, CH_2P], 1.59 [m, 4H, CH_2], 1.37 [sbr, 4H, CH_2]; $\delta(^{31}P) = 36.01$ (s). *Anal.* Calc. for $C_{42}H_{40}Au_2P_2S_3$: C, 45.99; H, 3.68. Found: C, 45.37; H, 3.70%. [S(4-$C_6H_4SAu)_2$(μ-*trans*-$Ph_2PCH{=}CHPPh_2$)] (**12g**). Yield: 76%. *Anal.* Calc. for $C_{38}H_{30}Au_2P_2S_3$: C, 43.94; H, 2.91. Found: C, 43.45; H, 2.69%.

[(–$CH_2OCOCH_2SAu)_2$(μ-$Ph_2PCH_2PPh_2$)] (**13a**). To a solution of [Au_2Cl_2(μ-$Ph_2PCH_2PPh_2$)] (0.130 g, 0.15 mmol) in thf (10 mL), a solution of silver trifluoroacetate (0.071 g, 0.31 mmol) was added in MeOH (2 mL). The reaction mixture was stirred for 20 min, then filtered through celite to remove AgCl. Dithiol **6** (27 μL, 0.15 mmol) was added. The solution was stirred for 3 h, then the product was precipitated by addition of pentane (100 mL). The resulting colorless powder was collected by filtration and washed

with acetone and ether. Yield: 0.108 g, 71%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40–7.65$ [m, 20H, Ph], 4.25 [s, 4H, CH_2O], 3.63 [s, 4H, CH_2S], 3.95 [sbr, 2H, CH_2P]. $\delta(^{31}P) = 30.42$ (s). IR(Nujol): $\nu(C{\equiv}O) = 1728\ cm^{-1}$. *Anal.* Calc. for $C_{31}H_{30}Au_2O_4P_2S_2$: C,37.74; H,3.06. Found: C, 37.88; H, 3.03%.

Similarly, by use of the appropriate diphosphine ligand, the following were prepared: [(–$CH_2OCOCH_2SAu)_2$(μ-$Ph_2P(CH_2)_2PPh_2$)] (**13b**). Yield: 77%. NMR in CD_2Cl_2: $\delta(^1H) = 7.45–7.70$ [m, 20H, Ph], 4.23 [s, 4H, CH_2O], 3.55 [s, 4H, CH_2S], 2.83 [m, 4H, CH_2P]. $\delta(^{31}P) = 35.61$ (s). *Anal.* Calc. for $C_{32}H_{32}Au_2O_4P_2S_2$: C, 38.41; H, 3.22. Found: C, 38.68; H, 3.19%. [(–$CH_2OCOCH_2SAu)_2$(μ-$Ph_2P(CH_2)_3P$-Ph_2)] (**13c**). Yield: 79%. NMR in CD_2Cl_2: $\delta(^1H) = 7.45–7.70$ [m, 20H, Ph], 4.15 [s, 4H, CH_2O], 3.45 [s, 4H, CH_2S], 2.80 [m, 4H, CH_2P], 2.02 [m, 2H, CH_2]; $\delta(^{31}P) = 32.19$ (s). *Anal.* Calc. for $C_{33}H_{34}Au_2O_4P_2S_2$: C, 39.06; H, 3.38. Found: C, 38.77; H, 3.26%. [(–$CH_2OCOCH_2SAu)_2$ (μ-$Ph_2P(CH_2)_4PPh_2$)], [**13d** · (dppb)] (**10d**). Yield: 87%. NMR in CD_2Cl_2: $\delta(^1H) = 7.45–7.70$ [m, 20H, Ph], 4.24 [s, 4H, CH_2O], 3.55 [s, 4H, CH_2S], 2.51 [m, 4H, CH_2P], 1.86 [m, 4H, CH_2]; $\delta(^{31}P) = 34.68$ (s). *Anal.* Calc. for $C_{34}H_{36}Au_2O_4P_2S_2$: C, 39.70; H, 3.53. Found: C, 39.53; H, 3.42%. [(–$CH_2OCOCH_2SAu)_2$(μ-$Ph_2P(CH_2)_5PPh_2$)] (**13e**). Yield: 0.208 g, 72%. NMR in CD_2Cl_2: $\delta(^1H) = 7.44–7.71$ [m, 20H, Ph], 4.17 [s, 4H, CH_2O], 3.51 [s, 4H, CH_2S], 2.49 [m, 4H, CH_2P], 1.72 [m, 6H, CH_2]; $\delta(^{31}P) = 34.86$ (s). *Anal.* Calc. for $C_{35}H_{38}Au_2O_4P_2S_2$: C, 40.32; H, 3.67. Found: C, 39.76; H, 3.53%. [(–$CH_2OCOCH_2SAu)_2$(μ-$Ph_2P(CH_2)_6$-PPh_2)] (**13f**). Yield: 85%. NMR in CD_2Cl_2: $\delta(^1H) = 7.45–7.70$ [m, 20H, Ph], 4.23 [s, 4H, CH_2O], 3.52 [s, 4H, CH_2S], 1.65 [m, 4H, CH_2P], 1.54 [m, 8H, CH_2]; $\delta(^{31}P) = 34.79$ (s). *Anal.* Calc. for $C_{36}H_{40}Au_2O_4P_2S_2$: C, 40.92; H, 3.82. Found: C, 40.54; H, 3.92%. [(–$CH_2OCOCH_2SAu)_2$(μ-*trans*-$Ph_2PCH{=}CHP$- Ph_2)] (**13g**). Yield: 0.323 g, 93%. The compound is insoluble in all common organic solvents. *Anal.* Calc. for $C_{32}H_{30}Au_2O_4P_2S_2$: C, 38.49; H, 3.03. Found: C, 38.06; H, 2.86%.

[4,4′-$C_6H_4C_6H_4${$(OCH_2CH_2)_3OCOCH_2SAu$}$_2$(μ-Ph_2P-CH_2PPh_2)] (**14a**). To a solution of [Au_2Cl_2(μ-Ph_2PCH_2-PPh_2)] (0.250 g, 0.29 mmol) in CH_2Cl_2(10 mL), a solution of silver trifluoroacetate (0.136 g, 0.59 mmol) was added in MeOH (2 mL). The reaction mixture was stirred for 30 min, then filtered through celite to remove AgCl. Dithiol **7** (27 μL, 0.15 mmol) was added. The solution was stirred for 3 h., then the product was precipitated by addition of pentane (100 mL). The resulting colorless powder was collected by filtration and washed with ether. Yield: 0.230 g, 57%. NMR in CD_2Cl_2: $\delta(^1H) = 7.21–7.47$ [m, 24H, Ph, ArH], 6.92 [d, 4H, $^3J(HH) = 7$ Hz, ArH], 4.20 [sbr, 4H, CH_2O], 4.10 [sbr, 4H, CH_2O] 3.80 [sbr, 8H, CH_2O] 3.64 [sbr, 8H, CH_2O] 3.62 [s, 4H, CH_2S], 3.60 [m, 2H, CH_2P]; $\delta(^{31}P) = 30.49$ (s). *Anal.* Calc. for $C_{53}H_{58}$- $O_{10}P_2S_2Au_2$: C, 46.30; H, 4.25. Found: C, 45.96; H, 4.03%. [4,4′-$C_6H_4C_6H_4${$(OCH_2CH_2)_3OCOCH_2SAu$}$_2$(μ-$Ph_2P(CH_2)_2$-PPh_2)] (**14b**). Yield: 68%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40–7.64$ [m, 24H, Ph, ArH], 6.93 [d, 4H, $^3J(HH) = 8$ Hz, ArH], 4.28 [m, 4H, CH_2O], 4.11 [m, 8H, CH_2O], 3.80 [m, 4H, CH_2O], 3.71 [m, 4H, CH_2O], 3.62 [m, 4H, CH_2O], 3.57 [s, 4H, CH_2S], 3.09 [m, 4H, CH_2P]. $\delta(^{31}P) = 33.50$ (s). *Anal.* Calc. for $C_{54}H_{60}O_{10}P_2S_2Au_2$: C, 46.69; H, 4.35. Found: C, 46.26; H, 4.15%. [4,4′-C_6H_4- C_6H_4{$(OCH_2$-$CH_2)_3OCOCH_2SAu$}$_2$(μ-Ph_2P- $(CH_2)_3PPh_2$)] (**14c**). Yield: 83%. NMR in CD_2Cl_2: $\delta(^1H) = 7.40–7.68$ [m, 24H, Ph, ArH], 6.91 [d, 4H, $^3J(HH) = 8$ Hz, ArH], 4.11 [m, 8H, CH_2O], 3.79 [t, 4H, $^3J(HH) = 5$ Hz, CH_2O], 3.60 [m, 12H, CH_2O] 3.52 [s, 4H, CH_2S], 2.81 [m, 4H, CH_2P], 1.86 [m, 2H, CH_2]; $\delta(^{31}P) = 29.92$ (s). *Anal.* Calc. for $C_{55}H_{62}O_{10}P_2S_2Au_2$: C, 47.08; H, 4.45. Found: C, 47.39; H, 4.28%. [4,4′-$C_6H_4C_6H_4${$(OCH_2CH_2)_3OCOCH_2$-SAu}$_2$(μ-Ph_2P- $(CH_2)_4PPh_2$)] (**14d**). Yield: 77%. NMR in CD_2Cl_2: $\delta(^1H) = 7.39–7.64$ [m, 24H, Ph, ArH], 6.92 [d, 4H, $^3J(HH) = 9.0$ Hz, ArH], 4.12 [m, 8H, CH_2O], 3.80 [t, 4H, $^3J(HH) = 4.5$ Hz, CH_2O] 3.63 [m, 12H, CH_2O], 3.60 [s, 4H, CH_2S], 2.45 [m, 4H, CH_2P], 1.80 [m, 4H, CH_2]; $\delta(^{31}P) = 33.61$ (s). *Anal.* Calc. for $C_{56}H_{64}O_{10}P_2S_2Au_2$: C, 47.46; H, 4.55. Found: C, 47.88; H, 4.41%. [4,4′-$C_6H_4C_6H_4${$(OCH_2CH_2)_3OCOCH_2SAu$}$_2$(μ-$Ph_2P(CH_2)_5$-PPh_2)] (**14e**). Yield: 75%. NMR in CD_2Cl_2: $\delta(^1H) = 7.42–7.69$ [m, 24H, Ph, ArH], 6.94 [s, 4H, $^3J(HH) = 8$ Hz, ArH], 4.18 [t, 4H, $^3J(HH) = 5$ Hz, CH_2O], 4.13 [t, 4H, $^3J(HH) = 5$ Hz, CH_2O] 3.80 [t, 4H, $^3J(HH) = 5$ Hz, CH_2O] 3.64 [m, 12H, CH_2O], 3.60 [s, 4H, CH_2S], 2.46 [m, 4H, CH_2P], 1.86 [m, 2H, CH_2], 1.60 [m, 4H, CH_2]; $\delta(^{31}P) = 32.70$ (s). *Anal.* Calc. for $C_{58}H_{66}O_{10}P_2S_2Au_2$: C, 47.84; H, 4.65. Found: C, 47.83; H, 4.47%. [4,4′-$C_6H_4C_6H_4${$(OCH_2CH_2)_3OCOCH_2SAu$}$_2$(μ-$Ph_2P(CH_2)_6$-PPh_2)] (**14f**). Yield: 88%. NMR in CD_2Cl_2: $\delta(^1H) = 7.43–7.68$ [m, 24H, Ph, ArH], 6.93 [d, $^3J(HH) = 8$ Hz, ArH], 4.17 [t, 4H, $^3J(HH) = 5$ Hz, CH_2O], 4.11 [t, 4H, $^3J(HH) = 5$ Hz, CH_2O] 3.79 [t, 4H, $^3J(HH) = 5$ Hz, CH_2O] 3.63 [m, 12H, CH_2O], 3.58 [s, 4H, CH_2S], 2.44 [m, 4H, CH_2P], 1.66 [m, 4H, CH_2], 1.50 [m, 4H, CH_2]; $\delta(^{31}P)$ 34.82 (s). *Anal.* Calc. for $C_{59}H_{68}O_{10}P_2S_2Au_2$: C, 48.20; H, 4.74. Found: C, 48.14; H, 4.05%. [4,4′-C_6H_4-C_6H_4{$(OCH_2CH_2)_3OCOCH_2SAu$}$_2$(μ-*trans*-$Ph_2PCH{=}CH$-PPh_2)] (**14g**). Yield: 80%. NMR in CD_2Cl_2: $\delta(^1H)$ 7.40–7.63 [m, 24H, Ph, ArH], 6.93 [s, 4H, $^3J(HH) = 9$ Hz, ArH], 6.96 [t, 2H, $^2J(PH) = 18$ Hz, $=CHP$] 4.12 [m, 4H, CH_2O], 4.07 [m, 4H, CH_2O] 3.80 [m, 4H, CH_2O] 3.58 [m, 16H, CH_2O, CH_2S]; $\delta(^{31}P) = 35.06$ (s). *Anal.* Calc. for $C_{54}H_{58}O_{10}P_2$-S_2Au_2: C, 46.76; H, 4.21. Found: C, 47.05; H, 4.01%.

5. X-ray structure determinations

Single crystals were mounted on glass fibers. Data were collected using a Nonius Kappa CCD diffractometer, using the program COLLECT for data collection, DENZO for cell refinement and data reduction, SCALEPACK for the absorption correction, SHELXTL-NT 6.1 for structure solution by direct methods and least squares refinement [47]. Crystal and experimental details are given in Table 1.

For complex **12d**, all non-hydrogen atoms, including those of the nitrobenzene solvate molecule, were refined

Table 1
Crystal data and experimental details

Complex	**12d** · $PhNO_2$	**8g*** · $2C_2H_4Cl_2$	**9g*** · CH_2Cl_2
Formula	$C_{46}H_{41}Au_2NO_2P_2S_3$	$C_{44}H_{38}Au_2Cl_4O_6P_2S_2$	$C_{45}H_{42}Au_2Cl_2O_6P_2S_2$
Formula weight	1191.85	1324.24	1269.68
T (K)	297(2)	294(2)	200(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2/n$	$P2/n$
Unit cell dimensions			
a (Å)	12.2798(3)	14.8337(8)	16.0701(12)
b (Å)	13.5635(4)	8.3956(4)	8.5562(3)
c (Å)	14.0911(4)	19.2351(10)	19.9827(14)
α (°)	105.296(1)	90	90
β (°)	98.423(2)	98.642(3)	105.700(2)
γ (°)	99.449(2)	90	90
V (Å^3)	2188.24(10)	2368.3(2)	2645.1(3)
Z	2	2	2
D_{calc} (Mg/m^3)	1.809	1.857	1.594
Absorption coefficient (mm^{-1})	6.951	6.614	5.820
F(000)	1152	1276	1228
Number of reflections	26731	25101	10575
Number of independent reflections	10012	4662	5880
Absorption correction	integration	integration	integration
Data/restraints/parameters	10012/0/505	4662/30/301	5880/0/267
Goodness-of-fit on F^2	0.930	0.967	0.947
R_1 [$I > 2\sigma(I)$]	0.0366	0.0548	0.0635
wR_2 [$I > 2\sigma(I)$]	0.0790	0.1285	0.1666

with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms.

In complex **9g***, the centroid of the $C_{10}H_6$ ring, the center of the *trans*-ethylene bond, and the carbon atom of the dichloromethane solvate molecule sit on symmetry elements. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in the calculated geometrical positions. The complex **8g*** was similar. The two dichloroethane solvate molecules were treated with fixed C–Cl and C–C distances.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006. 01.018.

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