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Synthesis of dinuclear gold-(I) and -(II) complexes by reaction of $[Au^{I}_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ with protonic acids

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The reaction of the bis(ylide) gold complex $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ with strong acids (such as $HClO_4$) in the presence of diphosphines L–L afforded a mixture of heterobridged gold(I) complexes $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}L\text{–}L)]^+$ (L–L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2PPh_2$) and $[PPh_2Me_2]^+$. After addition of Li(tcnq), $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}L\text{–}L)]_2[ClO_4][tcnq]$ were obtained pure (tcnq = 7,7,8,8-tetracyanoquinodimethane). The crystal structure of the $Ph_2PCH_2CH_2PPh_2$ derivative shows an intramolecular gold–gold distance of 3.1294(9) Å. The use of weak protonic acids such as pyridine-2-thiol (C_5H_5NS) or 2-sulfanylbenzothiazole ($C_7H_5NS_2$), in the presence of atmospheric oxygen, led to complexes of gold(II). The crystal structure of $[Au^{II}_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(C_5H_4NS)_2]$ shows a gold–gold bond length of 2.6686(13) Å.

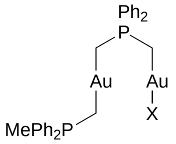
Dinuclear gold-(I) and -(II) complexes containing the bis(ylide) ligand $(CH_2)_2PR_2^-$ have been extensively studied because of their high stability, which provides a handle for the study of gold–gold bonds and weak gold–gold interactions.[1–5]

Fackler and co-workers[6] have shown elegantly that the isomerization of *trans*-$[Au_2\{\mu\text{-}(CH_2)_2PPhMe\}_2]$ to a *cis–trans* mixture is acid catalysed, *via* a nucleophilic attack of the gold atoms on the Lewis acids. However, the use of stronger protonic acids resulted in rupture of the dimer to give two monomeric units.[7]

Here we describe the reactions of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ with a strong acid in the presence of phosphine or diphosphine ligands, which afford dinuclear gold(I) derivatives, whereas the use of weak protonic acids (that are able to act as ligands) leads to gold(II) derivatives. The structures of $[Au^{I}_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-dppe})]_2[ClO_4][tcnq]$ (dppe = 1,2-bis(diphenylphosphino)ethane; tcnq = 7,7,8,8-tetracyanoquinodimethane) and $[Au^{II}_2\{\mu\text{-}(CH_2)_2PPh_2\}_2(C_5H_4NS)_2]$ (C_5H_4NS = pyridine-2-thiolate) have been determined by X-ray diffraction analyses.

Results and Discussion

As stated above, the symmetrical ring cleavage of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ by hydrogen halides gives mononuclear derivatives $[AuX(CH_2PPh_2Me)]$. It has been suggested that these processes involve a dinuclear intermediate **I** with one bridging bis(ylide) ligand and terminal ylide and halide ligands.[7] We have now carried out reactions between $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ and $HClO_4$ in the presence of (*i*) triphenylphosphine or (*ii*) diphosphine [dppm = bis(diphenylphosphine)methane or dppe] ligands (Scheme 1); NMR studies showed the presence of dinuclear gold(I) complexes (previously reported by us)[8] and phosphonium salts, although we could not separate the two components. These processes can evolve through the intermediate proposed if the second protonation takes place at the terminal ylide instead of the bridging bis(ylide) ligand.



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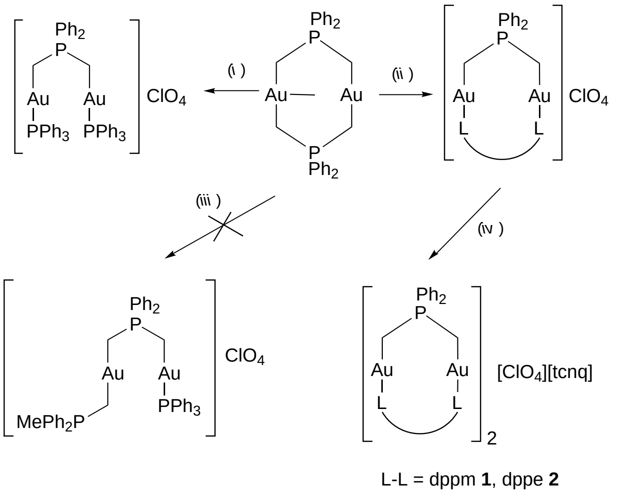


Scheme 1 (*i*) $HClO_4 + PPh_3$; (*ii*) $HClO_4$ + L–L, − $[PPh_2Me_2][ClO_4]$; (*iii*) $HClO_4 + PPh_3$ (1:1:1); (*iv*) Li(tcnq), − $LiClO_4$

Therefore, we tried to isolate this intermediate from the reaction of $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ with triphenylphosphine and perchloric acid in a 1:1:1 molar ratio [reaction (*iii*), Scheme 1]; the result was a mixture of starting material and doubly protonated product, but not the intermediate species.

In order to eliminate the phosphonium salt, metatheses (*iv*) with Li(tcnq) were carried out to afford complexes **1** and **2** as green solids from which the phosphonium salt can be eliminated by fractional crystallization (Scheme 1).

Complexes **1** and **2** were characterized by elemental analyses and NMR spectroscopy (see Experimental section). The IR spectra show bands at 2180s, 2154s and 828m cm^{-1} from the tetracyanoquinodimethane anion,[9–11] 1098s (br) and 623s cm^{-1} from the perchlorate anion,[12] 587m (**1**) and 582m cm^{-1} (**2**) assignable to $Au\text{–}C_{ylide}$.[13] In the positive-ion liquid secondary ion mass spectra (LSIMS) the parent ion $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}L\text{–}L)]^+$ is the base peak at m/z = 991 and 1005 respectively.

The nature of these double salts was confirmed by an X-ray diffraction analysis of complex **2**. The asymmetric unit consists of one cation $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}L\text{–}L)]^+$, one half-occupied perchlorate anion (disordered over an inversion centre) and half a tetracyanoquinodimethane anion (also associated with

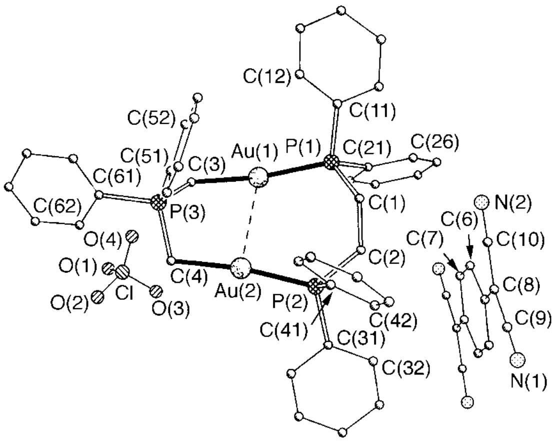


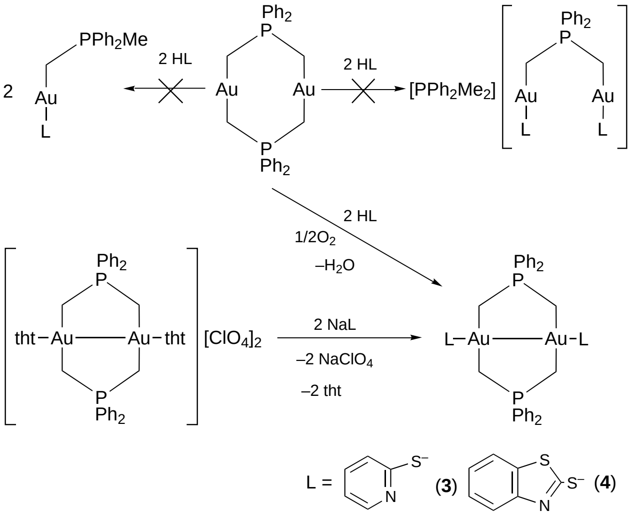
Fig. 1 Structure of the cation of complex **2** in the crystal (H atoms omitted, radii arbitrary) showing the atom numbering scheme

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Au(1)–C(3)	2.083(7)	Au(1)–P(1)	2.276(2)
Au(1)–Au(2)	3.1294(9)	Au(2)–C(4)	2.098(7)
Au(2)–P(2)	2.271(2)	P(1)–C(11)	1.819(7)
P(1)–C(21)	1.822(6)	P(1)–C(1)	1.827(6)
P(2)–C(31)	1.816(6)	P(2)–C(41)	1.823(7)
P(2)–C(2)	1.829(6)	P(3)–C(4)	1.763(7)
P(3)–C(3)	1.774(7)	P(3)–C(51)	1.798(7)
P(3)–C(61)	1.810(7)	C(1)–C(2)	1.554(8)
C(3)–Au(1)–P(1)	172.2(2)	C(3)–Au(1)–Au(2)	84.1(2)
P(1)–Au(1)–Au(2)	101.39(5)	C(4)–Au(2)–P(2)	172.5(2)
C(4)–Au(2)–Au(1)	88.5(2)	P(2)–Au(2)–Au(1)	98.69(5)
C(11)–P(1)–C(21)	108.0(3)	C(11)–P(1)–C(1)	103.1(3)
C(21)–P(1)–C(1)	103.5(3)	C(11)–P(1)–Au(1)	110.2(2)
C(21)–P(1)–Au(1)	114.8(2)	C(1)–P(1)–Au(1)	116.2(2)
C(31)–P(2)–C(41)	107.6(3)	C(31)–P(2)–C(2)	105.2(3)
C(41)–P(2)–C(2)	101.7(3)	C(31)–P(2)–Au(2)	109.7(2)
C(41)–P(2)–Au(2)	113.4(2)	C(2)–P(2)–Au(2)	118.4(2)
C(4)–P(3)–C(3)	108.3(4)	C(4)–P(3)–C(51)	109.8(3)
C(3)–P(3)–C(51)	111.0(3)	C(4)–P(3)–C(61)	110.1(3)
C(3)–P(3)–C(61)	110.8(3)	C(51)–P(3)–C(61)	106.9(3)
C(2)–C(1)–P(1)	113.1(4)	C(1)–C(2)–P(2)	113.3(4)
P(3)–C(3)–Au(1)	110.0(3)	P(3)–C(4)–Au(2)	108.5(3)

an inversion centre) (Fig. 1). Selected bond lengths and angles are collected in Table 1. The structure of the cation displays a nine-membered dimetallacycle in which the atoms Au(1,2), P(1,2), C(3,4) are approximately coplanar (mean deviation 0.13 Å) and P(3), C(1) and C(2) lie 0.9, 0.6 and −0.5 Å out of this plane. The intramolecular gold–gold distance is 3.1294(9) Å, which is longer than found in other nine-membered dinuclear gold(I) complexes: 2.867(1) Å in [Au_2(μ-mnt)(μ-dppen)][14] [mnt = maleonitriledithiolate, dppen = 1,2-bis(diphenylphosphino)ethylene], 2.90 Å in [Au_2(μ-mnt)(μ-dadpe)][14] [dadpe = 1-(diphenylarsino)-2-(diphenylphosphino)ethane)], 3.026(1) Å in [NBu_4][Au_2(μ-C_3S_5){μ-$(CH_2)_2PPh_2$}].[15] The Au···Au contact is however similar to that found in the ten-membered ring [Au_2{μ-$S(CH_2)_3S$}(μ-dppm)] [3.128(1) Å].[16] The bond lengths in the tcnq are very similar to those found in Rb(tcnq),[17] as would be expected for $tcnq^-$. The tcnq anions are essentially planar (mean deviation <0.04 Å) and are associated in planes at $z = 0$, coplanar rather than stacked; the shortest contact is N(2)···N(2) ($2 - x$, $1 - y$, $2 - z$) 3.45 Å.

We have also realized reactions of [Au_2{μ-$(CH_2)_2PPh_2$}$_2$] with weak protonic acids such as pyridine-2-thiol (C_5H_5NS) or 2-sulfanylbenzothiazole ($C_7H_5NS_2$), which can act as ligands either in the protonated or in the deprotonated form. Following the latter pattern, dinuclear gold(I) derivatives containing one bridging bis(ylide) ligand and two deprotonated S-donor ligands should be obtained, whereas mononuclear gold(I) derivatives with one ylide ligand and one deprotonated S-donor ligand would be expected if symmetrical ring cleavage occurs. Unexpectedly the gold(II) derivatives **3** and **4** are obtained (Scheme 2).



Scheme 2 tht = Tetrahydrothiophene

These complexes were obtained as orange solids, air and moisture stable at room temperature. Complex **3** is non-conducting in acetone solutions (**4** is too insoluble). Their IR spectra show medium-intensity bands at 573 (**3**) and 571 cm^{-1} (**4**) from Au–C_{ylide}, and the absorptions from N–H or S–H have disappeared. The ^{31}P-{^1H} NMR spectrum shows a singlet at δ 39.7 (s) for **3** (**4** is too insoluble). The ^1H NMR spectrum shows the ylide methylene proton resonance as a doublet at δ 1.59, and the absence of the MeP resonance rules out the formation of phosphonium. The LSIMS mass spectrum of **3** shows the parent peak at *m*/*z* (%) = 1041 (8) whilst the base peak appears at *m*/*z* = 930, corresponding to the loss of one pyridine-2-thiolate ligand from the parent peak.

It is known that by bubbling a Lewis acid such as SO_2 into a solution of [Au_2{μ-$(CH_2)_2PR$}$_2$] (R = Ph or Me) the coloured gold(I) adducts [Au_2{μ-$(CH_2)_2PR$}$_2$$(SO_2)_2$] are obtained, for which crystal structures, albeit disordered, have been determined.[6] Therefore, in order to confirm the oxidation state of the gold centres, complexes **3** and **4** have been also synthesized by a well established method of obtaining dinuclear gold(II) derivatives: substitution reactions. Thus the neutral tetrahydrothiophene in the gold(II) complex [Au_2{μ-$(CH_2)_2PPh_2$}$_2$$(tht)_2$][$ClO_4$]$_2$ can readily be displaced by addition of a freshly prepared solution of the corresponding anionic ligand (Scheme 2).

As further confirmation, the crystal structure of complex **3** has been established by X-ray crystallography (Fig. 2). Selected bond lengths and angles are collected in Table 2. The structure determination shows an octadiauracycle with chair geometry, as is common for dinuclear gold(II) derivatives; the P atoms lie 0.76 Å out of the mean plane of the other ring atoms (mean deviation <0.01 Å). The molecule displays crystallographic inversion symmetry. The Au–Au bond length 2.6686(13) Å is similar to that found in other S-bonded gold(II) systems such as [Au_2{μ-$(CH_2)_2PPh_2$}$_2$$(S_2CNMe_2)_2$] [2.6585(12) and 2.6444(8) Å][18] and clearly shorter than that in [Au_2{μ-$(CH_2)_2PPh_2$}$_2$$(SO_2)_2$] [2.835(1) Å].[6] The Au^{II}–S bond 2.437(3) Å is also similar to that found in [Au_2{μ-$(CH_2)_2PPh_2$}$_2$$(S_2CNMe_2)_2$] [2.439(2) and 2.431(1) Å] and shorter than in [Au_2{μ-$(CH_2)_2PPh_2$}$_2$$(SO_2)_2$] [2.587(5) Å].

It is clear that the reactions of Scheme 2 involve oxidation, for which we suggest atmospheric oxygen as the agent; these processes are not sensitive to light and are accelerated by bubbling oxygen through the solutions, whereas they are prevented by the use of deoxygenated solvents. The first step could be an approach of the sulfur donor ligand to give an adduct (similar to that

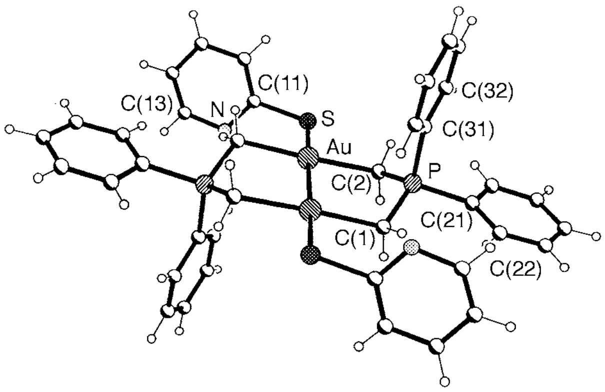


Fig. 2 The molecule of complex **3** in the crystal (H atoms omitted, radii arbitrary) showing the atom numbering scheme

Table 2 Selected bond lengths (Å) and angles (°) for complex **3**

Au–C(1$^{\mathrm{I}}$)	2.09(2)	Au–C(2)	2.128(14)
Au–S	2.437(3)	Au–Au$^{\mathrm{I}}$	2.6686(13)
S–C(11)	1.78(2)	P–C(1)	1.715(14)
P–C(2)	1.77(2)	P–C(31)	1.80(2)
P–C(21)	1.814(14)	C(11)–N	1.35(2)
C(11)–C(16)	1.36(2)	N–C(13)	1.38(2)
C(13)–C(14)	1.31(3)	C(14)–C(15)	1.35(3)
C(15)–C(16)	1.41(2)		

C(1$^{\mathrm{I}}$)–Au–C(2)	175.8(5)	C(1$^{\mathrm{I}}$)–Au–S	92.7(4)
C(2)–Au–S	83.4(4)	C(1$^{\mathrm{I}}$)–Au–Au$^{\mathrm{I}}$	89.5(4)
C(2)–Au–Au$^{\mathrm{I}}$	94.5(4)	S–Au–Au$^{\mathrm{I}}$	176.29(10)
C(11)–S–Au	109.1(5)	C(1)–P–C(2)	107.7(8)
C(1)–P–C(31)	110.7(7)	C(2)–P–C(31)	113.3(7)
C(1)–P–C(21)	111.2(6)	C(2)–P–C(21)	112.3(6)
C(31)–P–C(21)	101.7(6)	P–C(1)–Au$^{\mathrm{I}}$	114.8(8)
P–C(2)–Au	108.8(7)	N–C(11)–C(16)	124(2)
N–C(11)–S	117.3(12)	C(16)–C(11)–S	118.4(14)
C(11)–N–C(13)	115(2)	C(14)–C(13)–N	125(2)
C(13)–C(14)–C(15)	120(2)	C(14)–C(15)–C(16)	119(2)
C(11)–C(16)–C(15)	118(2)		

Symmetry transformation used to generate equivalent atoms: I $-x + 1, -y + 1, -z + 1$.

reported for SO$_2$) which should be very easy to oxidize. To the best of our knowledge that is the first example in which oxidation of gold(I) complexes to gold(II) is brought about by oxygen. Other examples affording gold(III) complexes have recently been reported.[19] Reactions with perchloric acid take place irrespective of the use of distilled and deoxygenated solvents.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets, ^{1}H and ^{31}P NMR spectra on a Varian UNITY 300 spectrometer in CDCl$_3$ solutions with chemical shifts quoted relative to SiMe$_4$ (external, ^{1}H) or H$_3$PO$_4$ (external, ^{31}P). Analyses (C, H and N) were performed with a Perkin-Elmer 2400 microanalyser. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Melting points were measured on a Büchi apparatus and are uncorrected. Mass spectra were recorded on a VG Autospec using positive-ion LSIMS techniques. All reactions were carried out at room temperature.

CAUTION: perchlorate salts or derivatives must be manipulated with care, as far as possible avoiding evaporation to dryness.

Syntheses

[Au$_2${μ-(CH$_2$)$_2$PPh$_2$}(L–L)]$_2$[ClO$_4$][tcnq] (L–L = dppm 1 or dppe 2). To a solution of [Au$_2${μ-(CH$_2$)$_2$PPh$_2$}$_2$][20] (0.082 g, 0.1 mmol) in dichloromethane (30 cm^3) was added HClO$_4$ (0.2 mmol, 0.020 g) and L–L (0.1 mmol; dppm, 0.038 g; dppe, 0.039 g). After stirring for 2 h the solvent was removed, the residue dissolved in acetone (20 cm^3) and Li(tcnq)[21] (0.021 g, 0.1 mmol) added. After 2 h the solvent was concentrated to *ca.* 5 cm^3 and addition of ethanol (15 cm^3) led to green solids, which were filtered off and dried *in vacuo*. Yields: **1**, 80%; **2**, 75%. NMR: ^{1}H, **1**; δ 7.9–7.5 (34 H, m, Ph and tcnq), 3.6 (2 H, s, br, dppm) and 1.9 (4 H, sd, CH$_2$P); ^{31}P-{^{1}H}, **1**; δ 36.5 (s br) and 34.8 (t, *J* 12.1); ^{1}H, **2**; δ 7.8–7.5 (34 H, m, Ph and tcnq), 2.7 (4 H, s br, dppe) and 1.95 (4 H, s, CH$_2$P); ^{31}P-{^{1}H}, **2**; δ 38.2 (d) and 35.2 (t, *J* 10.7 Hz). M.p. 205 (**1**), 110 °C (**2**) (Found: C, 46.95; H, 3.25; N, 2.45. Calc. for $C_{90}H_{76}Au_4ClN_4O_4P_6$ **1**: C, 47.3; H, 3.35; N, 2.45. Found: C, 47.7; H, 3.3; N, 2.35. Calc. for $C_{92}H_{80}Au_4ClN_4O_4P_6$ **2**: C, 47.75; H, 3.3; N, 2.4%). Λ_M = 226 (**1**), 234 ohm^{-1} cm^2 mol^{-1} (**2**).

[Au$_2${μ-(CH$_2$)$_2$PPh$_2$}$_2$L$_2$] (L = C$_5$H$_4$NS 3 or C$_7$H$_4$NS$_2$ 4). (*a*) To a solution of [Au$_2${μ-(CH$_2$)$_2$PPh$_2$}$_2$] (0.082 g, 0.1 mmol) in dichloromethane (30 cm^3) was added HL (0.2 mmol; C$_5$H$_5$NS, 0.022 g; or C$_7$H$_5$NS$_2$, 0.033 g). After stirring for 9 h (**3**) or 2 d (**4**), complex **4** appeared as an insoluble orange solid, whereas **3** was obtained by concentration to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3). Complex **3** was washed with diethyl ether and **4** with dichloromethane. Yields: **3**, 80%; **4**, 85%.

(*b*) To a solution of [Au$_2${μ-(CH$_2$)$_2$PPh$_2$}$_2$(tht)$_2$][ClO$_4$]$_2$[22] (0.06 g, 0.05 mmol) in dichloromethane (30 cm^3) was added a slight excess of freshly prepared NaL (0.11 mmol) in ethanol (10 cm^3). After stirring for 90 min (**3**) or 3 h (**4**), complex **4** appeared as an insoluble orange solid, whereas **3** was obtained by concentration to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3); **3** was washed with diethyl ether and **4** with dichloromethane. Yields: **3**, 91%; **4**, 73%. NMR: ^{1}H, **3**; δ 8.3–6.8 (28 H, m, Ph and C$_5$H$_4$NS) and 1.59 [8 H, d, ^2J(HP) 10.3 Hz, CH$_2$P]; ^{31}P-{^{1}H}, **3**; δ 39.7 (s). M.p. 160 (decomp.) (**3**), 215 °C (**4**), Λ_M = 9 ohm^{-1} cm^2 mol^{-1} (**3**) (Found: C, 43.75; H, 3.25; N, 2.6. Calc. for $C_{38}H_{36}Au_2N_2P_2S_2$ **3**: C, 43.85; H, 3.5; N, 2.7. Found: C, 43.35; H, 3.15; N, 2.4. Calc. for $C_{42}H_{36}Au_2N_2P_2S_4$ **4**: C, 43.75; H, 3.15; N, 2.4%).

Crystallography

Compound 2. *Crystal data.*_ $C_{92}H_{80}Au_4ClN_4O_4P_6$, M = 2314.74, triclinic, space group $P1$, a = 9.278(3), b = 10.689(3), c = 22.192(5) Å, α = 101.00(2), β = 95.91(2), γ = 105.11(2)°, U = 2058.5 Å^3, Z = 1, D_c = 1.867 Mg m^{-3}, F(000) = 1115, λ(Mo-Kα) = 0.710 73 Å, μ = 7.3 mm^{-1}, T = 173 K.

Data collection and reduction. Single crystals of compound **2** were obtained by slow diffusion of diethyl ether into a dichloromethane solution. A green prism with dimensions 0.80 × 0.20 × 0.12 mm was mounted on a glass fibre in inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3). A total of 7707 intensities were measured to 2θ$_{max}$ 50°, of which 7220 were independent (R_{int} = 0.027). An absorption correction based on ψ scans was applied, with transmission factors 0.72–1.00. Cell constants were refined from setting angles of 52 reflections in the range 2θ 20–22°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on F^2 (program system SHELXL 93).[23] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included by using a riding model. Refinement proceeded to $wR(F^2)$ 0.0829 for all reflections, conventional $R(F)$ 0.0347 and $S(F^2)$ 1.03 for 503 parameters and 445 restraints (to light atom displacement parameters and local ring symmetry), maximum Δρ 1.7 e Å^{-3}.

Compound 3. *Crystal data.* $C_{38}H_{36}Au_2N_2P_2S_2$, M = 1040.618, monoclinic, space group $P2_1/n$, a = 10.791(3), b = 8.763(3), c = 19.407(4) Å, β = 104.78(2)°, U = 1774.4(9) Å^3, Z = 2,

$D_c = 1.948$ Mg m^{-3}, $F(000) = 996$, λ(Mo-Kα) = 0.710 73, $\mu = 8.5$ mm^{-1}, $T = 173(2)$ K.

Data collection and reduction. Single crystals of compound **3** were obtained by slow diffusion of diethyl ether into a dichloromethane solution. An orange plate with dimensions 0.75 × 0.20 × 0.02 mm was mounted as above (Siemens P4) and used to collect 3025 intensities (3013 independent) to $2\theta_{max}$ 50°. Transmission factors 0.42–1.00.

Structure solution and refinement. The structure was solved and refined as above: $wR(F^2)$ 0.146, $R(F) = 0.057$, $S(F^2)$ 1.085 for 208 parameters and 277 restraints, maximum $\Delta\rho$ 2.8 e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/528.

Acknowledgements

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