Complexes of Gold(I) with a Chiral Diphosphine Ligand: A Polymer with Both Au···Ag and Ag···Ag Metallophilic Bonds

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Dedicated to Professor Hubert Schmidbaur, the grand master of gold chemistry, on the occasion of his 75th birthday

The chemistry of gold(I) with the ligand binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl is reported. Reaction of $[Au_2Cl_2(\mu\text{-binap})]$ with silver trifluoroacetate gave the corresponding complex $[Au_2(O_2CCF_3)_2(\mu\text{-binap})]$, and crystallization in the presence of excess silver trifluoroacetate gave the unusual syndiotactic polymeric complex $[\{Au_2Ag_2(\mu\text{-}O_2CCF_3)_4(\mu\text{-binap})\}_n]$, which contains both Au···Ag and Ag···Ag metallophilic bonds. The trifluoroacetate ligands in $[Au_2(O_2CCF_3)_2(\mu\text{-binap})]$ can be replaced by nitrogen or phosphorus donor ligands to give complexes $[Au_2(\kappa^1\text{-}4,4'\text{-bipyridine})_2(\mu\text{-binap})](CF_3CO_2)_2$ or *meso*-$[Au_2(\mu\text{-binap})_2](CF_3CO_2)_2$.

Key words: Gold, Diphosphine, Chiral, Aurophilic, Polymer

Introduction

The synthesis and characterization of chiral complexes of gold is a topical subject [1], based on applications in asymmetric catalysis [2, 3], chiral nanoparticles and clusters [4],and stereoregular molecular materials [5]. In studying stereoselective self-assembly of polymeric and oligomeric gold(I) complexes, several complexes of gold(I) both with the ligand binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl were prepared and structurally characterized. The ligand binap has been used extensively in catalysis but less often in materials chemistry [2 – 6]; it usually acts as a chelate [6] but, in its known complexes with gold(I), it acts as a bridging ligand [3, 5]. Thus it had promise for extending studies of coordination macrocycles and polymers of gold(I) by forming chiral derivatives [5, 7, 8]. One of the complexes described below is a mixed gold(I)-silver(I) complex which contains both Au···Ag and Ag···Ag metallophilic bonds in a syndiotactic polymer. The field of metallophilic bonding has been pioneered by the experimental research of Schmidbaur and by the theoretical work of Pyykkö [9], while Schmidbaur has also discovered interesting examples of Au···Ag metallophilic bonds [10] and general interest in metalophilic bonding continues to grow [1, 9 – 13].

Results and Discussion

Synthesis of gold(I) complexes of binap

Some of the synthetic procedures are illustrated in Scheme 1. The complex $[Au_2Cl_2(\mu\text{-binap})]$, **1**, was readily prepared by displacement of dimethylsulfide from $[AuCl(SMe_2)]$ by the phosphorus donors of the binap ligand, by analogy with the method established with other diphosphine ligands [7, 8]. The complexes **1a** and **1b** were prepared by using either *S*-binap or *rac*-binap as ligand. It is noted that the corresponding complex **1c**, with *R*-binap, has been prepared independently by a different route [3]. Reaction of **1b** with silver trifluoroacetate gave insoluble silver chloride and the corresponding digold(I) trifluoroacetate complex **2**. The trifluoroacetate ligands in **2** are bound sufficiently strongly to give a stable complex, but sufficiently weakly that they can be displaced by 4,4′-bipyridine to give the complex $[Au_2(\kappa^1\text{-}4,4'\text{-bipy})_2(\mu\text{-binap})](CF_3CO_2)_2$, **3**. Finally, reaction of **2** with *rac*-binap gave crystals of the complex *meso*-$[Au_2(\mu\text{-binap})_2](CF_3CO_2)_2$, **4a**. Most of the complexes gave singlet resonances in the ^{31}P NMR spectra ($\delta(^{31}P)$ = 24.71, 18.41, and 18.45 in **1**, **2** and **3**, respectively), but complex **4** gave two broader resonances at $\delta(^{31}P)$ = 41.2 and 43.1 in relative ratio 1.5 : 1. The product of the similar reaction using *S*-binap gave only the reso-

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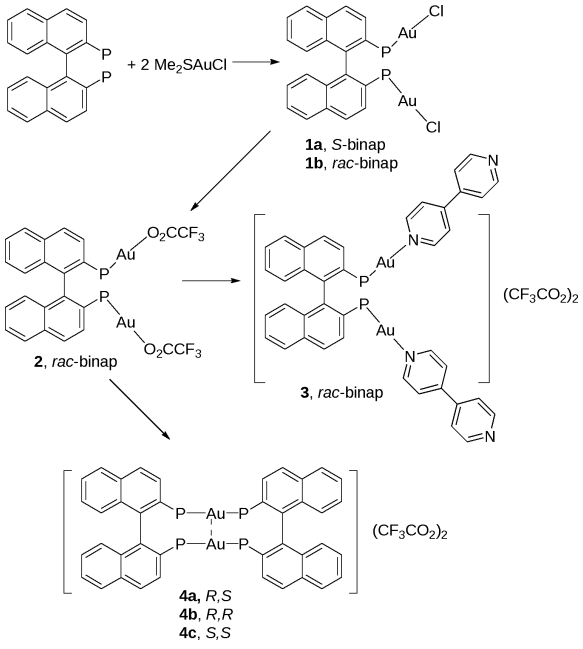


Scheme 1. (P = PPh_2).

nance at $\delta(^{31}P)$ = 43.1, so this resonance is assigned to the *S,S* isomer **4c**. Statistically, the reaction using *rac*-binap would give **4a** : **4b** : **4c** = 2 : 1 : 1 and, because **4b** and **4c** will have identical NMR spectra, this would lead to the presence of two equal-intensity resonances. The observed intensity ratio of 1.5 : 1 for **4a** : **4b** + **4c** indicates a modest selectivity for the *meso*-**4a** over *racemic*-**4b** + **4c**. Crystallization gave only **4a**.

Structures of binap complexes of gold(I)

The structure of the chiral gold(I) complex **1a**, prepared from *S*-binap and [AuCl(SMe_2)], is shown in Fig. 1. The asymmetric unit contains only half of the molecule, with the symmetrically equivalent half generated by a C_2 rotation. Therefore the two AuCl vectors are oriented away from each other in an *anti* conformation. As expected, the gold(I) coordination geometry is approximately linear, with the bond angle P–Au–N = 175.2(1)°. The binaphthyl torsion angle C(2)C(1)C(1A)C(2A) = 98.4(3)°, only slightly distorted from orthogonality. The molecule contains no gold···gold interactions, with an intramolecular contact of 5.42 Å and shortest intermolecular separation of 8.63 Å. The most significant intermolecular contact is a C–H···π interaction involving a C(4)–H(4) unit of each naphthalene ring acting as a donor to a phenyl

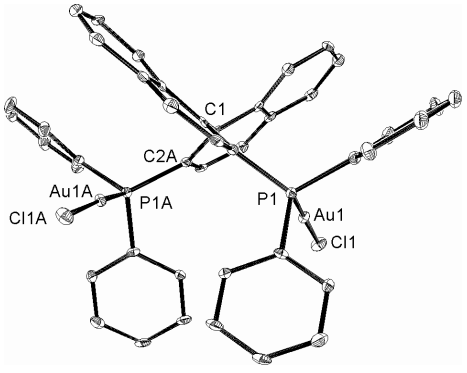


Fig. 1. The structure of complex **1a**. Hydrogen atoms and a dichloromethane molecule are excluded for clarity. Selected bond parameters (Å, deg): Au(1)–Cl(1) 2.282(3), Au(1)–P(1) 2.227(3); P(1)–Au(1)–Cl(1) 175.2(1). Symmetry equivalent half molecules: x, y, z; $1-x, y, 1-z$.

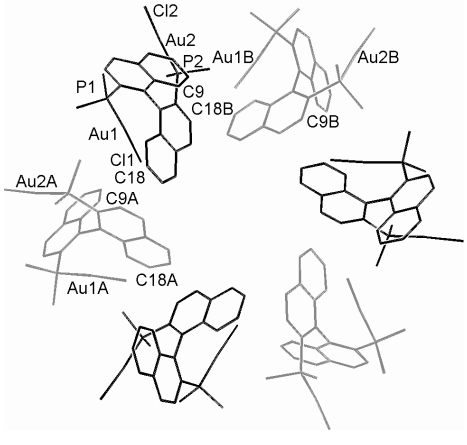


Fig. 2. The supramolecular hexameric structure of complex **1b**. Only the *ipso* carbon atoms of phenyl groups are shown, and solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths and angles (Å, deg): Au(1)–Cl(1) 2.299(2), Au(1)–P(1) 2.235(2), Au(2)–Cl(2) 2.277(3), Au(2)–P(2) 2.232(2); P(1)–Au(1)–Cl(1) 176.64(9), P(2)–Au(2)–Cl(2) 174.77(10).

ring of the neighboring molecule, at a distance of approximately 2.6 Å.

The structure of **1b** is shown in Fig. 2. In this case, the asymmetric unit contains one full molecule of the complex but otherwise the molecular structure is similar to that of **1a**. The rhombohedral unit cell contains eighteen symmetry-related molecules, with nine molecules of each enantiomer. The coordination geometry at gold(I) is approximately linear, with bond angles P–Au–Cl = 174.8(1)° and 176.64(9)° for Au(2) and Au(1), respectively. No aurophilic interaction is present, with the shortest Au···Au con-

tact being the intramolecular distance Au(1)···Au(2) = 5.48 Å. Through significant C–H···π stacking interactions, in which one naphthalene ring of each molecule acts as a donor as well as an acceptor, the molecules are organized in groups of six into large ring structures (Fig. 2). The main intermolecular interaction involves the C(9)H(9)···π interaction between naphthyl groups, with a contact distance of approximately 2.9 Å. The hexamer in Fig. 2 contains 3 molecules of each enantiomer with alternating chirality *RSRSRS*. These rings stack directly on top of one another, creating a small channel which is occupied by disordered solvent molecules. This remarkable difference between the crystal packing of **1a** and **1b** is an excellent example of *chirality-directed self-assembly*, showing how supramolecular structures can be significantly altered by variation of only the chiral features of the components [14].

The structure of complex **2c**, prepared by reaction of **1b** with silver trifluoroacetate, is depicted in Fig. 3. The asymmetric unit contains two similar but independent molecules of the complex. Each molecule is chiral, but a crystallographic center of inversion generates the molecules of opposite chirality, thus giving a racemic mixture within the crystal. The molecular structure is similar to the chloride analogs **1a** and **1b** (Figs. 1 and 2), with approximately linear coordination geometry at gold(I), and with the ligand binaphthyl torsion angle C(11)C(20)C(40)C(31) = 101°.

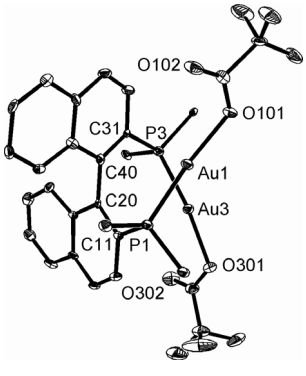


Fig. 3. Molecular structure of one of the two independent molecules of complex **2**. Hydrogen atoms and solvent molecules are omitted and only the *ipso* carbon atoms of the phenyl rings are shown for clarity. Selected bond parameters (Å, deg): Molecule 1: Au(1)–O(101) 2.06(1), Au(1)–P(1) 2.209(5), Au(3)–O(301) 2.09(1), Au(3)–P(3) 2.211(5); O(101)–Au(1)–P(1) 174.0(4), O(301)–Au(3)–P(3) 171.8(4). Molecule 2: Au(2)–O(201) 2.05(1), Au(2)–P(2) 2.220(5), Au(4)–O(401) 2.08(1), Au(4)–P(4) 2.216(5); O(201)–Au(2)–P(2) 177.8(4), O(401)–Au(4)–P(4) 176.3(4).

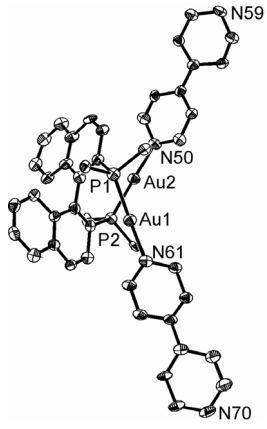
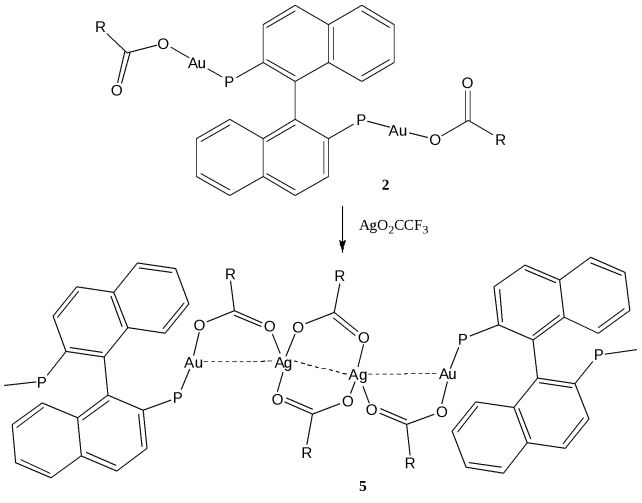


Fig. 4. Structure of the cationic complex **3**. Hydrogen atoms have been omitted, and only the *ipso* carbon atoms of phenyl groups are shown for clarity. Selected bond parameters (Å, deg): Au(1)–N(61) 1.95(3), Au(1)–P(1) 2.174(10), Au(2)–N(50) 1.95(3), Au(2)–P(2) 2.199(9); N(61)–Au(1)–P(1) 174.2(6), N(50)–Au(2)–P(2) 179.0(7).

The intramolecular Au···Au distance, Au(1)Au(3) = 3.966(2) Å, is shorter than analogous distances in **1a** and **1b**, but still outside the range of significant aurophilic attractions.

The structure of complex **3** is shown in Fig. 4. The molecule contains two gold atoms with a bridging binap ligand and with a monodentate 4,4′-bipyridine ligand bound to each gold atom. The coordination at gold(I) is close to the expected linear geometry (P–Au–N = 174.2(6)°, 179.0(7)°). The trifluoroacetate anions are not bound to gold(I), with the closest approaches being Au···O = 3.56 and 4.14 Å, and there is no intramolecular Au···Au contact (Au(1)···Au(2) = 4.66 Å). The primary supramolecular interaction is weak face-to-face π-π stacking between the noncoordinated pyridine rings of adjacent molecules with an interaction distance of approximately 3.5 Å. These interactions occur in a head-to-tail fashion between complexes of the same stereochemical configuration, giving loosely associated isotactic sequences. The opposite enantiomers are generated through crystallographic symmetry in the racemic product.

The structure of the complex [Au_2(μ-*R*-binap)(μ-*S*-binap)](CF_3CO_2)$_2$, **4a**, is shown in Fig. 5. The unit cell contains two similar but independent heterochiral macrocycles, each containing one *R*-binap and one *S*-binap ligand. There is a strong intramolecular aurophilic interaction, with the distance Au(1)···Au(2) = 2.8700(4) Å in one macrocycle and Au(3)···Au(4) = 2.9125(4) Å in the other. The close Au···Au ap-



Scheme 2. P = PPh_2, R = CF_3.

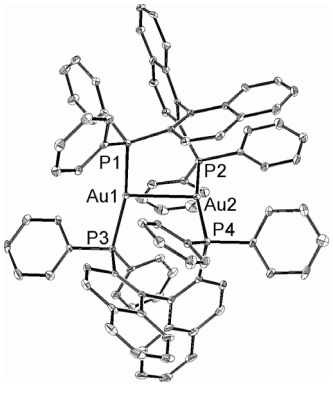


Fig. 5. One of two independent macrocycles in the structure of **4a**. Hydrogen atoms, anions and solvent molecules are omitted for clarity. Selected bond parameters (Å, deg): Molecule 1: Au(1)–P(1) 2.332(2), Au(1)–P(3) 2.328(2), Au(2)–P(2) 2.336(2), Au(2)–P(4) 2.323(2), Au(1)···Au(2), 2.8700(4); P(1)–Au(1)–P(3) 162.06(7), P(2)–Au(2)–P(4) 163.67(7). Molecule 2: Au(3)–P(5) 2.334(2), Au(3)–P(6) 2.343(2), Au(4)–P(7) 2.319(2), Au(4)–P(8) 2.328(2), Au(3)···Au(4) 2.9125(4); P(5)–Au(3)–P(6) 163.12(7), P(7)–Au(4)–P(8) 164.52(7).

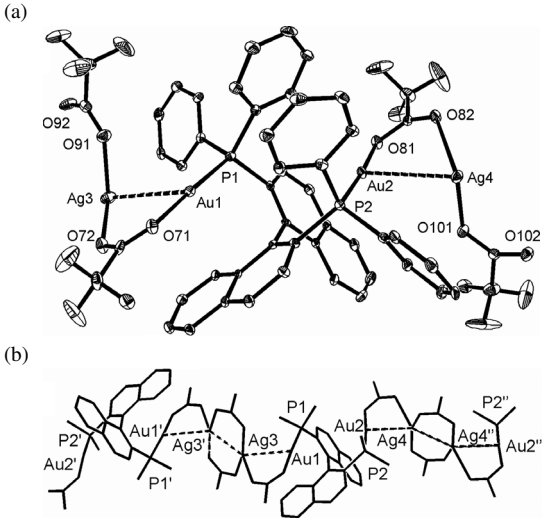
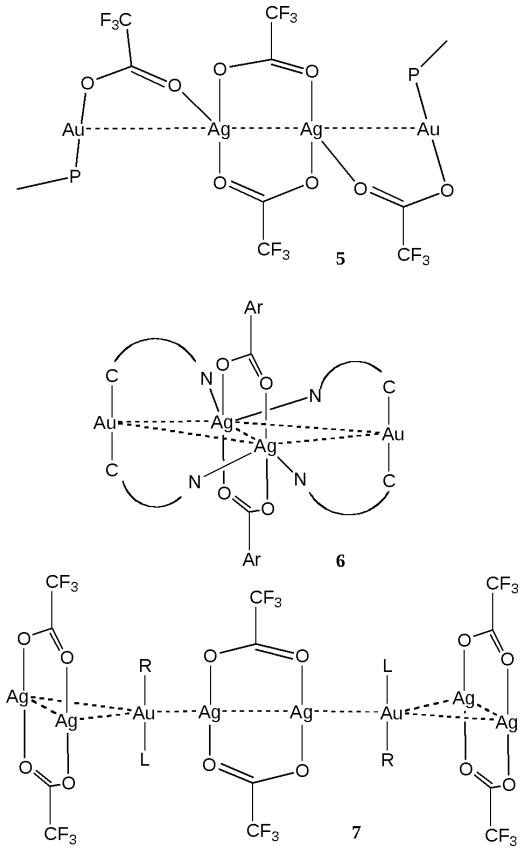


Fig. 6. Structure of the polymeric complex **5**: (a) A view of the asymmetric unit; (b) a section of the polymeric chain with fluorine atoms and all but the *ipso* carbon atoms of phenyl groups omitted for clarity. Selected bond parameters (Å, deg): Au(1)–O(71) 2.058(5), Au(1)–P(1) 2.205(2), Au(1)–Ag(3) 3.2989(9), Au(2)–O(81) 2.066(5), Au(2)–P(2) 2.209(2), Au(2)–Ag(4) 3.0373(8), Ag(3)–O(91) 2.201(6), Ag(3)–O(92A) 2.207(6), Ag(3)–O(72) 2.380(6), Ag(3)–Ag(3A) 2.938(1), Ag(4)–O(101) 2.179(6), Ag(4)–O(102B) 2.191(6), Ag(4)–O(82) 2.500(6), Ag(4)–Ag(4B) 2.973(1); O(71)–Au(1)–P(1) 176.4(2), O(81)–Au(2)–P(2) 175.8(2), O(91)–Ag(3)–O(92A) 161.1(2), O(91)–Ag(3)–O(72) 101.5(2), O(92A)–Ag(3)–O(72) 96.7(2), Ag(3A)–Ag(3)–Au(1) 141.23(4), O(101)–Ag(4)–O(102B) 156.9(2), O(101)–Ag(4)–O(82) 109.5(2), O(102B)–Ag(4)–O(82) 93.4(2), Ag(4B)–Ag(4)–Au(2) 147.78(4).

proaches are accompanied by distortion of the gold(I) centers from linearity, with angles P(1)–Au(1)–P(3) = 162.06(7)° and P(2)–Au(2)–P(4) = 163.67(7)°. There is no association between the anions and the gold atoms, and there are no notable intermolecular interactions.

A polymer with gold(I)-silver(I) metallophilic interactions

The reaction of complex **2** (Scheme 1) with excess silver trifluoroacetate gave the complex *rac*-$[\{Au_2Ag_2(O_2CCF_3)_4(\mu\text{-binap})\}_n]$, **5** (Scheme 2). The ^1H and ^{31}P NMR spectra of **5** were very similar to



Scheme 3. Some complexes with Au···Ag metallophilic bonds.

those of complex **2**, indicating that the complex is largely dissociated in solution. The structure of complex **5** was determined and is shown in Fig. 6.

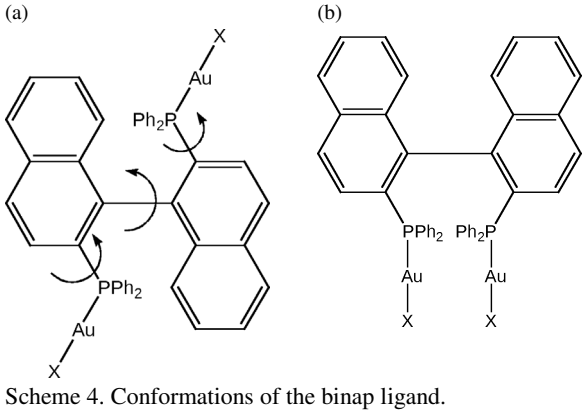
In the structure of complex **5**, there are two non-equivalent $Ag_2(\mu\text{-}O_2CCF_3)_2$ units which bridge between molecules of $[Au_2(O_2CCF_3)_2(\mu\text{-binap})]$ by forming, in each case, a weak Ag–O bond to a carbonyl oxygen atom (Ag(3)–O(72) = 2.380(6), Ag(4)–O(82) = 2.500(6) Å) and a metallophilic Au···Ag bond (Au(1)–Ag(3) 3.2989(9), Au(2)–Ag(4) 3.0373(8) Å). The gold(I) centers (ignoring the metal-metal interactions) are roughly linear (O(71)–Au(1)–P(1) = 176.4(2), O(81)–Au(2)–P(2) 175.8(2)°), while the silver(I) centers have highly distorted trigonal or T-shaped coordination (angles O–Ag–O range from 93.4 – 156.9°).

Fig. 6(b) shows that the complex **5** forms a syndiotactic coordination polymer with alternating *RSRS*··· chirality of the binap ligands. It is an unusual compound, in the sense that it is a polymer with both chiral ligands [5] and with metallophilic bonds [11, 13] as part of the backbone. It should be noted that there are several recent examples of complexes in which $Ag_2(\mu\text{-}O_2CR)_2$ units form metallophilic bonds to gold(I), as illustrated in Scheme 3 [12, 13]. Complex **5** forms roughly linear Au···Ag···Ag···Au linkages, but complex **6**, in which C-N represents a pyridyl-carbene ligand, forms triangular AuAgAg units, while complex **7**, in which R = C_6F_5 and L = $Ph_3P{=}CH_2$, contains both of the above structural units [13h, 13i].

Discussion

The conformation of the binap ligand can change by rotation about either the central binaphthyl C–C bond or about the phosphorus-carbon bonds, as illustrated in Scheme 4. The binaphthyl torsion angle remains fairly constant at approximately 90° in the complexes studied, as discussed above, so the rotation about the phosphorus-carbon bonds is the most important single factor in determining the conformation. A useful parameter to define the binap conformation in the complexes is the Au–P···P–Au torsion angle, which can vary from 180° to 0°, as illustrated in Scheme 4.

The Au–P···P–Au torsion angles for the complexes **1** – **5** range from 37 – 176°, from which it is clear that there is no very large barrier to rotation about the Ph_2P–C bonds. The complexes **1a**, **1b**, and **5** have the most linear conformations, with Au–P···P–Au = 157, 176 and 172°respectively. Complex **4** has the approximately eclipsed conformation, with Au–P···P–Au ranging from 37 – 57°, as required for formation of the macrocyclic structure. Complexes **2** and **3** have intermediate values with torsion angles Au–P···P–Au = 110 and 126°, respectively. There are no obvious constraints for the conformations of complexes **1** – **3** and **5**, from which it can be concluded that there is

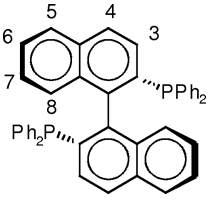


Scheme 4. Conformations of the binap ligand.

little steric hindrance within the torsion angle range Au–P···P–Au = 110 – 176°. Within this range, the gold atoms are well separated and do not form an intramolecular aurophilic interaction, while steric effects of the bulky binap ligands prevent formation of intermolecular Au···Au bonds. In complex **5**, the smaller $[Ag_2(O_2CCF_3)_2]$ units are able to form metallophilic bonds of the form Au···Ag···Ag···Au. For complex **4**, the increase in steric strain in forming the more eclipsed structure must be small enough that it can be balanced by the bond energy gained in forming the aurophilic attraction in the macrocyclic complex. This relative freedom of rotation within the binap ligand may be problematic in the use of complexes such as **2** in chiral catalysis, because the greatest selectivity tends to be observed when the catalyst structure is relatively rigid [2, 3]. However, the preference for the roughly linear conformation is useful in forming polymeric gold(I) complexes from the precursor complex **2** [5].

Experimental Section

NMR spectra were recorded using either a Varian Inova 400 NMR spectrometer or a Varian Mercury 400 NMR spectrometer. ^{1}H and ^{13}C chemical shifts are reported relative to tetramethylsilane (TMS), while ^{31}P chemical shifts are reported relative to 85 % H_3PO_4 as an external standard. ESI mass spectra were recorded using a Micromass LCT spectrometer and dichloromethane solutions of the compounds. The ^{1}H NMR labeling system is shown below for the binap ligand.



[Au$_2$(μ-R,S-binap)Cl$_2$], ***1b***

A solution of *R,S*-binap (0.304 g, 0.488 mmol) in acetone (30 mL) was added to a suspension of [AuCl(SMe$_2$)] (0.283 g, 0.961 mmol) in acetone (60 mL). The mixture was stirred for two hours to give a white precipitate, which was collected by filtration, washed with acetone, diethyl ether, and pentane, and dried under vacuum. Yield 0.381 g, 73 %. – Anal. for $C_{44}H_{32}Au_2Cl_2P_2$: calcd. C 48.60, H 2.97; found C 48.29, H 2.73. – ^{1}H NMR (CD_2Cl_2): $\delta(^1H)$ = 8.20 (d, 2H, 4-H binap), 7.98 (d, 2H, 5-H binap), 7.65 (d, 2H, *o*-H Ph), 7.63 (d, 2H, *o*-H Ph), 7.56 – 7.45 (m, 6H, 3-H binap + 6-H binap + *m*-H Ph), 7.45 – 7.35 (m, 6H, *m*-H Ph), 7.26 (d of t, 4H, *p*-H Ph), 7.19 (d, 2H, *o*-H Ph), 7.17(d, 2H, *o*-H Ph), 6.90 (t, 2H, 7-H, binap), 6.66 (d, 2H, 8-H binap). – ^{31}P NMR: δ = 24.71 (s).

Complex **1a** was prepared by the same procedure from *S*-binap, giving similar yield and identical ^{1}H NMR spectra.

[Au$_2$(μ-binap)(CF$_3$CO$_2$)$_2$], ***2***

Silver trifluoroacetate (40.6 mg, 0.184 mmol) was added to a suspension of **1b** (100 mg, 0.092 mmol) in dichloromethane (10 mL). The mixture was stirred for 30 min and filtered through celite to remove silver chloride. The solvent was removed, and the compound was purified by reprecipitation from a concentrated dichloromethane solution by addition of pentane. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield 0.102 g, 89 %. – Anal. for $C_{48}H_{32}Au_2F_6O_4P_2$: calcd. C 46.40; H 2.60; found C 46.08, H 2.45. – ^{1}H NMR (CD_2Cl_2): $\delta(^1H)$ = 8.10 (d, 2H, 4-H binap), 7.97 (d, 2H, 5-H binap), 7.63 (d, 2H, *o*-H Ph), 7.61 (d, 2H, *o*-H Ph), 7.57 – 7.35 (m, 12H, 3-H binap + 6-H binap + *m*-H Ph), 7.29 (t, 4H, *p*-H Ph), 7.19 (d, 2H, *o*-H Ph), 7.17 (d, 2H, *o*-H Ph), 7.00 (t, 2H, 7-H, binap), 6.72 (d, 2H, 8-H binap). – ^{31}P NMR: δ = 18.41(s).

Complex **5** was prepared similarly, but using silver trifluoroacetate (81.2 mg, 0.368 mmol). Yield: 95 mg, 61 %. – Anal. for $C_{52}H_{32}Ag_2Au_2F_{12}O_8P_2$: calcd. C 37.08, H 1.91; found C 36.75, H 2.14. – NMR data are the same as for **2**.

[Au$_2$(κ^1-4,4′-bipy)$_2$(μ-binap)](CF$_3$CO$_2$)$_2$, ***3***

To a solution of 4,4′-bipy (28.7 mg, 0.184 mmol) in CH_2Cl_2 (10 mL) was added a filtered solution of [Au$_2$(μ-*R,S*-binap)(CF$_3$CO$_2$)$_2$] (0.092 mmol), prepared from [Au$_2$(μ-*R,S*-binap)Cl$_2$] (0.100 g, 0.092 mmol) and AgO_2CCF_3 (0.041 g, 0.184 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 2 h. The solvent was then removed and the crude product dissolved in a minimum of dichloromethane. The product was precipitated from solution as a white powder by addition of pentane, collected by filtration, washed with diethyl ether and pentane, and dried under vacuum. Yield: 0.0612 g, 42 %. – Anal. for $C_{68}H_{48}Au_2P_2N_4O_4F_6$: calcd. C 52.52, H 3.11, N 3.60; found C 52.11, H 2.85, N 3.53. – ^{1}H NMR (CD_2Cl_2 + CD_3OD): $\delta(^1H)$ = 8.69 (s, 8H, *o*-H py), 8.08 (d, 2H, 4-H binap), 7.93 (d, 2H, 5-H binap), 7.63 (d, 2H, *o*-H Ph), 7.62 (d, 2H, *o*-H Ph), 7.57 (d, 8H, *m*-H py), 7.52 – 7.42 (m, 6H, 3-H binap + 6-H binap + *m*-H Ph), 7.38 (t, 6H, *m*-H Ph), 7.22 (m, 4H, *p*-H Ph), 7.16 (d, 2H, *o*-H Ph), 7.14 (d, 2H, *o*-H Ph), 6.96 (t, 2H, 7-H, binap), 6.68 (d, 2H, 8-H binap). – ^{31}P NMR: δ = 18.45 (s).

[Au$_2$(μ-binap)$_2$](CF$_3$CO$_2$)$_2$, ***4***

To a solution of [Au$_2$(μ-*R,S*-binap)(CF$_3$CO$_2$)$_2$] (0.092 mmol) in tetrahydrofuran was added 58.5 mg (0.092 mmol)

Table 1. Crystallographic data for the complexes.

Complex	**1a**·CH_2Cl_2	**1b**·0.93 $(CH_3)_2SO$	**2**·0.5 CH_2Cl_2	**3**·3 CH_2Cl_2	**4**·0.74 CH_2Cl_2	**5**·1.5 CH_2Cl_2
Formula	$C_{55}H_{42}Au_2Cl_4P_2$	$C_{45.86}H_{37.58}Au_2Cl_2O_{0.93}P_2S_{0.93}$	$C_{48.5}H_{33}Au_2ClF_6O_4P_2$	$C_{71}H_{54}Au_2Cl_6F_6N_4O_4P_2$	$C_{92.74}H_{66.2}Au_2Cl_{1.48}F_6O_4P_4$	$C_{53.5}H_{35}Ag_2Au_2Cl_3F_{12}O_8P_2$
M_r	1170.38	1160.18	1285.07	1809.80	1928.91	1811.78
T, K	150	150	150	150	150	150
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	rhombohedral	triclinic	monoclinic	triclinic	triclinic
Space group	$C2$	$R\bar{3}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	19.5457(8)	30.199(1)	11.9800(4)	16.853(8)	14.7650(3)	13.5887(5)
b, Å	8.6328(3)	30.199(1)	15.5702(6)	22.64(1)	22.7024(5)	14.1199(5)
c, Å	14.0179(5)	28.2091(9)	24.4784(9)	18.407(7)	23.3878(5)	15.7540(6)
α, deg	90	90	74.579(2)	90	88.9490(8)	85.894(2)
β, deg	122.112(2)	90	89.400(2)	114.03(3)	89.6320(8)	86.299(2)
γ, deg	90	120	74.197(2)	90	79.0320(9)	66.574(2)
V, Å^3	2003.4(1)	22279(1)	4225.8(3)	6414(2)	7695.1(3)	2764.3(2)
Z	2	18	4	4	4	2
D_{calc}, Mg m^{-3}	1.94	1.46	2.02	1.83	1.65	2.18
μ, mm^{-1}	7.7	6.1	7.1	4.9	4.0	6.3
Data / restr. / param.	3328 / 1 / 241	8631 / 0 / 403	14616 / 1045 / 1043	5766 / 1353 / 801	26578 / 3384 / 1786	9724 / 677 / 710
x (Flack)	0.14(2)	–	–	–	–	–
$R1$ / $wR2$ [$I \geq 2\sigma(I)$]	0.0408 / 0.1085	0.0542 / 0.1284	0.0781 / 0.1988	0.0938 / 0.2617	0.0500 / 0.1247	0.0440 / 0.0950
$R1$ / $wR2$ (all data)	0.0421 / 0.1099	0.0804 / 0.1388	0.1143 / 0.2164	0.1895 / 0.3129	0.0633 / 0.1308	0.0748 / 0.1054
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	3.56 / −2.33	0.76 / −1.83	3.42 / −2.61	1.25 / −1.44	1.77 / −2.52	1.86 / −1.44

of *R,S*-binap. The solution was stirred for 2 h. The solvent was removed and the crude product dissolved in a minimum of dichloromethane. The product was precipitated from solution as a white powder by addition of pentane, collected by filtration, washed with diethyl ether and pentane, and dried under vacuum. Yield: 0.172 g, 96 %. – Anal. for $C_{92}H_{64}Au_2F_6O_4P_4$: calcd. C 59.24, H 3.46; found C 58.98, H 3.54. – ^{31}P NMR (CD_2Cl_2): δ = 41.16 (s); 43.07 (s, broad). Single crystals of **4a** were grown by slow diffusion of *n*-hexane into a dichloromethane solution of the compound.

X-Ray structure determinations

Data were collected at low temperature (−123 °C) with a Nonius Kappa-CCD area detector diffractometer using COLLECT [15] software, with MoK_α radiation (λ = 0.71073 Å). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN [16]. The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK) [16]. The SHELXTL [17] software package was used to solve the structures by Direct Methods, with subsequent refinement carried out using successive difference Fouriers. All hydrogen atoms were calculated geometrically as riding on their respective carbon atoms. Crystal data are summarized in Table 1, and further details of the structures can be found in the CIF files CCDC 743981–743986 deposited with The Cambridge Crystallographic Data Centre. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

*[Au_2(μ-*S*-binap)Cl_2], **1a***

Crystals of **1a** were grown by slow diffusion of pentane into a dichloromethane solution of the compound. The asymmetric unit contains only one half of a structural unit of the compound, the other being related by symmetry.

*[Au_2(μ-binap)Cl_2], **1b***

Crystals of **1b** crystallized from a dimethylsulfoxide (DMSO) solution of the compound. Voids in the lattice were filled with disordered molecules of DMSO. The SQEEZE procedure of the PLATON suite of programs [18] was used to account for this solvent electron density. A total of 701.7 electrons were removed in a volume of 7299.9 Å^3 (32.8 % of the unit cell). These electrons are assigned to 16.7 molecules of dimethylsulfoxide (This equates to 0.93 DMSO molecules per asymmetric unit). The SQUEEZE-processed data were used for all subsequent refinement cycles.

*[Au_2(μ-binap)(CF_3CO_2)$_2$], **2***

Crystals of **2** were grown by slow diffusion of pentane into a dichloromethane solution of the compound. There are two distinct molecules in the asymmetric unit, and a solvent CH_2Cl_2 molecule, which was restrained to have equal C–Cl distances.

*[Au_2(κ^1-4,4′-bipy)$_2$(μ-binap)](CF_3CO_2)$_2$, **3***

Crystals of **3** were grown by slow diffusion of pentane into a dichloromethane solution. The CH_2Cl_2 molecules of

solvation were restrained to have C–Cl = 1.65 Å, and phenyl groups were restrained to be ideal hexagons.

meso-[Au$_2$(μ-R-binap)(μ-S-binap)](CF$_3$CO$_2$)$_2$, ***4a***

Crystals of **4a** were grown by slow diffusion of *n*-hexane into a concentrated dichloromethane solution of the compound **4**. The asymmetric unit contains two similar but independent macrocyclic structures. Two of the four trifluoroacetate anions were disordered in which the -CO_2 group was modeled over two sites, one at 50 : 50 and the other at 60 : 40 occupancy. All atoms of the macrocycles were modeled anisotropically with the exception of C144. Several anion and solvent atoms were also not modeled anisotropically, including O304, O401, C404, F405, and C700. A single small void in the lattice was assumed to be filled with disordered dichloromethane solvent, and was accounted for using the SQUEEZE procedure of the PLATON suite of programs [18]. A total of 40.4 electrons were removed from a volume of 159.7 Å^3 (2.1 % of the unit cell). These electrons are assigned to 0.96 molecules of dichloromethane. The SQUEEZE-processed date were used for all subsequent refinement cycles.

[Au$_2$Ag$_2$(μ-O$_2$CCF$_3$)$_4$(μ-R,S-binap)], ***5***

Crystals of [Au_2Ag_2(μ-O_2CCF_3)$_4$(μ-*R,S*-binap)]·1.5-CH_2Cl_2 were grown from a concentrated dichloromethane chloride solution of **2** containing excess silver trifluoroacetate by slow diffusion of pentane. The C–Cl and Cl–Cl distances of the CH_2Cl_2 molecules were fixed.

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