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Binuclear diorganophosphinothioformamido complexes of gold(I): synthesis and crystal structure of $[Au(Ph_2PC(S)NPh)]_2$ and related systems

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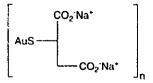
Abstract

Binuclear gold compounds, $[Au(R_2PC(S)NR')]_2$, were characterized from the reactions of $HAuCl_4$ or Ph_3PAuCl with $R_2PC(S)N(H)R'$. The complexes feature bidentate bridging ligands that link two gold centres leading to eight-membered metallacycles and linear S–Au–P coordination geometries. In the case of $[Au(Ph_2PC(S)NPh)]_2$, crystal structure analysis shows the presence of two conformations in the one lattice, i.e. an extended chair and a twisted conformation.

Keywords: Gold complexes; Thioformamide complexes; Thiolate complexes; Crystal structures

1. Introduction

Interest in gold thiolate chemistry arises, in part, from the use of gold compounds in the treatment of rheumatoid arthritis [1–4], with a number of gold thiolates such as aurothiomalate (Myocrisin, **1**) and aurothioglucose (Solganol, **2**) used in this context. These polymeric species, which are generally water soluble, may be broken down to monomeric complexes on the addition of triorganophosphine; this can also lead to potent species. Thus, monomeric lipid soluble auranofin, [(1-thio-β-D-glucopyranose-2,3,4,6-tetraacetato-*S*)(triethylphosphine)gold(I)] **3**, is used clinically and can be administered orally rather than by injection as for the polymeric species. Given the clinical use of such complexes, it is not surprising that these and related species have been examined for potential anti-tumour activity. Recent studies have demonstrated that a number of phosphinegold(I) thiolates, with the thiolate derived from a thionucleobase such as 6-mercaptopurine, possess significant in vitro and in vivo anti-tumour activity [5–8]. As a continuation of studies in this area, the interaction of the potentially polydentate ligand diorganophosphinothioformamide, $R_2PC(S)N(H)R'$, R = alkyl, aryl, **4**, with gold was investigated.



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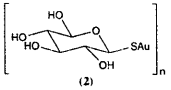

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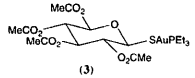

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Anions derived from **4** have been shown to coordinate principally in an S-,P-chelating mode, however, monodentate

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P-, chelating S-,N- and bidentate bridging S-,P-,S-,N- and P-,N-modes have also been observed crystallographically [9]. In this study, the reactions of $R_2PC(S)N(H)R'$ with $HAuCl_4$ and R_3PAuCl each yielded binuclear gold(I) complexes with the general formula $[Au(R_2PC(S)NR')]_2$ which were characterized spectroscopically as well as crystallographically for R = Ph, R' = Ph and cHex.

2. Experimental

2.1. Materials and reagents

All chemicals used were of reagent grade or better. The Ph_2PH [10] and $R_2PC(S)N(H)R'$ phosphines [11] and gold salts $HAuCl_4$ [12] and Ph_3PAuCl [13] were prepared by literature methods. The Ph_3P and $cHex_2PH$ phosphines were obtained from Aldrich.

2.2. Physical measurements

IR spectra were recorded as KBr discs on a Perkin-Elmer 1720X FT spectrophotometer, proton (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra on a Bruker ACP-300 NMR spectrometer with $CDCl_3$ as the solvent and $SiMe_4$ as the internal reference in each case. Proton-decoupled ^{31}P NMR spectra were recorded as $CHCl_3$ solutions on a Bruker AM-360 NMR spectrometer at 36.44 MHz with 85% H_3PO_4 in D_2O as the internal reference. Fast atom bombardment (FAB) mass spectra were recorded with the assistance of T. Blumenthal on a VG ZAB-2HF spectrometer (using 3-nitrobenzyl alcohol as matrix, exciting gas argon, FAB gun voltage 7 kV, current 1 mA and accelerating potential 8 kV). Microanalytical data were obtained at the Universität Hamburg.

2.3. Syntheses

Two methods were employed to prepare $Au(R_2PC(S)NR')_2$; details are given in Table 1.

2.3.1. Method 1, reaction of $[Ph_2PC(S)N(H)Ph]$ with $HAuCl_4$

Under an inert atmosphere of dry N_2 and at 0°C (ice-bath), one molar equivalent of $HAuCl_4 \cdot 3H_2O$ (150 mg, 0.38 mmol) was dissolved in a solution of acetone and water (4:1 vol./vol., 5 cm^3). Three molar equivalents of thiodiglycol (0.12 cm^3, 1.15 mmol) were added dropwise to the yellow-orange solution over a period of 2 h, yielding a colourless solution. To this solution, a 1:1 molar equivalent of $[Ph_2PC(S)N(H)Ph]$ (134 mg, 0.42 mmol), dissolved separately in hot ethanol (~5 cm^3), was added dropwise over a period of 10 min. A solid precipitated out almost immediately and after the completion of the addition, the complex was collected by vacuum filtration and washed with cold ethanol. The crude product was recrystallized from a chloroform/ethanol solution (4:1 vol./vol., 5 cm^3) and the resulting crystals dried over P_2O_5 in vacuo.

Table 1
Crystallographic data

Formula	$[Au(Ph_2PC(S)NPh)]_2 \cdot 0.33CH_2Cl_2$	$[Au(cHex_2PC(S)NPh)]_2$
M	1063.0	1058.9
Colour	yellow	pale yellow
Crystal size (mm)	0.08×0.28×0.28	0.04×0.04×0.32
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	16.500(4)	10.061(1)
b (Å)	13.862(1)	13.301(2)
c (Å)	24.771(8)	7.862(4)
α (°)		104.32(2)
β (°)	92.58(5)	104.11(2)
γ (°)		77.14(1)
V (Å^3)	5659(1)	973.8(5)
Z	6	1
D_c (g cm^{-3})	1.871	1.805
$F(000)$	3036	516
μ (cm^{-1})	80.18	77.69
Range of transmission factors	0.064–0.365	0.483–0.568
No. data collected	12072	3830
No. unique data	9988	3438
No. unique data with $I \geq 2.5\sigma(I)$	5206	2848
R	0.042	0.027
R_w	0.046	0.028
Residual density (e Å^{-3})	1.51	1.85

Table 2
Fractional atomic coordinates for $Au(R_2PC(S)NR')_2$

Atom	x	y	z
R = R' = Ph			
Au(1)	−0.00563(4)	0.05897(3)	0.04863(2)
Au(2)	0.03976(4)	0.16526(4)	0.15805(2)
Au(3)	0.08357(5)	0.35488(4)	0.20149(3)
Cl(1)	0.4893(8)	0.1282(7)	0.0297(4)
Cl(2)	0.4630(8)	0.0781(7)	0.1369(4)
S(1a)	0.0391(3)	0.2029(2)	0.0128(1)
S(1b)	0.2125(3)	0.3632(2)	0.1700(2)
S(1c)	−0.0984(3)	0.1910(3)	0.1519(2)
P(1a)	0.0626(3)	0.0728(2)	−0.0861(1)
P(1b)	0.1756(3)	0.1462(2)	0.1708(2)
P(1c)	−0.0457(3)	0.3552(3)	0.2292(2)
N(1a)	0.0191(9)	0.2557(7)	−0.0922(4)
N(2b)	0.2737(9)	0.2315(8)	0.1020(5)
N(3c)	−0.176(1)	0.3604(9)	0.1621(5)
C(1a)	0.038(1)	0.1903(8)	−0.0567(5)
C(1b)	0.229(1)	0.2490(9)	0.1417(6)
C(1c)	−0.118(1)	0.307(1)	0.1759(6)
C(11a)	0.044(1)	0.0829(9)	−0.1576(6)
C(11b)	0.208(1)	0.1436(9)	0.2425(6)
C(11c)	−0.060(1)	0.280(1)	0.2868(7)
C(12a)	−0.036(1)	0.104(1)	−0.1778(7)
C(12b)	0.287(1)	0.159(1)	0.2586(7)
C(12c)	−0.003(2)	0.281(2)	0.3285(9)
C(13a)	−0.055(1)	0.103(1)	−0.2331(8)
C(13b)	0.312(1)	0.143(1)	0.3122(9)
C(13c)	−0.012(2)	0.220(3)	0.375(1)
C(14a)	0.002(2)	0.082(2)	−0.2684(8)
C(14b)	0.255(2)	0.114(1)	0.3485(8)
C(14c)	−0.077(3)	0.161(3)	0.378(2)
C(15a)	0.075(2)	0.062(1)	−0.2497(9)
C(15b)	0.176(1)	0.104(1)	0.3318(8)
C(15c)	−0.126(3)	0.157(2)	0.337(1)
C(16a)	0.098(1)	0.063(1)	−0.1937(7)
C(16b)	0.151(1)	0.1191(9)	0.2790(6)
C(16c)	−0.121(2)	0.216(1)	0.2910(8)
C(21a)	0.172(1)	0.070(1)	−0.0778(6)
C(21b)	0.217(1)	0.0355(9)	0.1435(6)
C(21c)	−0.085(1)	0.472(1)	0.2452(6)
C(22a)	0.218(1)	0.156(1)	−0.077(1)
C(22b)	0.204(1)	0.015(1)	0.0881(6)
C(22c)	−0.046(1)	0.550(1)	0.2234(8)
C(23a)	0.297(2)	0.152(2)	−0.076(1)
C(23b)	0.230(1)	−0.072(1)	0.0678(7)
C(23c)	−0.081(2)	0.645(1)	0.2297(9)
C(24a)	0.339(1)	0.063(2)	−0.074(1)
C(24b)	0.264(1)	−0.142(1)	0.1035(7)
C(24c)	−0.144(2)	0.656(1)	0.259(1)
C(25a)	0.294(2)	−0.018(1)	−0.0742(8)
C(25b)	0.276(1)	−0.123(1)	0.1563(7)
C(25c)	−0.184(1)	0.579(1)	0.2810(8)
C(26a)	0.213(1)	−0.016(1)	−0.0748(7)
C(26b)	0.253(1)	−0.034(1)	0.1775(6)
C(26c)	−0.152(1)	0.487(1)	0.2734(7)
C(31a)	−0.007(1)	0.353(1)	−0.0770(6)
C(31b)	0.312(1)	0.309(1)	0.0764(7)
C(31c)	−0.231(1)	0.334(1)	0.1187(7)
C(32a)	−0.078(1)	0.367(1)	−0.0545(7)
C(32b)	0.275(1)	0.350(1)	0.0317(9)
C(32c)	−0.310(2)	0.325(2)	0.1295(8)
C(33a)	−0.105(1)	0.459(1)	−0.0451(8)
C(33b)	0.312(2)	0.427(2)	0.004(1)
C(33c)	−0.366(1)	0.303(2)	0.085(1)
C(34a)	−0.056(2)	0.535(1)	−0.0598(8)
C(34b)	0.385(2)	0.460(2)	0.021(1)
C(34c)	−0.336(2)	0.295(2)	0.037(1)
C(35a)	0.013(2)	0.525(1)	−0.0811(8)
C(35b)	0.422(2)	0.420(2)	0.063(1)
C(35c)	−0.263(2)	0.307(2)	0.025(1)
C(36a)	0.041(2)	0.429(1)	−0.0901(6)
C(36b)	0.384(2)	0.345(1)	0.0924(8)
C(36c)	−0.208(2)	0.324(2)	0.0680(9)
C(100)	0.428(2)	0.071(2)	0.078(1)
R = cHex, R' = Ph			
Au	0.06404(2)	0.00648(2)	0.18572(3)
S(1)	−0.2302(2)	0.1435(1)	−0.1509(2)
P(1)	−0.0954(1)	0.1535(1)	0.2524(2)
N(1)	−0.1966(5)	0.3207(4)	0.1047(7)
C(1)	−0.1770(6)	0.2201(5)	0.0633(8)
C(11)	−0.0191(6)	0.2521(5)	0.4375(8)
C(12)	0.0420(8)	0.2019(6)	0.5999(8)
C(13)	0.1192(8)	0.2754(7)	0.7573(9)
C(14)	0.2298(7)	0.3122(6)	0.700(1)
C(15)	0.1693(8)	0.3643(6)	0.539(1)
C(16)	0.0965(7)	0.2891(6)	0.3836(9)
C(21)	−0.2421(6)	0.1240(5)	0.3211(8)
C(22)	−0.3622(7)	0.2195(5)	0.343(1)
C(23)	−0.4785(7)	0..926(6)	0.406(1)
C(24)	−0.5306(7)	0.0954(6)	0.287(1)
C(25)	−0.4136(8)	0.0025(5)	0.266(1)
C(26)	−0.2981(7)	0.0284(5)	0.1995(9)
C(31)	−0.2618(6)	0.3830(4)	−0.0260(8)
C(32)	−0.3972(7)	0.3829(6)	−0.120(1)
C(33)	−0.4570(8)	0.4504(6)	−0.234(1)
C(34)	−0.3807(9)	0.5168(6)	−0.262(1)
C(35)	−0.2459(9)	0.5181(6)	−0.170(1)
C(36)	−0.1875(7)	0.4519(5)	−0.050(1)

2.3.2. Method 2. Reaction of [Ph_3PAuCl] with [$Ph_2PC(S)N(H)Ph$]

One molar equivalent of [Ph_3PAuCl] (200 mg, 0.40 mmol) was dissolved in tetrahydrofuran (25 cm^3) with stirring. A 1.1 molar equivalent of solid [$Ph_2PC(S)N(H)Ph$] (141 mg, 0.44 mmol) was added. Stirring was continued until dissolution after which Et_3N (~2 cm^3) was added dropwise over a few minutes during which the colour of the solution faded. After 45 min stirring, the solution was filtered and the solvent removed in vacuo. The product was washed with ethanol and then recrystallized from a small quantity of an ethanol/dichloromethane mixture (1:4 vol./vol., 5 cm^3). A crystal suitable for X-ray analysis was shown to have occluded CH_2Cl_2 in the lattice.

2.4. Crystallography

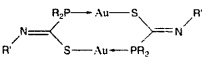
Intensity data for [$Au(Ph_2PC(S)NPh)]_2$ and [$Au(cHex_2PC(S)NPh)]_2$ were measured at room temperature on an

Enraf-Nonius CAD4F diffractometer equipped with Mo Kα radiation (graphite monochromator), $\lambda = 0.7107$ Å, using the ω–2θ scan technique to $\theta_{max} = 25.0°$. The data sets were corrected for Lorentz and polarization effects and for absorption employing an analytical procedure [14]; crystal data are collected in Table 1.

The structures were each solved by the Patterson method and refined by a full-matrix least-squares procedure based on F [14]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms included in the models at their calculated positions (C–H 0.97 Å). A weighting scheme of the form $w = 1/[\sigma^2(F)]$ was used for the R = R′ = Ph analysis, and $w = 1/[\sigma^2(F) + 0.0017F^2]$ for the second; both refinements were continued until convergence. The fractional atomic coordinates are listed in Table 2 and the numbering schemes employed are shown in Figs. 1 and 2 which were drawn with ORTEP [15] at the 45% probability level.

3. Results and discussion

The $[Au(R_2PC(S)NR')]_2$ compounds, **5**, were prepared from the reaction of $HAuCl_4$ with $R_2PC(S)N(H)R'$ (for R = Ph, R′ = Ph and Me; R = cHex, R′ = Ph) and from the reaction of R_3PAuCl and $R_2PC(S)N(H)R'$ in the presence of base; physical data are given in Table 3.



(5)

The complexes were characterized spectroscopically (IR, NMR and FAB mass) as well as crystallographically for R = R′ = Ph and R = cHex, R′ = Ph.

Selected IR bands are collected in Table 4. The ν(N–H) absorptions found in the $R_2PC(S)N(H)R'$ compounds were absent in the spectra of the complexes, indicating deprotonation. Two regions of the IR spectra are of particular interest, i.e. 1400–1600 (thioamide(I), mainly due to C–N) and around 1350 cm^{-1} (thioamide(II), mainly due to C–S). The thioamide(I) band, which occurs around 1500 cm^{-1} in the free ligand, shifts to higher frequencies in the complexes; the thioamide(II) band (around 1350 cm^{-1} in the ligands) is shifted to around 950 cm^{-1} [16]. These results suggest additional and reduced electron density in the C–N and C–S bonds respectively. Small shifts in the positions of the thioamide(I) and (II) bands in the spectra between the R′ = Ph and Me complexes are attributed to the differences in the inductive effects of these substituents.

The ^{1}H NMR spectra showed the expected resonances and integration. The notable feature of the ^{13}C NMR spectra was the shift upfield by approximately 40 ppm for the quaternary Cq, compared with the free ligands (Table 4). The ^{31}P NMR spectra showed one peak in each case, with the signal in the complex having moved downfield (~30 ppm) with respect to the free ligand, indicating coordination of the phosphorus atom; see Table 4.

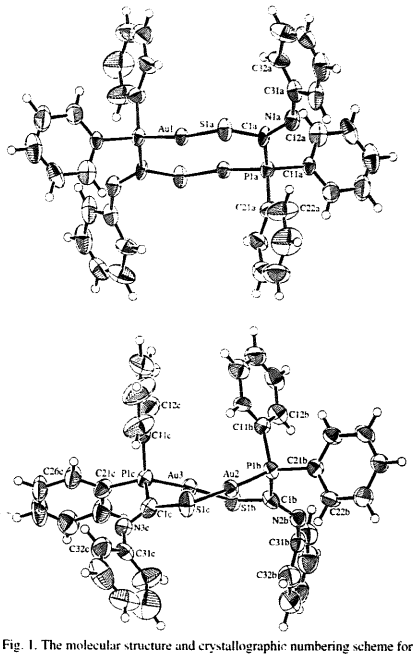


Fig. 1. The molecular structure and crystallographic numbering scheme for the two independent molecules of $[Au(Ph_2PC(S)NPh)]_2$: upper view, centrosymmetric molecule.

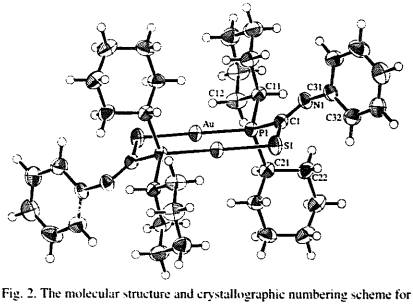


Fig. 2. The molecular structure and crystallographic numbering scheme for $[Au(cHex_2PC(S)NPh)]_2$.

The FAB mass spectra showed the presence of $[M]^+$ for each complex, however, in no case was this the most abundant

Table 3
Physical and microanalytical data for $Au(R_2PC(S)NR')_2$

	Colour	Yield (%)		M.p. (°C)	C (%) Found Calc.	H (%) Found Calc.	P (%) Found Calc.
		Method 1	Method 2				
R = Ph, R′ = Ph	pale yellow	91	80	250 (dec.)	43.9 44.1	2.8 2.9	6.0 6.0
R = Ph, R′ = Me	white	78	75	205–210 (dec.)	37.1 36.9	3.0 2.9	6.8 6.8
R = cHex, R′ = Ph	pale yellow	80	84	116–118	42.9 43.1	5.2 5.1	5.9 5.9
R = cHex, R′ = Me	pale yellow	[a]	78	145 (dec.)	36.2 36.0	5.5 5.4	6.3 6.6

[a] No reaction.

ion. The major ion observed in each of the spectra was as follows: for R = R′ = Ph, $[Au(Ph_2PC(S)NPh)_2]^+$ (*m/z* 838); for R = Ph, R′ = Me, $[Au_2S_2]^+$ (*m/z* 460); for R = cHex, R′ = Ph, $[M-(SCNPh,cHex)]^+$ (*m/z* 641); for R = cHex, R′ = Me, $[cHex_3PAu]^+$ (*m/z* 476). Except for the appearance of a fragment $[M-SCNR']^+$, no other common features in the spectra were noted.

Thus, the spectroscopic and microanalytical evidence indicates the formation of novel gold(I) complexes with deprotonated forms of $R_2PC(S)N(H)R'$ most likely coordinating via a thiolate sulfur and phosphorus. Unambiguous structure assignment is based on single crystal diffraction studies of two derivatives, namely R = R′ = Ph and R = cHex, R′ = Ph.

Crystals of $[Au(Ph_2PC(S)NPh)]_2$ crystallize with one and one-half molecules of $[Au(Ph_2PC(S)NPh)]_2$ as well as half a molecule of dichloromethane in the asymmetric unit. One of the independent molecules is centrosymmetric and the other occupies a general position. Crystals of $[Au(cHex_2PC(S)NPh)]_2$ are centrosymmetric with half a molecule comprising the asymmetric unit. The molecular geometries for $[Au(R_2PC(S)NPh)]_2$ are shown in Figs. 1 and 2 and selected interatomic parameters are collected in Table 5. The structures are binuclear with two gold atoms being bridged by a bidentate $[R_2PC(S)NPh]^-$ anion leading to eight-membered rings and approximately linear S–Au–P geometries. As can be seen from Table 5, the geometric parameters describing the four independent gold atoms are remarkably concordant. The S–C and C–N bond distances are consistent with single and double bonds respectively, i.e. structure **5**. Despite the similarity in the cited parameters, the structures are not identical owing to puckering in the metallacycles.

The centrosymmetric molecule in $[Au(Ph_2PC(S)NPh)]_2$ exists in an extended chair conformation with the mean deviation of the atoms from the 2 × (Au, S and P) least-squares plane being 0.072 Å; the C(1) atoms lie ±0.542(8) Å out of this plane. A similar conformation is found for $[Au(cHex_2PC(S)NPh)]_2$ where the comparable mean deviation is 0.024 Å with C(1) ±0.564(4) Å out of the plane. By contrast, significant puckering about the phosphorus atoms occurs in the second independent molecule of $[Au(Ph_2PC(S)NPh)]_2$; the mean deviation in this case is 0.346 Å. Thus, while there are only small differences in the Au/S(1)/C(1)/P(1), N(1) torsion angles, differences of up to 20° are found for the Au/P(1)/C(1)/S(1), N(1) torsion angles (Table 5). The adoption of two distinct conformations in the one lattice indicates that there is only a small difference in energy between them. The spectroscopic results do not show any evidence for more than one conformation in solution and, hence, the appearance of two conformations appears to be a solid state effect. As may be expected for complexes of this type, there are significant Au···Au interactions.

Table 4
Selected spectroscopic data for $R_2PC(S)N(H)R'$ and $Au(R_2PC(S)NR')_2$

	IR (cm^{-1})		NMR (ppm)	
	ν(C=N)	ν(C=S)	^{13}C Cq (^1J(P–C) (Hz))	^{31}P
R = Ph, R′ = Ph				
Ligand	1528	1388	206.6 (39.9)	19.2
Complex	1550	946	169.2 (65.3)	52.1
R = Ph, R′ = Me				
Ligand	1506	1338	208.5 (37.9)	14.7
Complex	1561	913	167.6 (70.8)	50.7
R = cHex, R′ = Ph				
Ligand	1502	1330	210.3 (34.4)	43.9
Complex	1548	945	168.3 (55.1)	78.3
R = cHex, R′ = Me				
Ligand	1521	1345	210.8 (34.9)	48.4
Complex	1558	924	165.8 (60.7)	76.6

The intramolecular Au···Au interactions in two independent molecules of $[Au(Ph_2PC(S)NPh)]_2$ and in $[Au(cHex_2PC(S)NPh)]_2$ are 2.924(1), 2.919(1) and 2.869(1) Å respectively. In $[Au(Ph_2PC(S)NPh)]_2$, there is an inter-

Table 5
Selected bond distances (Å), and angles (°) for [Au(Ph$_2$PC(S)NPh)]$_2$ and [Au(cHex$_2$PC(S)NPh)]$_2$

	R = R′ = Ph			R = cHex, R′ = Ph
	Ligand a	Ligand b	Ligand c	
Au–S(1)	2.318(3)	2.301(5)	2.306(5)	2.306(1)
Au–P(1)	2.271(4)	2.265(5)	2.271(5)	2.276(1)
S(1)–C(1)	1.73(1)	1.76(1)	1.75(2)	1.765(5)
P(1)–C(1)	1.84(1)	1.84(1)	1.85(2)	1.845(6)
N(1)–C(1)	1.29(2)	1.28(2)	1.25(2)	1.278(8)
S–Au–P(1)	173.4(2)	175.3(2)	175.3(1)	173.70(6)
Au–S(1)–C(1)	107.6(4)	104.8(6)	108.5(7)	107.3(2)
Au–P(1)–C(1)	116.5(4)	110.3(5)	111.4(5)	114.2(2)
S(1)–C(1)–P(1)	119.4(7)	117(1)	116(1)	119.1(3)
S(1)–C(1)–N(1)	126(1)	125(1)	127(1)	125.8(5)
P(1)–C(1)–N(1)	114(1)	117(1)	116(1)	114.9(4)
Au/S(1)/C(1)/P(1)	−35(1)	−29(1)	−30(1)	−38.6(4)
Au/S(1)/C(1)/N(1)	144(1)	149(1)	152(2)	145.7(6)
Au/P(1)/C(1)/S(1)	−44(1)	63(1)	57(1)	43.2(4)
Au/P(1)/C(1)/N(1)	135(1)	−115(1)	−125(1)	−140.6(4)

molecular Au(1)···Au(2) contact of 3.146(1) Å but no other Au···Au contacts less than 4.1 Å. Similarly, there are no Au···Au contacts less than 4.1 Å in the lattice of [Au(cHex$_2$PC(S)NPh)]$_2$. The absence of extensive intermolecular Au···Au contacts (and indeed other non-hydrogen contacts) may be rationalized in terms of the steric crowding owing to the bulky organic substituents as well as the presence of the close intramolecular Au···Au contacts.

Preliminary biological screening for anti-arthritic activity [9] and cytotoxicity [7] for the dinuclear gold(I) compounds did not show enhanced activity over related systems and, hence, biological studies were not continued.

4. Supplementary material

The Crystallographic Information File for the structures is available from one of the authors (etiekink@chemistry.adelaide.edu.au).

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