Coordination modes of diphenylphosphinothioformamide in its neutral and deprotonated forms at gold(I)

Olga Crespo,[a] Eduardo J. Fernández,[b] Peter G. Jones,[c] Antonio Laguna,*[a]
José M. López-de-Luzuriaga,[b] Miguel Monge,[b] M. Elena Olmos[b] and Javier Pérez[b]

[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain. E-mail: alaguna@posta.unizar.es.*
[b] *Departamento de Química, Universidad de la Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC, Complejo Científico Tecnológico, 26001 Logroño, Spain*
[c] *Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany*

The reaction of the polydentate ligand $Ph_2PC(S)N(H)Me$ with various Au(I) substrates and in different molar ratios leads to complexes with different geometries around the gold center, such as linear mononuclear complexes, $[AuCl\{Ph_2PC(S)N(H)Me\}]$ (**1**), $[Au(C_6F_5)\{Ph_2PC(S)N(H)Me\}]$ (**2**) or $[Au\{Ph_2PC(S)N(H)Me\}_2]ClO_4$ (**4**), linear polynuclear derivatives, $[Au_2(C_6F_5)_2\{Ph_2PC(S)N(H)Me\}]_2$ (**3**) and $[Au\{Ph_2PC(SAuCl)N(H)Me\}_2]ClO_4$ (**6**), or the three-coordinate complex $[Au\{Ph_2PC(S)N(H)Me\}_3]ClO_4$ (**5**). Treatment of **1** with Tl(acac) produces the deprotonated derivative $[Au\{Ph_2PC(S)NMe\}]_2$ (**7**), which can further react with other gold(I) starting materials leading to the synthesis of $[Au_2\{Ph_2PC(S)N(AuX)Me\}_2]$ (X = Cl (**8**) and C_6F_5 (**9**)). The crystal structures of complexes **1**, **3**, **5** and **7** have been determined by X-ray diffraction studies.

Introduction

A common strategy in the synthesis of polynuclear complexes is the use of ligands bearing various donor sites. In the case of gold, the most favorable ligands are polyfunctional molecules with P-, S-, or N-donor centers.[1] The combination of different donor atoms in the same ligand can offer a combination of stability and reactivity; some such ligands have recently been revealed as instrumental in the preparation of complexes that can be used for a number of applications including chemotherapy, diagnosis, electron microscopy, catalysis and surface technology.[2–6]

We have recently been able to isolate molecular and cationic species in which phosphorus and sulfur atoms {(phenylthiomethyl)diphenylphosphine (PPh_2CH_2SPh)}[7–9] or phosphorus and nitrogen atoms {3,4-bis(diphenylphosphinoamino)toluene (3,4-$(NHPPh_2)_2MeC_6H_3$), 1,2-bis(diphenylphosphinoamino)benzene (1,2-$(NHPPh_2)_2C_6H_4$)[10] or 2-(diphenylphosphino)aniline ($PPh_2C_6H_4NH_2$)}[11] act as nucleation centers giving rise to homo- or hetero-polynuclear species, associated with the different coordination abilities of the donor centers. As a part of our own ongoing investigations we wished to use a functionalised phosphine bearing nitrogen- and sulfur-donor substituents in addition to the phosphorus atom. Our choice fell on the diphenylphosphinothioformamide ligand $Ph_2PC(S)N(H)Me$ and its deprotonated derivative $[Ph_2PC(S)NMe]^-$ (See Chart 1) since they display some interesting features. First, these potentially polydentate ligands can promote selective heteroatom (P, S and/or N) coordination to gold(I) centers and, thus, allow the synthesis of different mono- and polynuclear gold(I) complexes in which Au(I)–Au(I) interactions or hydrogen bonds would play an important role. Second, the flexibility characteristics[12] of these ligands allow very different structural arrangements, even with the same donor centers bonded to the same metal.
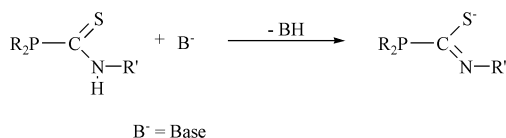
In this paper we report the synthesis of new mono- and polynuclear gold(I) complexes with the ligand $Ph_2PC(S)N(H)Me$ and its corresponding anion $[Ph_2PC(S)NMe]^-$ as a multi/mixed-functional donor for gold(I). Tiekink *et al.*[12,13] have summarized the coordination capabilities of this type of ligands to different organometallic or metallic substrates, but a systematic study of the coordination capabilities of this ligand without varying metal centers has not been reported to date. In this paper we present two- or three-coordinated mononuclear complexes, dinuclear compounds, and also one tetranuclear complex formed *via* gold(I)–gold(I) intermolecular interactions.

Results and discussion

The ligand diphenylphosphinothioformamide ($Ph_2PC(S)N(H)Me$) is readily prepared from diphenylphosphine and methyl isothiocyanate in equimolecular amounts according to the literature procedure.[14] It reacts with gold(I) species such as $[AuCl(tht)]$ or $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) in a 1 : 1 molar ratio, leading to the mononuclear derivatives $[AuCl\{Ph_2PC(S)N(H)Me\}]$ (**1**) or $[Au(C_6F_5)\{Ph_2PC(S)N(H)Me\}]$ (**2**), respectively, as illustrated in Scheme 1, by displacement of the weakly coordinated *tht* ligand. The elemental analysis and physical and spectroscopic properties of these products are in accordance with the proposed stoichiometry. Their molar conductivities in acetone solutions ($\Lambda_M = 4$ (**1**), 5 (**2**) Ω^{-1} cm^2 mol^{-1}) rule out an ionic formulation and, furthermore, their IR spectra show, among others, bands at 326 (**1**) and at 1503, 951 and 791 cm^{-1} (**2**), which are assigned to the Au–Cl[15] and Au–C_6F_5 [16,17] units, respectively. In the ^{1}H NMR spectra the aminic protons appear at 9.4 (**1**) and at 8.5 (**2**) ppm and in their ^{31}P{^{1}H} NMR spectra a single resonance appears, which is shifted more than 41 ppm downfield compared to that of the ligand, indicative of Au–P coordination.

A curious and exclusive characteristic of complex **2** is the progressive decoloration of the initially yellow chloroform solutions of this complex used in the NMR experiments, which begins after a few minutes and is complete in approximately one hour. In its ^{31}P{^{1}H} NMR spectrum a new signal at 50.7 ppm appears with increasing relative intensity, as the decoloration progresses. In the ^{1}H NMR spectrum the signal corresponding

$$R_2P{-}C\diagdown^{S}_{N{-}R'} \; + \; B^- \xrightarrow{\; -BH \;} R_2P{-}C\diagdown^{S^-}_{N{-}R'}$$

$B^- = Base$

Chart 1

Scheme 1
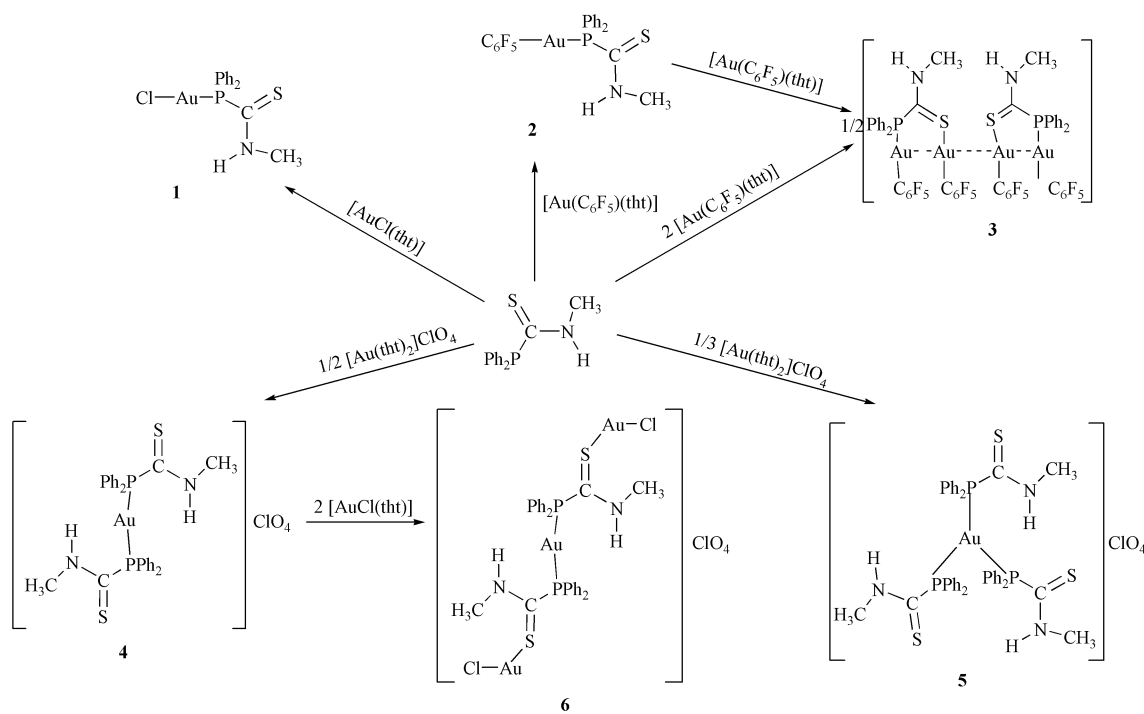
to the aminic proton of the starting material decreases in intensity until it disappears and, in addition, in its ^{19}F NMR spectrum the signals corresponding to the pentafluorophenyl rings bonded to gold(I) also disappear. The chemical shift of 50.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum is similar to that obtained for the previously reported dimeric complex [Au{Ph$_2$-PC(S)NMe}]$_2$.[13] These facts seem to be in accordance with a process of simultaneous deprotonation of the aminic protons of two [Au(C$_6$F$_5$)(Ph$_2$PC(S)N(H)Me)] units by the pentafluorophenyl rings of the adjacent units; whereby these act as Lewis bases producing pentafluorobenzene. An example of the deprotonating ability of the pentafluorophenyl group has previously been described[18] in the gold complex [Au(C$_6$F$_5$)PhP(O)H] and is in good agreement with our results.

Notwithstanding, the crystal structure of complex **1** has been unequivocally determined by X-ray diffraction studies. The geometry at the gold atom (Fig. 1) is linear (P–Au–Cl 177.13(3)°, see Table 1). The Au–P and Au–Cl bond distances (2.2254(7), 2.2866(8) Å respectively) are very similar to those found in [AuCl(PPh$_3$)][19] or in the dinuclear [Au$_2$Cl$_2$(μ-dppf)]
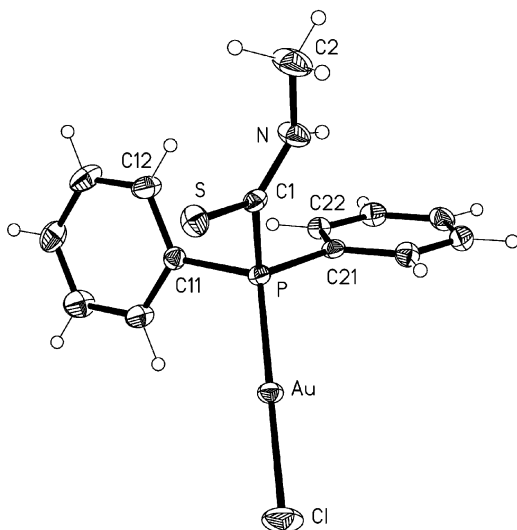
Table 1 Bond lengths [Å] and angles [°] for compound **1**

Au–P	2.2254(7)	P–C(1)	1.844(3)
Au–Cl	2.2866(8)	S–C(1)	1.658(3)
P–C(11)	1.809(3)	N–C(1)	1.318(3)
P–C(21)	1.814(3)	N–C(2)	1.461(4)
P–Au–Cl	177.13(3)	C(1)–P–Au	107.87(8)
C(11)–P–C(21)	106.55(12)	C(1)–N–C(2)	123.4(3)
C(11)–P–C(1)	102.65(12)	N–C(1)–S	125.5(2)
C(21)–P–C(1)	107.36(12)	N–C(1)–P	118.5(2)
C(11)–P–Au	115.75(8)	S–C(1)–P	115.92(14)
C(21)–P–Au	115.62(9)		

(dppf = 1,1′-bis(diphenylphosphino)ferrocene).[20,21] Molecules adjacent by translation parallel to the *y* axis are connected by rather long (2.64 Å) hydrogen bonds N–H · · · Cl. Further contacts C–H · · · Cl and C–H · · · Au, 2.94 and 3.18 Å respectively, might be considered as weak hydrogen bonds (Table 2).

The presence of various donor centers in these mononuclear species allows the synthesis of polynuclear derivatives. For instance, the reaction of the ligand Ph$_2$PC(S)N(H)Me with two equivalents of the mononuclear gold complex [Au(C$_6$F$_5$)(tht)] or, starting from the mononuclear derivative [Au(C$_6$F$_5$)-{Ph$_2$PC(S)N(H)Me}] (**2**), the reaction with one more equivalent of [Au(C$_6$F$_5$)(tht)], gives rise to the tetranuclear species [Au$_2$(C$_6$F$_5$)$_2${Ph$_2$PC(S)N(H)Me}]$_2$ (**3**), as an air-stable yellow solid. All the analytical data are in accordance with the proposed stoichiometry, and the presence of ^{19}F NMR signals corresponding to two inequivalent pentafluorophenyl groups confirms the presence of two types of magnetically different Au(C$_6$F$_5$) units in the molecule. Its $^{31}P\{^1H\}$ NMR spectrum also shows a displacement of the signal to low field with respect to the free ligand, indicating the coordination of this nucleus to one of these units (see Experimental). Nevertheless, the sulfur or nitrogen atoms could be involved in the coordination to the other Au(C$_6$F$_5$) fragment. Based on its infrared spectrum, it is difficult to distinguish these two possibilities, since both the *v*(C=N) stretching mode and *v*(C=S) appear at energies very close to those observed in the free ligand, which would indicate an electronic delocalization between these bonds.[13,22] Nevertheless, previous work in gold chemistry with S,N-donor ligands

Fig. 1 Molecular structure of complex **1**.

Table 2 Hydrogen bond lengths [Å] and angles [°]

Compound 1[a] D–H ⋯ A	d(D–H)	d(H ⋯ A)	d(D ⋯ A)	<(DHA)
N–H(0) ⋯ Cl#1	0.88	2.60	3.294(3)	136.3
C(23)–H(23) ⋯ Cl#2	0.95	2.94	3.665(3)	133.9
C(26)–H(26) ⋯ Au#3	0.95	3.18	3.944(3)	139.1

Compound 3[b] D–H ⋯ A	d(D–H)	d(H ⋯ A)	d(D ⋯ A)	<(DHA)
N(1)–H(1) ⋯ F(12)#1	0.86	2.42	3.062(9)	132.0

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $y - 1$, z; #2 $-x + 1$, $-y + 1$, $-z + 1$; #3 $-x$, $-y + 1$, $-z + 1$.
[b] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $y + 1/2$, $-z + 1/2$.

has shown that the sulfur atom is the preferred site for coordination to the gold center.[23]

The crystal structure of complex **3** has been determined by X-ray diffraction analysis and confirms the phosphorus– and sulfur–gold coordination. Crystals of **3** were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. Compound **3** (Fig. 2) crystallizes forming tetranuclear units formed by an intermolecular Au ⋯ Au interaction of 3.2712(5) Å (Table 3) between two [$Au_2(C_6F_5)_2${PPh$_2$-C(S)N(H)Me}] units; intermetallic distances between adjacent tetranuclear units are approximately 6 Å. This intermolecular Au ⋯ Au interaction is longer than those found in the related complex [Au(Ph$_2$PC(S)NPh)]$_2$[13] (3.146(1) Å) or in other dinuclear bridged gold(I) complexes that display inter- and intramolecular metal–metal interactions[24–27] (intermolecular Au ⋯ Au distances between 2.954(1)[24] and 3.171(3) Å[26]) and similar to that observed in the polymer [ClAu{Ph$_2$P(CH$_2$)$_8$-PPh$_2$}AuCl]$_\infty$[28] (3.264(2) Å). Both independent dinuclear units of complex **3** also show intramolecular Au ⋯ Au contacts of 3.0391(5) and 3.1631(5) Å, respectively. These distances are also longer than those in the related complexes [Au(Ph$_2$PC(S)-NPh)]$_2$[13] (2.9241(1) and 2.919(1) Å), [Au(cHex$_2$PC(S)NPh)]$_2$[13] (2.869(1) Å) or [Au(Ph$_2$PCH$_2$SPh)]$_2$(CF$_3$SO$_3$)$_2$[7] (2.9020(5) Å), that are doubly coordinated by the P,S-donor ligands. The gold atoms in complex **3** exhibit linear geometry at the gold centres (C–Au–P angles of 175.9(2) and 176.4(2)° and C–Au–S angles of 175.1(2) and 174.8(2)°) with typical Au–C distances between 2.029(8) and 2.074(7) Å. The Au–P distances, of 2.273(2) and 2.270(2) Å, are slightly longer than in complex **1** (2.2254(7) Å) and compare well with those observed in [Au(Ph$_2$PC(S)NPh)]$_2$[13] (2.265(5) and 2.271(5) Å), [Au(cHex$_2$PC(S)NPh)]$_2$[13] (2.276(1) Å) or [Au(Ph$_2$PCH$_2$SPh)]$_2$(CF$_3$SO$_3$)$_2$[7] (2.2721(11) Å), while the Au–S distances in **3** (2.315(2) and 2.316(2) Å) are shorter
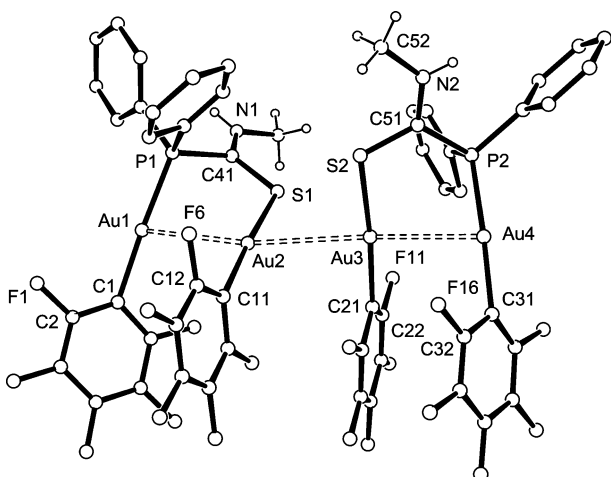

Fig. 2 Molecular structure of complex **3**. Aromatic H atoms are omitted for clarity.

Table 3 Selected bond lengths [Å] and angles [°] for complex **3**

Au(1)–C(1)	2.068(8)	Au(1)–P(1)	2.273(2)
Au(2)–C(11)	2.029(8)	Au(2)–S(1)	2.315(2)
Au(3)–C(21)	2.041(8)	Au(3)–S(2)	2.316(2)
Au(4)–C(31)	2.074(7)	Au(4)–P(2)	2.270(2)
Au(1)–Au(2)	3.1631(5)	Au(2)–Au(3)	3.2712(5)
Au(3)–Au(4)	3.0391(5)	S(1)–C(41)	1.679(8)
C(41)–N(1)	1.314(10)	C(41)–P(1)	1.843(9)
N(1)–C(42)	1.477(12)	P(1)–C(61)	1.801(8)
P(1)–C(71)	1.804(9)	S(2)–C(51)	1.693(9)
C(51)–N(2)	1.316(10)	C(51)–P(2)	1.840(9)
N(2)–C(52)	1.455(11)	P(2)–C(81)	1.802(9)
P(2)–C(91)	1.802(8)		
C(1)–Au(1)–P(1)	175.9(2)	C(11)–Au(2)–S(1)	174.8(2)
C(21)–Au(3)–S(2)	175.1(2)	C(31)–Au(4)–P(2)	176.4(2)
Au(1)–Au(2)–Au(3)	161.06(1)	Au(4)–Au(3)–Au(2)	170.13(1)
P(1)–Au(1)–Au(2)	76.97(6)	C(1)–Au(1)–Au(2)	99.1(2)
C(11)–Au(2)–Au(1)	92.9(2)	S(1)–Au(2)–Au(1)	88.35(6)
C(11)–Au(2)–Au(3)	105.5(2)	S(1)–Au(2)–Au(3)	72.93(6)
C(21)–Au(3)–Au(4)	93.2(2)	S(2)–Au(3)–Au(4)	91.13(6)
C(21)–Au(3)–Au(2)	87.7(2)	S(2)–Au(3)–Au(2)	87.66(6)
C(31)–Au(4)–Au(3)	97.9(2)	P(2)–Au(4)–Au(3)	79.33(6)
C(41)–S(1)–Au(2)	108.5(3)	N(1)–C(41)–S(1)	121.0(7)
N(1)–C(41)–P(1)	117.3(6)	S(1)–C(41)–P(1)	121.7(5)
C(41)–N(1)–C(42)	122.8(7)	C(51)–S(2)–Au(3)	108.9(3)
N(2)–C(51)–S(2)	120.3(7)	N(2)–C(51)–P(2)	119.2(7)
S(2)–C(51)–P(2)	120.5(5)	C(51)–N(2)–C(52)	124.2(8)

than the Au–S distance in [Au(Ph$_2$PCH$_2$SPh)]$_2$(CF$_3$SO$_3$)$_2$[7] (2.3619(11) Å) and closer to those found in [Au(Ph$_2$PC-(S)NPh)]$_2$[13] (from 2.306(5) to 2.318(3) Å) or in [Au(cHex$_2$PC-(S)NPh)]$_2$[13] (2.306(1) Å). Complex **3** also shows an N–H ⋯ F hydrogen bond between adjacent tetranuclear units with an H ⋯ F distance of 2.42 Å (Table 2).

Cationic complexes can be synthesized in similar ways using the complex [Au(tht)$_2$]ClO$_4$ as gold precursor. Thus, its reactions with diphenylphosphinothioformamide in a 1 : 2 or 1 : 3 molar ratio give rise to the mononuclear derivatives [Au-{Ph$_2$PC(S)N(H)Me}$_2$]ClO$_4$ (**4**) or [Au{Ph$_2$PC(S)N(H)Me}$_3$]-ClO$_4$ (**5**), respectively, in high yield, by displacement of both tetrahydrothiophene ligands. The analytical data are in accordance with the proposed formulation. For both complexes, the molar conductivity in dilute acetone solutions (see Experimental), and also the presence in the infrared spectra of bands due to the ionic perchlorate at around 1100 (br,vs) and 620 (m) cm^{-1},[29] are in accordance with an ionic formulation. Also, in both cases, the presence of only one resonance in their ^{31}P{^{1}H} NMR spectra and the downfield shift, more than 40 ppm compared with the starting material, is indicative of the equivalence of all the phosphorus atoms in each complex, and also of the coordination of the ligands through the phosphorus centers.

In the case of complex **5**, the three-coordination around the gold(I) center is confirmed in solid state by the X-ray diffraction analysis and, significantly, the absence of any other phosphorus resonance in the spectrum of this complex suggests that the

Table 4 Selected bond lengths [Å] and angles [°] for compound **5**[a]

Au–P(1)	2.3759(13)	S–C(1)	1.645(5)
P–C(11)	1.814(5)	N–C(1)	1.319(7)
P–C(21)	1.818(5)	N–C(2)	1.452(7)
P–C(1)	1.860(5)		
P#1–Au–P	119.429(9)	C(1)–P–Au	115.02(17)
C(11)–P–C(21)	104.7(2)	C(1)–N–C(2)	123.7(5)
C(11)–P–C(1)	106.1(2)	N–C(1)–S	124.7(4)
C(21)–P–C(1)	101.7(3)	N–C(1)–P	113.3(4)
C(11)–P–Au	107.64(17)	S–C(1)–P	122.0(3)
C(21)–P–Au	120.43(17)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-y + 1, x - y, z$.

Table 5 Selected bond lengths [Å] and angles [°] for compound **7**[a]

Au–P	2.2685(16)	Au–Au#1	2.9104(6)
Au–S#1	2.3276(17)		
P–Au–S#1	170.52(6)	C(1)–S–Au#1	104.9(2)
P–Au–Au#1	78.64(4)	C(1)–N–C(2)	118.7(6)
S#1–Au–Au#1	93.74(4)	N–C(1)–S	126.6(5)
C(11)–P–Au	117.5(2)	N–C(1)–P	115.6(5)
C(21)–P–Au	114.59(19)	S–C(1)–P	117.8(3)
C(1)–P–Au	107.2(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, -y + 1/2, z$.

three-coordination remains also in solution. The molecule (Fig. 3) crystallizes in the trigonal system. The gold center lies on a three-fold axis 0.13 Å out of the plane formed by the three phosphorus atoms. The Au–P distance (2.3759(13) Å) (Table 4) is very close to those found in [Au{Ph$_2$P(C$_6$H$_4$)NH$_2$}$_3$]ClO$_4$ (2.3688(12), 2.3738(12) Å).[11] These values lie between those found in [Au(PPh$_3$)$_3$]ClO$_4$ (2.345–2.408 Å, three independent determinations)[30–32] or in other three-coordinated complexes of the type [Au(P–P)P]$^+$ in which P–P is a diphosphine and P a monophosphine bonded to gold. In such cases the Au–P (monodentate phosphine) distance (opposite to the narrowest angle) is shorter than the other two, some examples are [Au{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}(PPh$_3$)]ClO$_4$ (2.318(1)–2.417(1) Å),[33] [Au{(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}(PPh$_3$)] (2.2831(13)–2.3952(12) Å) or [Au$_2${μ-dppp}{(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}$_2$] (2.288(3)–2.443(3) Å).[34]
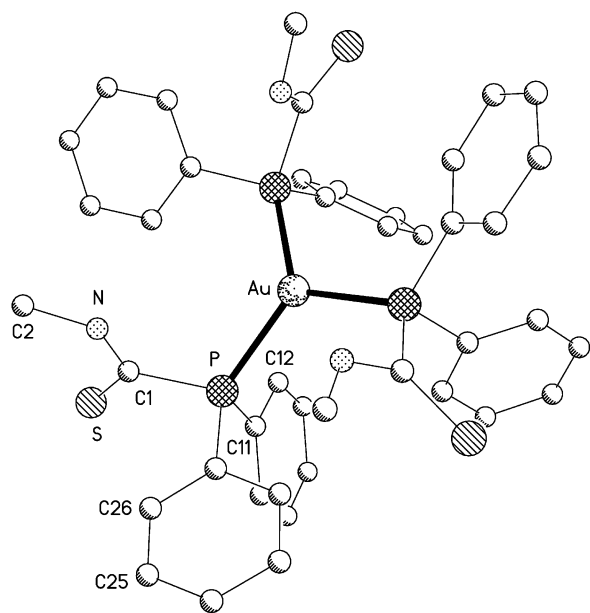
Fig. 3 Structure of the cation of complex **5**. H atoms omitted for clarity.

In the same way as before, the presence of poly-donor substituents permits further coordination of gold centers. Thus, the reaction of [Au{Ph$_2$PC(S)N(H)Me}$_2$]ClO$_4$ (**4**) and two equivalents of the precursor [AuCl(tht)] leads to the synthesis of the pale-yellow complex [Au{Ph$_2$PC(SAuCl)N(H)Me}$_2$]ClO$_4$ (**6**) (see Scheme 1). Its infrared spectrum, in addition to the bands from the thioformamide ligand and the ionic perchlorate, displays a broad absorption at 327 cm^{-1}. This can be assigned to the stretching v(Au–Cl) and v(Au–S) vibration modes, which appear at similar energies; this is indicative of the coordination of the new Au–Cl units to the starting material through the sulfur centers. Its ionic nature is also confirmed by the conductivity measurement in acetone solution (126 Ω^{-1} cm^2 mol^{-1}),

typical of 1 : 1 electrolytes. Also, its ^{31}P{^{1}H} NMR spectrum displays one single resonance, which indicates that the equivalence of both phosphorus centers in the starting material is not affected for the new metal coordination.

Attempts to synthesize polynuclear molecules starting from the three-coordinate complex **5** and gold(I) precursor complexes bearing weakly coordinated ligands led to the dissociation of one of the ligands and to the isolation of a mixture of products, in which we could identify the mononuclear complex **4**.

As has been observed for complex **2**, the phosphinodithioformamide ligand Ph$_2$PC(S)N(H)Me is reactive towards Lewis bases, deprotonating the amide group and leading to a new anionic ligand [Ph$_2$PC(S)NMe]$^-$ in which the redistribution of the electron density allows a new reactivity towards gold(I) precursors.

Thus, the reaction between complex [AuCl{Ph$_2$PC(S)N(H)-Me}] (**1**) and Tl(acac) (acac = acetylacetonate) in equimolecular amounts leads to the formation of [Au{Ph$_2$PC(S)NMe}] units in solution, accompanied by precipitation of TlCl and deprotonation by the acetylacetonate ligand. These mononuclear units self-associate giving the diauracyclic complex [Au{Ph$_2$-PC(S)NMe}]$_2$ (**7**) (Scheme 2). This complex was already described by Tiekink *et al.*[13] and synthesized by a different route. Its analytical and spectroscopic data are in accordance with those already reported.

The crystal structure of complex **7** has been elucidated by X-ray diffraction analysis (Fig. 4). The molecule possesses crystallographic two-fold symmetry. The gold centers display distorted linear geometry (P–Au–S#1 170.52(6)°) (Table 5), associated with the presence of intramolecular gold ··· gold contacts of 2.9014(6) Å. These interactions are shorter than those found in **3**. The Au–P (2.2685(13) Å) distance is shorter than that found in **3**, whereas the Au–S#1 (2.3276(17) Å) bond distance is slightly shorter in **3** than in **7**. Both the phosphorus and sulfur donor heteroatoms are coordinated to gold(I) centers, forming an eight-membered metallacyclic ring, while the nitrogen atoms are in an exocyclic disposition that could be appropriate for the coordination of further metal centers, thus, enhancing the nuclearity of the starting complex. Accordingly, reaction of complex [Au{Ph$_2$PC(S)NMe}]$_2$ (**7**) with two
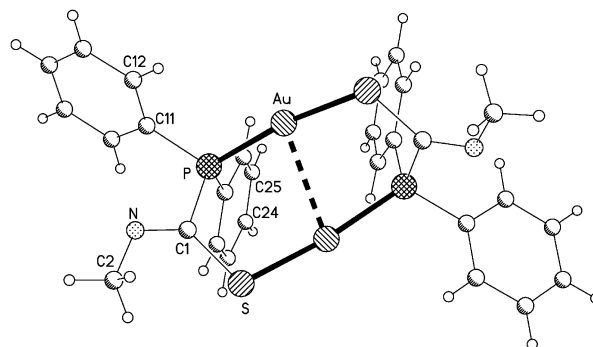
Fig. 4 Molecular structure of complex **7**.
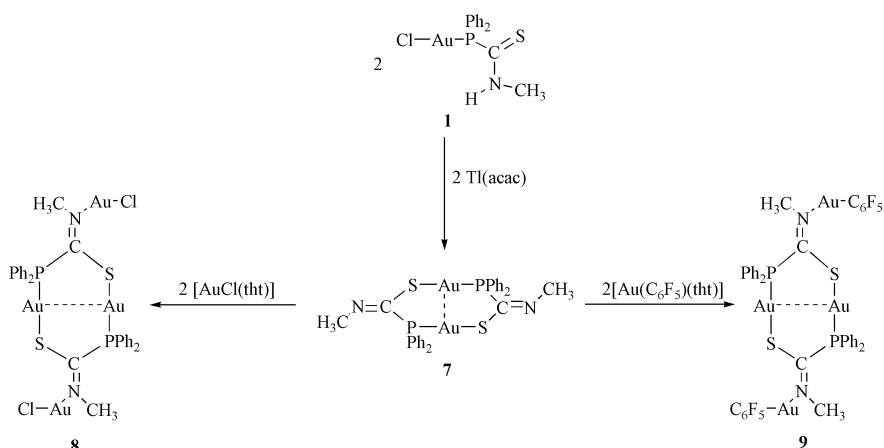
Scheme 2

equivalents of [AuX(tht)] (X = Cl or C_6F_5) leads to the formation of derivatives [Au$_2${Ph$_2$PC(S)N(AuX)Me}$_2$] (X = Cl (**8**) and C_6F_5 (**9**)) by displacement of the weakly coordinated tetrahydrothiophene ligand and coordination of the [AuX] fragments to the nitrogen atoms of complex **7** (See Scheme 2). The analytical data for both complexes are in accordance with the proposed formulation. The infrared spectrum for each complex show common ν(C=N) vibrations at 1602 (**8**) and 1592 cm^{-1} (**9**), respectively, appearing at 1561 cm^{-1} for **7**.[13] Besides, complex **8** displays a vibration at 328 cm^{-1} corresponding to the ν(Au–Cl) vibration, while complex **9** shows the ν(Au(I)–C$_6$F$_5$) pattern at 795, 955 and 1504 cm^{-1}. In both cases these new vibrations arise from the coordinated [AuX] fragments. The ^{31}P{^{1}H} NMR spectra of these complexes show one singlet in each case at 48.0 (**8**) and 48.0 ppm (**9**). This chemical shifts are not very different from that of the starting complex **7** (50.7 ppm), which would indicate a similar coordination behavior for the phosphorus centers.

Experimental

General

Caution! Perchlorate salts may be explosive. The compounds Ph$_2$PC(S)N(H)Me,[14] [Au(tht)$_2$]ClO$_4$,[35] [AuCl(tht)] [36] and [Au(C$_6$F$_5$)(tht)] [37] were prepared by literature methods.

Instrumentation

Infrared spectra were recorded in the 4000–200 cm^{-1} range on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer, using Nujol mulls between polyethylene sheets. C, H, N, S analysis were carried out with a C.E. Instrument EA-1110 CHNS-O microanalyser. Mass spectra were recorded on a HP-5989B Mass Spectrometer API-Electrospray with interface 59987A. ^{1}H, ^{19}F and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker ARX 300 in (CD$_3$)$_2$CO or CDCl$_3$ solutions. Chemical shifts are quoted relative to SiMe$_4$ (^{1}H external), CFCl$_3$ (^{19}F external) and H$_3$PO$_4$ (85%) (^{31}P, external).

Synthesis

[AuCl(Ph$_2$PC(S)N(H)Me)] (1). To a dichloromethane solution (20 mL) of [AuCl(tht)] (0.1 g, 0.3 mmol) was added Ph$_2$PC(S)N(H)Me (0.08 g, 0.3 mmol) and after one hour of stirring the solvent was evaporated to *ca.* 5 mL. Addition of n-hexane (20 mL) led to precipitation of complex **1** as a pale-yellow solid. Yield: 83%. Mass spectrum: [M − Cl]$^+$ at *m/z* = 456 (100%). Anal. Calcd. for: C$_{14}$H$_{14}$AuClNPS (**1**): C, 34.20; H, 2.85; N, 2.85; S, 6.5. Found: C, 33.65; H, 2.45; N, 2.65; S, 6.25%. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 55.5 (s). ^{1}H NMR (CDCl$_3$) δ: 3.99 [m, CH$_3$], 7.62–7.19 [m, aromatic protons], 9.44 [m, N–H]. Λ_M = 4.4 Ω^{-1} cm^2 mol^{-1}.

[Au(C$_6$F$_5$)(Ph$_2$PC(S)N(H)Me)] (2). To a dichloromethane solution (20 mL) of [Au(C$_6$F$_5$)(tht)] (0.2 g, 0.44 mmol) was added Ph$_2$PC(S)N(H)Me (0.115 g, 0.44 mmol) and the mixture was stirred for one hour. After evaporation of the solvent to *ca.* 5 mL, addition of n-hexane (20 mL) gave complex **2** as a yellow solid. Yield: 77%. Mass spectrum: [2M − C$_6$F$_5$]$^+$ at *m/z* = 1080 (100%). Anal. Calcd. for: C$_{20}$H$_{14}$AuF$_5$NPS (**2**): C, 38.55; H, 2.25; N, 2.25; S, 5.15. Found: C, 38.55; H, 2.40; N, 2.45; S, 4.75%. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 56.0(s). ^{19}F NMR (CDCl$_3$) δ: −116.33 [m, 2F, *o*-F], −156.66 [t, 1F, *p*-F, ^3J(F$_p$–F$_m$) 19.9 Hz], −162.09 [m, 2F, *m*-F]. ^{1}H NMR (CDCl$_3$) δ: 4.34 [d, CH$_3$, J(H–P) 7.4 Hz], 7.70–7.25 [m, aromatic protons], 8.50 [m, N–H]. Λ_M = 5.5 Ω^{-1} cm^2 mol^{-1}.

[Au$_2$(C$_6$F$_5$)$_2$(Ph$_2$PC(S)N(H)Me)] (3). Method 1. To a solution (20 mL) of [Au(C$_6$F$_5$)(tht)] (0.4 g, 0.88 mmol) in 20 mL of dichloromethane was added Ph$_2$PC(S)N(H)Me (0.115 g, 0.44 mmol) and after one hour of stirring the solvent was evaporated to *ca.* 5 mL. Addition of n-hexane (20 mL) led to precipitation of complex **3** as a pale-yellow solid. Yield: 72%. Method 2. To a dichloromethane solution (20 mL) of [Au(C$_6$F$_5$)(tht)] (0.2 g, 0.44 mmol) was added [Au(C$_6$F$_5$)-(Ph$_2$PC(S)N(H)Me)] (**2**) (0.274 g, 0.44 mmol) and the mixture was stirred for one hour. Evaporation of the solvent in a vacuum to *ca.* 5 mL and addition of n-hexane (20 mL) gave **3** as a pale-yellow solid. Yield: 65%.

Mass spectrum: [M − C$_6$F$_5$] at *m/z* = 820 (10%). Anal. Calcd. for: C$_{26}$H$_{14}$Au$_2$F$_{10}$NPS (**3**): C, 31.65; H, 1.45; N, 1.40; S, 3.25. Found: C, 31.5; H, 1.30; N, 1.45; S, 3.2%. ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO) δ: 60.0(s). ^{19}F NMR ((CD$_3$)$_2$CO) δ: −114.53 [m, 2F, *o*-F], −115.23 [m, 2F, *o*-F], −160.49 [t, 1F, *p*-F, ^3J(F$_p$–F$_m$) 20.0 Hz] −161.84 [t, 1F, *p*-F, ^3J(F$_p$–F$_m$) 20.0 Hz], −163.84 [m, 2F, *m*-F], −164.30 [m, 2F, *m*-F]. ^{1}H NMR ((CD$_3$)$_2$CO) δ: 3.55 [s, CH$_3$], 7.96–7.71 [m, aromatic protons], 9.5 [m, N–H]. Λ_M = 5 Ω^{-1} cm^2 mol^{-1}.

[Au(Ph$_2$PC(S)N(H)Me)$_2$]ClO$_4$ (4). To a solution of [Au-(tht)$_2$]ClO$_4$ (0.5 g, 1.00 mmol) was added Ph$_2$PC(S)N(H)Me (0.548 g, 2.1 mmol) in 20 mL of dichloromethane and the solution was stirred for one hour. Evaporation of the solvent to *ca.* 5 mL and further addition of diethyl ether (20 mL) led to the precipitation of complex **4** as a yellow solid. Yield: 93%. Mass spectrum: [M]$^+$ at *m/z* = 715 (100%). Anal. Calcd. for: C$_{28}$H$_{28}$AuClN$_2$O$_4$P$_2$S$_2$ (**4**): C, 41.25; H, 3.45; N, 3.45; S, 7.85. Found: C, 41.35; H, 3.70; N, 3.90; S, 7.25%. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 54.2(s). ^{1}H NMR (CDCl$_3$) δ: 4.16 [d, CH$_3$, J(H–P) 6.2 Hz], 7.71–7.00 [m, aromatic protons], 9.25 [m, N–H]. Λ_M = 117.4 Ω^{-1} cm^2 mol^{-1}.

[Au(Ph$_2$PC(S)N(H)Me)$_3$]ClO$_4$ (5). To a dichloromethane solution (20 mL) of [Au(tht)$_2$]ClO$_4$ (0.075 g, 0.16 mmol) was

Table 6 Details of data collection and structure refinement for complexes **1**, **3**, **5** and **7**

Compound	1	3	5	7
Formula	$C_{14}H_{14}AuClNPS$	$C_{52}H_{28}Au_4F_{20}N_2P_2S_2$	$C_{42}H_{42}AuClN_3OP_3S_3$	$C_{28}H_{26}Au_2N_2P_2S_2$
M	491.71	1974.69	1074.29	910.50
Crystal system	Monoclinic	Monoclinic	Trigonal	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P(-3)$	$Pccn$
a/Å	9.3007(9)	16.8870(2)	14.0697(9)	23.576(3)
b/Å	9.0894(8)	12.6690(2)	14.0697(9)	7.0362(10)
c/Å	18.4826(18)	25.0874(3)	14.7342(11)	16.6857(18)
α/°	90	90	90	90
β/°	98.385(3)	92.223(1)	90	90
γ/°	90	90	120	90
U/Å³	1545.8(3)	5363.20(12)	2526.0(3)	2768.0(6)
Z	4	4	2	4
μ(Mo-Kα)/mm^{-1}	9.913	11.155	3.223	10.876
No. of reflections measured	12477	56611	4944	4112
No. of unique reflections	4494	12730	2960	2440
No. of reflections used	4494	11295	2960	2440
R_{int}	0.0410	0.1010	0.0230	0.0284
$R^a(F > 4\sigma(F))$	0.0219	0.0469	0.0318	0.0281
$wR^b(F^2$, all refl.)	0.0432	0.0957	0.0901	0.0652

^{a} $R(F) = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. ^{b} $wR(F^2) = [\Sigma\,\{w(F_o^2 - F_c^2)^2\}/\Sigma\,\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

added Ph$_2$PC(S)N(H)Me (0.123 g, 0.48 mmol) and after one hour of stirring the solvent was evaporated to *ca.* 5 mL. Addition of diethyl ether (20 mL) gave to the precipitation of complex **5** as a yellow solid. Yield: 76%. Mass spectrum: [M]$^+$ at *m/z* = 974 (1%). Anal. Calcd. for: C$_{42}$H$_{42}$AuClN$_3$O$_4$P$_3$S$_3$ (**5**): C, 46.95; H, 3.95; N, 3.90; S, 8.95. Found: C, 46.50; H, 4.35; N, 3.75; S, 8.45%. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 53.1(s). ^{1}H NMR (CDCl$_3$) δ: 3.83 [d, CH$_3$, *J*(H–P) 6.5 Hz], 7.72–7.03 [m, aromatic protons], 9.35 [m, N–H]. Λ_M = 114.2 Ω^{-1} cm^2 mol^{-1}.

[Au(Ph$_2$PC(S)N(H)Me)$_2$\{AuCl\}$_2$]ClO$_4$ (6). To a solution of [Au(Ph$_2$PC(S)N(H)Me)$_2$]ClO$_4$ (**4**) (0.08 g, 0.1 mmol) in 20 mL of dichloromethane was added [AuCl(tht)] (0.063 g, 0.2 mmol) and the mixture was stirred for one hour. Evaporation of the solvent to 5 mL and addition of diethyl ether (20 mL) led to precipitation of complex **6** as a yellow solid. Yield: 83%. Mass spectrum: [M]$^+$ at *m/z* = 1179 (40%). Anal. Calcd. for: C$_{28}$H$_{28}$Au$_3$Cl$_3$N$_2$O$_4$P$_2$S$_2$ (**6**): C, 26.30; H, 2.20; N, 2.15; S, 5.01. Found: C, 25.90; H, 2.55; N, 2.15; S, 5.15%. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 58.2(s). ^{1}H NMR (CDCl$_3$) δ: 5.58 [m, CH$_3$], 8.10–7.52 [m, aromatic protons], 10.59 [m, N–H]. Λ_M = 125.6 Ω^{-1} cm^2 mol^{-1}.

[Au$_2$\{Ph$_2$PC(S)NMe\}$_2$] (7). To a dichloromethane solution (20 mL) of [AuCl(Ph$_2$PC(S)N(H)Me)] (**1**) (0.100 g, 0.2 mmol) was added [Tl(acac)] (0.062 g, 0.2 mmol) and after four hours of stirring the TlCl precipitate was filtered off. Then the solvent was evaporated to *ca.* 5 mL. Addition of n-hexane (20 mL) led to precipitation of complex **7** as a pale-yellow solid. Yield: 56%.

[Au$_2$\{Ph$_2$PC(S)N(AuCl)Me\}$_2$] (8). To a dichloromethane solution (20 mL) of [Au(Ph$_2$PC(S)NMe)]$_2$ (**7**) (0.075 g, 0.08 mmol) was added [AuCl(tht)] (0.053 g, 0.16 mmol) and the solution was allowed to stir for one hour. The solvent was evaporated to *ca.* 5 mL. Addition of n-hexane (20 mL) led to precipitation of complex **8** as a pale-yellow solid. Yield: 40%. Mass spectrum: [M + H]$^+$ at *m/z* = 1376 (2%). Anal. Calcd. for: C$_{28}$H$_{26}$Au$_4$Cl$_2$N$_2$P$_2$S$_2$ (**8**): C, 24.5; H, 1.90; N, 2.05; S, 4.80. Found: C, 24.75; H, 1.80; N, 2.05; S, 4.80%. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 48.0(s). ^{1}H NMR (CDCl$_3$) δ: 3.42 [m, CH$_3$], 7.85–7.18 [m, aromatic protons].

[Au$_2$\{Ph$_2$PC(S)N(Au(C$_6$F$_5$))Me\}$_2$] (9). To a solution of [Au(Ph$_2$PC(S)NMe)]$_2$ (**7**) (0.075 g, 0.8 mmol) in dichloromethane (20 mL) was added [AuCl(tht)] (0.063 g, 0.2 mmol) and after one hour of stirring the solvent was evaporated to

ca. 5 mL. Addition of diethyl ether (20 mL) gave complex **9** as a yellow solid. Yield: 40%. Mass spectrum: [M − AuC$_6$F$_5$]$^+$ at *m/z* = 1275 (15%). Anal. Calcd. for: C$_{40}$H$_{26}$Au$_4$F$_{10}$N$_2$P$_2$S$_2$ (**9**): C, 29.30; H, 1.60; N, 1.70; S, 3.90. Found: C, 29.20; H, 2.05; N, 1.80; S, 4.20%. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 48.0(s). ^{19}F NMR (CDCl$_3$) δ: −115.10 [m, 4F, −159.60 [m, 2F, *p*-F], −163.20 [t, 4F, *m*-F]. ^{1}H NMR (CDCl$_3$) δ: 3.75 [m, CH$_3$], 7.70–7.20 [m, aromatic protons].

Crystal structure determinations

The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Bruker SMART 1000-CCD (**1**), Siemens P4 (**5**, **7**) and a Nonius Kappa CCD (**3**) diffractometer. Data were collected using monochromated Mo Kα radiation (λ 0.71073 Å). Absorption correction were based on ψ-scans (**5**, **7**) or multiple scans (Sadabs (**1**), Scalepack (**3**)). The structures were refined on F^2 using the program SHELXL-97.[38] All non-hydrogen atoms were refined anisotropically. H atoms were included using a riding model or rigid methyl groups. Special features of refinement: restraints to light atom U value components and to local ring symmetry were employed to improve stability of refinement. Further crystallographic details are given in Table 6. Compound **5**: Ill-defined residual electron density close to the threefold axis may be caused by disordered solvent (possibly petrol ether components). The largest such peak was arbitrarily refined as an isotropic C atom. Values for M, density, *etc.*, do not include any solvent.

CCDC reference numbers 200117–200119 & 200468.

See http://www.rsc.org/suppdata/dt/b2/b211865c/ for crystallographic data in CIF or other electronic format.

References

1 H. Schmidbaur, in *Gold: Progress in Chemistry, Biochemistry and Technology*, ed. H. Schmidbaur, J. Wiley & Sons, Chichester, 1999.
2 W. S. Rapson and T. Groenewald, in *Gold Usage*, Academic Press, London, 1978.
3 P. J. Sadler, *Gold Bull.*, 1976, **9**, 110.
4 K. C. Dash and H. Schmidbaur, in *Metal Ions in Biological Systems*, ed. H. Sigel, M. Dekker, New York–Basel, 1982, vol. 14, pp. 179ff.

5 A. Ulman, *Chem. Rev.*, 1996, **96**, 1533 and references therein.
6 C. F. Shaw III, in *Gold: Progress in Chemistry, Biochemistry and Technology*, ed. H. Schmidbaur, J. Wiley & Sons, Chichester, 1999, pp. 259ff.
7 E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. A. Rodríguez, O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *Inorg. Chem.*, 1998, **37**, 6002.
8 E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. A. Rodríguez, O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *Chem. Eur. J.*, 2000, **6**, 636.
9 O. Crespo, A. Laguna, E. J. Fernández, J. M. López-de-Luzuriaga, P. G. Jones, M. Teichert, M. Monge, P. Pyykkö, N. Runeberg, M. Schütz and H.-J. Werner, *Inorg. Chem.*, 2000, **39**, 4786.
10 P. Bella, O. Crespo, E. J. Fernández, A. K. Fischer, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga and M. Monge, *J. Chem. Soc., Dalton Trans.*, 1999, 4009.
11 O. Crespo, E. J. Fernández, M. Gil, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga and M. E. Olmos, *J. Chem. Soc., Dalton Trans.*, 2002, 1319.
12 G. Siasios and E. R. T. Tiekink, *Malays. J. Sci.*, 1996, **17B**, 1.
13 D. Clajus, R. Kramolowsky, G. Siasios and E. R. T. Tiekink, *Inorg. Chim. Acta*, 1998, **281**, 64.
14 K. Issleib and G. Hárzfeld, *Z. Anorg. Allg. Chem.*, 1967, **351**, 19.
15 R. Usón, A. Laguna and J. Vicente, *Rev. Acad. Cienc. Zaragoza*, 1976, **31**, 211.
16 H. Werner and J. Gotzig, *Organometallics*, 1983, **2**, 547.
17 J. Gotzig, R. Werner and H. Werner, *J. Organomet. Chem.*, 1985, **285**, 99.
18 C. Hollatz, A. Schier and H. Schmidbaur, *J. Am. Chem. Soc.*, 1997, **119**, 8115.
19 N. C. Baeziger, K. M. Dittemore and J. R. Doyle, *Inorg. Chem.*, 1974, **13**, 805.
20 F. Canales, M. C. Gimeno, P. G. Jones, A. Laguna and C. Sarroca, *Inorg. Chem.*, 1997, **36**, 5206.
21 D. T. Hill, G. R. Girard, F. L. McGabe, R. K. Johnson, P. D. Stupik, J. H. Zhang, W. H. Reiff and D. S. Eggleston, *Inorg. Chem.*, 1989, **28**, 3529.
22 W. Carr, R. Colton and D. Dakternieks, *Inorg. Chem.*, 1984, **23**, 720.
23 M. López-de-Luzuriaga, A. Sladek, W. Schneider and H. Schmidbaur, *Chem. Ber.*, 1997, **130**, 641.
24 W. E. van Zyl, J. M. López-de-Luzuriaga, A. A. Mohamed, R. J. Staples and J. P. Fackler, Jr., *Inorg. Chem.*, 2002, **41**, 4579.
25 W. E. van Zyl, J. M. López-de-Luzuriaga, J. P. Fackler, Jr. and R. J. Staples, *Can. J. Chem.*, 2001, **79**, 896.
26 P. Bishop, P. Marsh, A. K. Brisdon, B. J. Brisdon and M. F. Mahon, *J. Chem. Soc., Dalton Trans.*, 1998, 675.
27 S. S. Tang, C.-P. Chang, I. J. B. Lin, L.-S. Liou and J.-C. Wang, *Inorg. Chem.*, 1997, **36**, 2294.
28 P. M. Van Calcar, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1997, **36**, 5231.
29 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.
30 P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1980, 1031.
31 L. J. Guggenberger, *J. Organomet. Chem.*, 1984, **81**, 271.
32 P. G. Jones, *Acta Crystallogr., Sect. B*, 1980, **36**, 1105.
33 O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1992, 1601.
34 O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Inorg. Chem.*, 1996, **33**, 1361.
35 R. Usón, A. Laguna, M. Laguna, J. Jiménez, M. P. Gómez, A. Sainz and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1990, 3457.
36 E. A. Allen and W. Wilkinson, *Spectrochim. Acta*, 1972, **28A**, 2257.
37 R. Usón, A. Laguna and J. Vicente, *J. Chem. Soc., Chem. Commun.*, 1976, 353.
38 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.