PERGAMON

Polyhedron 18 (1999) 593–600

POLYHEDRON

The preparation and coordination chemistry of substituted benzenethiols. Triphenylphosphine gold(I) complexes of sterically demanding and nondemanding arenethiols. The absence of gold(I)–gold(I) interactions

Laila S. Ahmed[a], William Clegg[b], Dominic A. Davies[a,1], Jonathan R. Dilworth[c], Mark R. J. Elsegood[b], D. Vaughan Griffiths[a,2], Lynne Horsburgh[b], John R. Miller[a], Nigel Wheatley[a,*]

[a]*Department of Biological and Chemical Sciences, University of Essex, Central Campus, Wivenhoe Park, Colchester CO4 3SQ, U.K.*
[b]*Department of Chemistry, University of Newcastle-upon-Tyne, Newcastle-upon-Tyne NE1 7RU, U.K.*
[c]*Inorganic Chemical Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.*

Received 25 May 1998; accepted 16 September 1998

Abstract

Novel substituted benzenethiols can be easily prepared via aryl thiocyanates or aryl bromides. Reaction of [$(Ph_3P)AuCl$] with the sterically-nondemanding benzenethiols $HSC_6H_4NMe_2$-*p* and $HSC_6H_4NMe_3^+$-*p* and with the sterically-demanding benzenethiols $HSCMe_2H_2NMe_2$-*p*, HSC_6Me_4H-*p* and in the presence of triethylamine yields the monomeric gold(I) complexes [$(Ph_3P)Au(SAr)$], which are analogous to the gold-based antiarthritic drug Auranofin. Reaction with the sterically demanding dithiol HSC_6Me_4SH-*p* in the presence of NEt_3 yields the dimeric complex [$\{(Ph_3P)Au\}_2(\mu$-SC_6Me_4S-*p*)]. Spectrochemical and electrochemical data are reported. The crystal structures of [$(Ph_3P)Au(SC_6H_4NMe_2$-*p*)] and [$(Ph_3P)Au(SC_6H_4NMe_3$-*p*)]PF_6 have been solved: both complexes are monomeric in the solid state, lacking the short gold–gold interaction which is commonly found in gold(I) complexes of soft ligands, e.g., $[(Ph_3P)Au(SPh)]_2$.

Keywords: Gold; Metal–metal interactions; Cyclic voltammetry; Thiols

1. Introduction

The use of copper and gold to combat connective tissue disorders dates back to the Bronze Age; in more modern times, gold thiolates are increasingly important in the control and treatment of arthritis, especially since the introduction of the orally-administered drug Auranofin [1,2], [$(Et_3P)Au(SR)$] (HSR = tetraacetylthioglucose). The mode of action of gold-based anti-arthritic drugs is still not well understood [3], although it is known that gold is transported in the blood stream bound to serum albumin cysteine-34 [4,5]. The exchange of gold between physiological thiol groups is thought to be important in its biodistribution and pharmacological activity [6–8].

The phenomenon of "gold–gold bonding" [9,10], interaction between two d^{10} gold(I) centres less than the sum of the van der Waals radii [11], 3.32 Å, has received both theoretical [12–15] and experimental attention [16–27]. The reversible formation of gold(I)–gold(I) interactions in the solid state by a gold dithiocarbamate complex leads to luminescence in the presence of organic vapours, offering a basis for the detection of volatile organic compounds in the atmosphere [28].

The energy of these interactions has been estimated to be 25–30 kJ mol^{-1} for a gold–gold distance of 3 Å [29,30], of the same order of magnitude as hydrogen bonding. There has been much debate as to the exact nature of the interaction between the two formally closed-shell centres, although it is generally agreed that the relativistic contraction of the ns orbitals due to the extremely high angular momentum of the electrons in the gold atom

* Corresponding author. Current address: Laboratoire de Catalyse, Chimie Fine et Polymères, Ecole Nationale Supérieure de Chimie de Toulouse, 118 route de Narbonne, F-31077 Toulouse cedex 4, France. Tel.: +33-561-175-692; fax: +33-561-175-600; e-mail: nwheatley@ensct.fr

[1] Current address: School of Chemical and Life Sciences, University of Greenwich, Wellington Street, London SE18 6PF, UK.

[2] Current address: Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London, E1 4NS, UK.

0277-5387/99/$ - see front matter
PII: S0277-5387(98)00339-8

($Z = 79$) is an important element of the phenomenon [31–34]. Recent *ab initio* studies [35,36] failed to reproduce an attractive gold–gold interaction at the HF level, although inclusion of electron correlation produced a energy minimum of *ca.* 0.01 au ($\approx 25\,kJ\,mol^{-1}$) at the MP2 level. The energy minimum is quite soft with respect to gold–gold distance, in accordance with the large range of gold–gold distances observed [9,10].

Much of the recent interest in the coordination chemistry of sterically-demanding thiols [37] has been directed at the modelling of active sites in proteins such as ferredoxins [38]. In such complexes, both the metal centre and the thiolate anion possess considerable reactivity, and a degree of steric protection of the sulfur atom is necessary to allow the isolation of stable complexes. Most sterically hindered thiols studied to date have been substituted with relatively inert carbon- or silicon-based substituents, partly due to the limitations on synthetic procedures based on the Newmann–Kwart rearrangement [39] or chlorosulfonation [40,41]: however, this has meant that there has been little attempt to separate the electronic effects of the sterically-demanding substituents from those caused purely by their size.

In a recent paper [42], Schmidbaur *et al.* compared the properties of (benzenethiolato)(triphenylphosphine)-gold(I), [(Ph_3P)Au(SPh)], which exists as a gold–gold bonded dimer in the solid-state, with analogous complexes of sterically-demanding thiols, which are monomeric. In this paper, we discuss the synthesis of a number of sterically-demanding and -nondemanding benzenethiols and their complexation to (triphenylphosphine)gold(I) centres in an attempt to separate the effects of size and electronic properties on the properties of the complexes, with particular reference to short gold(I)–gold(I) interactions.

2. Experimental

Chloro(triphenylphosphine)gold(I) [43], 4-(dimethylamino)benzenethiol [44] and 2,3,5,6-tetramethylbenzenethiol [45,46] were prepared by literature methods; solvents were dried by normal methods [47], and distilled under dry oxygen-free nitrogen prior to use; all other chemicals were obtained from normal commercial sources and used as received. Microanalyses were performed by Mr S. Hodder (University of Essex). NMR spectra were obtained on an JEOL EX-270 spectrometer [^1H 270 MHz, ^{13}C 67.9 MHz, standard $SiMe_4$; ^{13}P 109.3 MHz, standard 85% H_3PO_4 (ext.)].

2.1. Trimethyl(4-thiocyanatophenyl)ammonium iodide (**1**)

4-(Dimethylamino)phenyl thiocyanate [48,49] (6.0 g, 34 mmol) and iodomethane (5.3 ml, 12.1 g, 85 mmol) were refluxed in methanol for 24 h. The mixture was allowed to cool and a small amount of diethyl ether added to ensure complete precipitation, yielding trimethyl(4-thiocyanatophenyl)ammonium iodide (5.8 g, 88%) as a yellow precipitate. m.p. 165°C (from EtOH). Found C, 37.2; H, 3.9; N, 8.6. $C_{10}H_{13}IN_2S$ requires C, 37.5; H, 4.1; N, 8.75. δ_H (DMSO-d_6) 3.5 (9H, s, Me), 7.9 [2H, d, *J*(HH) 9.3 Hz, Ar], 8.2 [2H, d, *J*(HH) 9.3 Hz, Ar]. δ_C (DMSO-d_6) 65.4 (s, Me), 110.8 (s, NCS), 122.7 (s, Ar), 127.6 (s, Ar), 130.9 (s, Ar), 147.4 (s, Ar).

2.2. 4-(Trimethylammonio)benzenethiol tetraphenylborate (**2**)

(Trimethyl (4-thiocyanatophenyl)ammonium iodide) (2.0 g, 6.3 mmol) and sodium borohydride (0.47 g, 13 mmol) were refluxed in methanol (50 ml) for 24 h under an atmosphere of dry oxygen-free nitrogen. The mixture was allowed to cool, and acidified to pH 6 with 10% aq. hydrochloric acid. The mixture was filtered, and a solution of sodium tetraphenylborate (2.17 g, 6.3 mmol) in the minimum quantity of methanol was added, yielding 4-(trimethylammonio)benzenethiol tetraphenylborate (2.2 g, 72%) as a white precipitate. m.p. 173–175°C. Found C, 80.9; H, 6.9; N, 2.9. Calc. for $C_{33}H_{34}BNS$ C, 81.3; H, 7.0; N, 2.9. δ_H (DMSO-d_6) 3.5 (1OH, s, Me), 6.7–7.3 (20H, m), 7.45 [2H, d, *J*(HH) 9.1 Hz, Ar], 7.64 [2H, d, *J*(HH) 9.1 Hz, Ar]. δ_C (DMSO-d_6) 56.2 (s, Me), 120.9 (s, Ar), 121.6 (s, BPh_4), 125.4 (s, BPh_4), 128.8 (s, Ar), 135.5 (s, BPh_4), 136.2 (s, Ar), 143.8 (s, Ar), 164.4 [q, *J*(CB) 49.6 Hz, BPh_4]. The hexafluorophosphate salt was (m.p. 174–177°C [50]) was prepared by an analogous method.

2.3. 4-Dimethylamino-2,6-dimethylbenzenethiol (**3**)

4-Dimethylamino-2,6-dimethylphenyl thiocyanate [51] (1.0 g, 5.4 mmol), sodium sulfide nonahydrate (2.0 g, 26 mmol) and sodium hydroxide (0.25 g, 6.25 mmol) were refluxed in ethanol (25 ml) for 4 h under an atmosphere of dry oxygen-free nitrogen. The mixture was allowed to cool, and then poured in to a thoroughly degassed 10% aq. solution of ammonium chloride (50 ml). The mixture was extracted with degassed diethyl ether (3×15 ml). The ethereal solution was dried over magnesium sulfate and the solvent removed, yielding 4-dimethylamino-2,6-dimethylbenzenethiol.[1] δ_H ($CDCl_3$) 2.4 (6H, s, Ar–CH_3), 3.0 (6H, s, N–CH_3), 3.9 (1H, s, SH), 6.5 (2H, s, Ar–*H*).

2.4. 2,3,5,6-Tetramethylbenzene-1,4-dithiol (**5**)

1,4-Bis(butylthio)-2,3,5,6-tetramethylbenzene [51] (2.5 g, 6.6 mmol) was dissolved in liquid ammonia

[1] The product was usually found to be contaminated with *ca.* 20% bis(4-dimethylamino-2,6-dimethylphenyl)disulfide, δ_H ($CDCl_3$) 2.2, 2.9, 6.4.

(100 ml) under an atmosphere of dry oxygen-free nitrogen. Small portions of metallic sodium were added until a blue colour persisted in the solution for one hour. Solid ammonium chloride was added in small portions until the blue colour was just extinguished. The ammonia was allowed to evaporated off, leaving a white residue which was suspended in chloroform (200 ml). An excess of dry hydrogen chloride gas was passed through the suspension. The remaining solid was filtered off, and the chloroform removed on a rotary evaporator, giving 2,3,5,6-tetramethylbenzene-1,4-dithiol (1.3 g, 98%) as a yellow solid. δ_H ($CDCl_3$) 2.4 (12H, s, Me), 3.0 (2H, s, SH). δ_c ($CDCl_3$) 19.7 (s, Me), 128.9 (s, *C*–Me), 133.3 (s, C–SH).

2.5. Gold(I) complexes

[(Ph_3P)AuCl] (0.2 g, 400 μmol), thiol (400 μmol) and triethylamine (0.04 g, 410 μmol) were refluxed in methanol (30 ml) for 3 h under an atmosphere of dry oxygen-free nitrogen. Cooling yielded the (triphenylphosphine)gold(I) complex as a white or off-white precipitate. Analytical and other data for the complexes are given in Tables 1 and 2.

2.6. Cyclic voltammetry

Measurements were made using a custom-made glass cell housing the three electrodes and a nitrogen bubbler. The working and secondary electrode were constructed from platinum wire fused in glass: a silver reference electrode was also used. The cell was powered by a EG and G PAR 362 scanning potentiostat, and the data recorded on a 386 microcomputer using the ConDecon program. Test solutions were approximately 100 μM in complex and 1000 μM in $Bu_4N^+BF_4^-$ (support electrolyte): solvents and results (quoted relative to $Cp_2Fe/Cp_2Fe^+ = 0$ mV) are given in Table 3.

2.7. Crystal structure determination

Crystal data and experimental details are given in Table 4. The structures were solved by Patterson methods followed by normal heavy atom procedures, and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically, while hydrogens were placed in calculated positions. Atomic coordinates, interatomic distances and angles, anisotropic displacement parameters and hydrogen atom positions have been deposited with the Cambridge Crystallographic Data Centre, Cambridge, with deposition codes 101689 for **6** and 101693 for **7**.

3. Results and discussion

3.1. Preparation of ligands

Thiocyanation has previously provided a convenient route to 4-(dimethylamino)benzenethiol [44,58], with the thiocyanate being reduced by either $LiAlH_4$ or sodium sulfide. Quaternisation of the amino group does not appear to interfere with the subsequent reduction, and so this method can also be used to prepare the unusual, electron-deficient trimethylammonio-substituted benzenethiols. However, the initial thiocyanation step is effective only with electron-rich phenyl rings: our attempts to prepare 1,2,4,5-tetramethyl-3,6-dithiocyanatobenzene (**14**) by this method were unsuccessful. We were also unable to prepare 2,3,5,6-tetramethylbenzene-1,4-disulfonyl dichloride (**15**) from any of a number of possible precursors. Hence we used an adaptation of the method of Adams and Ferretti [59–61] to prepare 2,3,5,6-tetramethylbenzene-1,4-dithiol (durene dithiol) (**5**) (see Scheme 1): this is a significant improvement [51] in terms of simplicity, cost and safety over the previous six-step synthesis of Raasch [62–64].

3.2. Preparation of gold(I) complexes

Our gold(I) complexes were stable indefinitely at room temperature in the solid state, in line with the findings of Schmidbaur et al. [42] and Fackler et al. [65] and contrary to the implications of the work of Kowala et al. [66,67]. However, we did notice a small degree of dis-

Table 1
Analytical[a] and other data for the gold(I) complexes

Complex	Yield[b] (%)	δ_P^c/ppm	C	H	N
6 [(Ph_3P)Au($SC_6H_4NMe_2$-*p*)]	77	+39.9	50.9 (51.1)	4.15 (4.1)	2.3 (2.3)
7 [(Ph_3P)Au($SC_6H_4NMe_3$-*p*)]PF_6	72	+39.9[d]	42.0 (42.0)	3.6 (3.7)	1.8 (1.8)
8 [(Ph_3P)Au($SC_6Me_2H_2NMe_2$-*p*)]	68	+38.7	53.7 (53.5)	4.5 (4.3)	2.4 (2.2)
9 [(Ph_3P)Au(SC_6Me_4H-*p*)]	70	+38.9	53.5 (53.8)	4.7 (4.5)	
10 [{(Ph_3P)Au}$_2$$SC_6Me_4S$-*p*]	65	+39.0	49.3 (49.6)	3.8 (3.8)	

[a] Required values are given in parentheses.
[b] Based on [(Ph_3P)AuCl].
[c] 109.3 MHz, standard 85% aq. H_3PO_4 (ext.), solvent $CDCl_3$ unless otherwise stated.
[d] Solvent acetone-d_6.

Table 2
^{1}H and $^{13}C\{^{1}H\}$-NMR[a] data for the gold(I) complexes

Compound	NMR-data
6	δ_H 2.9 (6H, s, N–CH_3), 6.15 [2H, d, J(HH) 8.6 Hz, Ar], 7.5 (17H[b], m, Ar).
	δ_C 41.2 (s, N–CH_3), 113.6 (s, C^3–H), 129.3 (s, C^2–H), 133.5 (s, C–S), 148.0 (s, C–NMe_2).
7	δ_H^c 3.8 (9H, s, N–CH_3), 7.6 (19H[b], m, Ar).
	δ_C^c 57.7 (s, N–CH_3), 120.9 (s, C^2–H), 130.7 (s, C^3–H), 133.3 (s, C–S), 139.4 (s, C–NMe_3).
8	δ_H 2.7 (6H, s, Ar–CH_3), 2.9 (6H, s, N–CH_3), 6.6 (1H, s, Ar).
	δ_C 35.1 (s, Ar–CH_3), 41.1 (s, N–CH_3), 112.8 (s, C–H), 139.5 (s, C–CH_3), 144.5 (s, C–S), 147.8 (s, C–NMe_2).
9	δ_H 2.3 (6H, s, C^2–CH_3), 2.7 (6H, s, C^3–CH_3), 6.75 (1H, s, Ar).
	δ_C 20.2 (s, C^2–CH_3), 21.3 (s, C^3–CH_3), 128.2 (s, C–H), 132.8 (s, C^3–CH_3), 136.9 (s, C^2–CH_3), 139.5 (s, C–S).
10	δ_H 2.8 (12H, s, Ar–CH_3).
	δ_C 22.3 (s, Ar–CH_3), 135.6 (s, C–S), 136.5 (s, C–CH_3).

[a] ^{1}H, 270 MHz; ^{13}C, 67.9 MHz; standard $SiMe_4$, solvent $CDCl_3$ unless otherwise specified; peaks assigned to triphenylphosphine are not recorded unless otherwise specified.
[b] Includes 15H corresponding to PPh_3.
[c] Solvent acetone-d_6.

Table 3
Electrochemical data[a] for the gold(I) complexes

	Solvent	E_{ox}	$E_{1/2}$	ΔE
6	$CHCl_3$	170	308	177
			591	151
7	DMSO-d_6	1233		
8	CH_2Cl_2	−114	−315	245
			397	203
9	CH_2Cl_2	452	954	166
10	CH_2Cl_2	274	706	216

[a] Potentials in mV relative to $Cp_2Fe/Cp_2Fe^+ = 0$ mV ($Cp_2Fe/Cp_2Fe^+ = +540$ mV vs SCE in THF).

proportionation of the complexes of sterically-demanding thiols on attempted recrystallisation, leading to deposition of metallic gold.

3.3. Electrochemistry

The five gold complexes showed a complex electrochemistry when studied by cyclic voltammetry. On the first sweep, the complexes showed a broad oxidation peak at −114 to +593 mV (see Table 3), with the more electron-rich thiols (e.g., **6** and **8**) giving the lower values for the oxidation potential. No corresponding reduction peak could be observed, even on increasing the sweep speed to 2000 mV s^{-1} and reducing the temperature to 200 K and the oxidation peak was substantially reduced in height or even absent in immediately subsequent scans, indicating an EC-type process, where an electrochemical oxidation is immediately followed by a chemical rearrangement. This can be explained by an initial transfer of an electron from the complex, followed by dissociation of a thiyl radical, which may then dimerise to form a disulfide or react with the solvent or adventitious water (see Scheme 2). The irreversibility of this process and the breadth of the peaks in the voltammagrams prevented a quantitative measurement of electron stoichiometry, although the results are consistent with a two electron transfer in the case of the dimeric complex **10**.

In all the complexes except **7**, there are additional oxidation processes at more positive potentials, one for **9** and **10** and two for **6** and **8**. These all have coupled reduction peaks, although these are much smaller than the oxidation peaks. The interpeak spacings and the observed variation of peak potential with sweep speed both indicate that the electron transfer in these processes is very slow, which may also explain the disparity in peak currents.

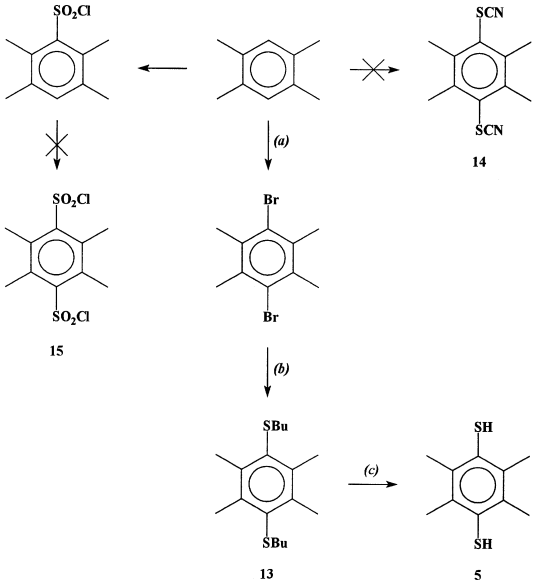
3.4. Crystal structures of 6 and 7

Both **6** and **7** crystallise in the triclinic $P\bar{1}$ space group, with two molecules per unit cell, related by a centre of symmetry. The molecular structures are shown in Figs 1 and 2, and significant interatomic distances and angles are given in Tables 5 and 6. The geometry around the gold atom is approximately linear, with P–Au–S being 176.53(5)° for **6** and 175.52(4)° for **7**. Perhaps surprisingly, given the very different electronic properties of the two thiol phenyl rings, there is no significant difference between the two Au–S distances; 2.298(2) Å for **6** and 2.293(3) Å for **7**. These distances are within the range of Au–S distances observed to date for (triphenylphosphine)gold(I) thiolates, 2.284–2.310 Å [3,9,10,42,65,68–79]: the angles at sulfur, 104.1(2)° for **6** and 103.6(2)° for **7** and the Au–P distances, 2.259(1) Å for **6** and 2.259(3) Å for **7**, are also typical for this type of complex.

The most striking feature of these crystal structures is the absence of any short gold(I)–gold(I) interaction, with

Table 4
Crystal data and experimental details of the structure determinations for **6** and **7**

	6	**7**
Colour and habit	orange–brown tablets	pale blue tablets
Crystal dimensions (mm)	$0.5 \times 0.6 \times 1.0$	$0.42 \times 0.13 \times 0.10$
Formula	$C_{26}H_{25}AuNPS$	$C_{27}H_{28}AuNPS \cdot PF_6$
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	9.7504(7)	8.652(9)
b (Å)	10.934(2)	10.644(12)
c (Å)	13.3872(9)	15.718(17)
α (°)	79.530(8)	87.52(9)
β (°)	68.934(6)	87.67(7)
γ (°)	65.368(9)	74.22(12)
U (Å^3)	1209.8(2)	1391(3)
Z	2	2
Diffractometer	Enraf-Nonius CAD4	Stoe–Siemens [55]
Radiation	Mo–Kα	Mo–Kα
Reflections measured	4240 ($1.5 \leq \theta \leq 25$)	5175 ($2.6 \leq \theta \leq 25$)
Unique reflections	4240	4892
Observed reflections	3902 [$F > 3\sigma(F)$]	4647 [$F > 2\sigma(F)$]
Transmission factors	max 1.0, min 0.79	max 0.450, min 0.228
Refinement	F	F^2
Weighting scheme (w^{-1})	$\sigma^2(F_o) + 0.0004F_o^2$	$\sigma^2(F_o^2) + 2.6393P + 0.0022P^2$ [$P = (F_o^2 + 2F_c^2)/3$]
Agreement analysis (S)	1.86	1.071
Final R	0.031	0.0256
Final R'	0.045	0.0720
Program	Molen [56]	SHELXTL [57]



Scheme 1.

minimum Au · · · Au distances of 6.181 Å for **6** and 5.627 Å for **7**. The possibility that a gold–gold interaction might be overtaken by a stacking interaction between the thiolate rings of **6** was investigated, as the rings are parallel; however, the closest approach is C(12) · · · C(12′) = 3.50(1) Å.

Short gold–gold interactions have been observed in a wide range of gold(I) compounds [9,10], including $[(Ph_3P)Au(SPh)]_2$ (**16**) [42,79] and $[(Ph_3P)Au(C{\equiv}CPh)]_2$ [80]. It has been proposed that the tendency to form gold–gold bonds increases with the softness of the ligand [9,10,81,82], and hence we would definitely expect **6** to show such a short contact, as the 4-(dimethylamino)benzenethiolato ligand is softer than the benzenethiolato ligand in **16**.

However, many gold(I) complexes of the type [LAuX], where X is a soft anionic ligand such as iodide, exist as chains or clusters of distinct anions and cations, $[L_2Au][AuX_2]$, in the solid state [9,10,83–87]. It would be expected that any gold–gold interactions in these compounds would be enhanced by the Coulombic attraction between the ions, although recent *ab initio* studies indicate that the electron populations on the gold centres in the two isomeric forms, $[LAuX]_2$ and $[L_2Au]^+[AuX_2]^-$, as well as their total energies, are very similar [88].

Schmidbaur et al. [42] have postulated that the steric demands of the thiol ligand prevent gold–gold inter-

Scheme 2.

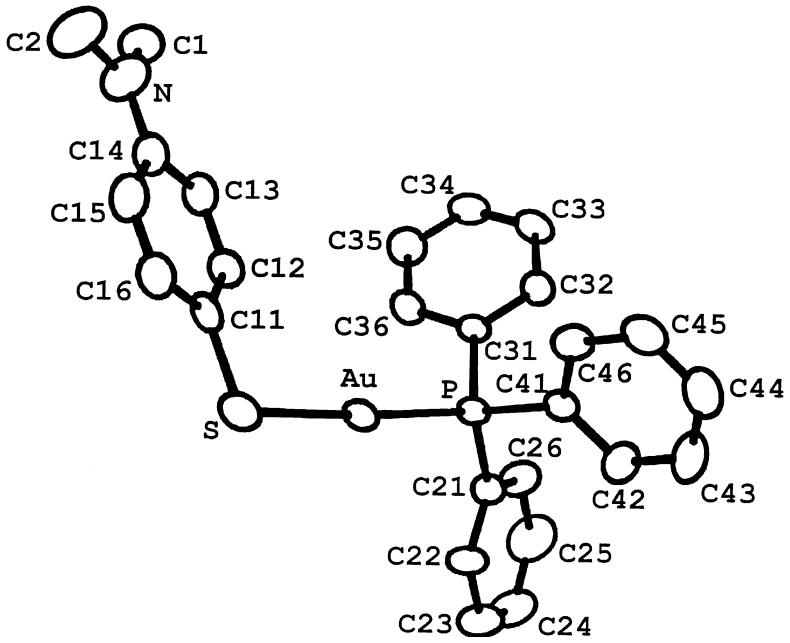


Fig. 1. The molecular structure of $[(Ph_3P)Au(SC_6H_4NMe_2\text{-}p)]$.

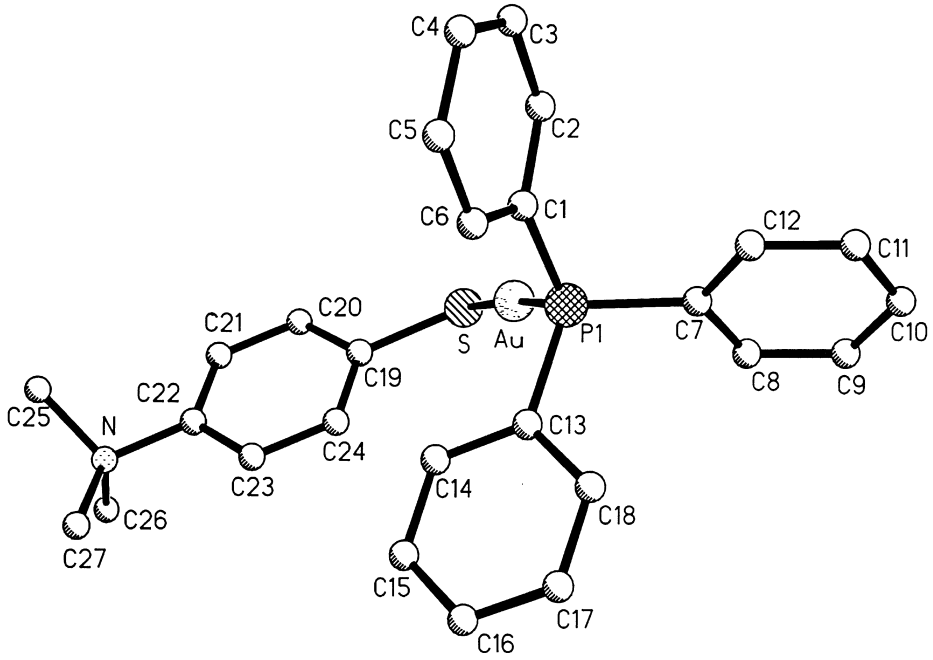


Fig. 2. The molecular structure of the $[(Ph_3P)Au(SC_6H_4NMe_3\text{-}p)]^+$ cation.

actions in $[(Ph_3P)Au(SC_6R_3H_2)]$ (R = Me, Et, Pr^i), despite the bending of the phenyl ring away from any obstacle (Au–S–C 101.7–110.8°) and the softer nature of the thiol ligands compared to the benzenethiolato ligand. This explanation for the absence of short gold–gold contacts has been applied in other systems [65,89,90]. However, in neither **6** nor **7** is the arenethiolate ligand significantly more sterically demanding than that in **16**.

The long Au...Au distances in **6** and **7** cannot be explained in terms of ligand softness or steric demands. Hence we are forced to conclude that explanations of the existence or absence of short gold(I)–gold(I) contacts which are based on the softness or steric demands of the anionic ligand are at best incomplete, and that such contacts should be viewed as just one of the many intermolecular interactions which occur to stabilise a crystal.

Table 5
Significant interatomic distances (Å) and angles (°) for [(Ph_3P)Au($SC_6H_4NMe_2$-*p*)] (**6**): figures in parentheses indicate the estimated standard deviation in the least significant digit

Complex	Distance or angle (Å or °)	Complex	Distance or angle (Å or °)
Au–P	2.259(1)	Au–S	2.298(2)
P–C(21)	1.816(5)	S–C(11)	1.763(6)
P–C(31)	1.818(5)	P–C(41)	1.808(5)
P–Au–S	176.53(5)	C(11)–S–Au	104.1(2)
C(21)–P–Au	115.4(2)	C(31)–P–Au	110.5(2)
C(41)–P–Au	113.3(2)	C(21)–P–C(31)	106.2(2)
C(21)–P–C(41)	105.3(2)	C(31)–P–C(41)	105.4(2)

Table 6
Significant interatomic distances (Å) and angles (°) for [(Ph_3P)Au($SC_6H_4NMe_3$-*p*)]PF_6 (**7**): figures in parentheses indicate the estimated standard deviation in the least significant digit

Complex	Distance or angle (Å or °)	Complex	Distance or angle (Å or °)
Au–P(1)	2.259(3)	Au–S	2.293(3)
P(1)–C(7)	1.814(4)	S–C(19)	1.778(5)
P(1)–C(1)	1.814(5)	P–C(13)	1.821(5)
P(1)–Au–S	175.52(4)	C(19)–S–Au	103.6(2)
C(1)–P(1)–Au	115.8(2)	C(13)–P(1)–Au	107.3(2)
C(7)–P(1)–Au	114.8(2)	C(1)–P(1)–C(13)	107.5(2)
C(7)–P(1)–C(1)	104.8(2)	C(7)–P(1)–C(13)	106.1(2)

Acknowledgements

The authors would like to thank Mr. N. L. Barnard (University of Essex) for his help in conducting the electrochemical experiments, Johnson Matthey for their gift of sodium tetrachloroaurate, and the following for studentships during the period of this work: European Social Fund (LSA), London Borough of Bromley (DAD), B. P. Chemicals Ltd. (NW). The authors also thank Professor Pekka Pyykkö (University of Helsinki), as well as one of the reviewers of the original submission, for bringing to our attention certain published articles.

References

[1] Sutton BM, Gusty E, Walz DT, DiMartino MJ. J. Med. Chem 1972;15:1095.
[2] Hill DT, Sutton BM. Cryst Struct Commun 1980;9:679.
[3] Brown DH, Brown WE. Chem Soc Rev 1980;9:217.
[4] Shaw III CF, Schaeffer NA, Elder RC, Eidsness MK, Trooster JM, Calis GHM. J Am Chem Soc 1984;106:3511.
[5] Coffer MT, Shaw III CF, Eidsness MK, Watkins II JW. Inorg. Chem 1986;25:33.
[6] Shaw III CF, Coffer MT, Kingbeil J, Mirabelli CK. J Am Chem Soc 1988;110:729.
[7] Isab AA, Sadler PJ. J. Chem Soc Dalton Trans. 1982;135.
[8] Snyder RM, Mirabelli CK, Crooke ST. Biochem Pharmacol 1986;35:923.
[9] Ahrland S, Dreisch K, Norén B, Oskarsson Å. Mat Chem Phys 1993;35:281.
[10] Pyykkö P. Chem Rev 1997;97:597.
[11] Bondi A. J. Phys Chem 1964;68:441.
[12] Jiang Y, Alvarez S, Hoffmann R. Inorg Chem 1985;24:749.
[13] Pyykkö P, Runeberg N, Mendizabal F. Chem Eur J 1997;3:1451.
[14] Pyykkö P, Mendizabal F. Chem Eur J 1997;3:1458.
[15] Pyykkö P, Mendizabal F. Inorg Chem 1998;37:3018.
[16] Balch AL, Fung EY, Olmstead MM. J Am Chem Soc 1990;112:5181.
[17] King C, Wang J-C, Khan MNI, Fackler Jr JP. Inorg Chem 1989;28:2145.
[18] Tzeng BC, Che CM, Peng SM. J. Chem Soc Dalton Trans 1996;1769.
[19] Tang SS, Lin IJB, Liu LS, Wang JC. J Chin Chem Soc 1996;43:327.
[20] Colacio E, Cuesta R, Gutierrez-Zorilla JM, Luque A, Roman P, Giraldi T, Taylor MR. Inorg Chem 1996;35:4232.
[21] Cerrada E, Jones PG, Laguna A, Laguna M. Inorg Chim Acta 1996;249:163.
[22] Toronto DV, Weissbart B, Tinbi DS, Balch AL. Inorg Chem 1996;35:2484.
[23] Van Calcar PM, Olmstead MM, Balch AL. Inorg Chem 1997;36:5231.
[24] Xiao H, Weng YX, Wong WT, Mak TCW, Che CM. J Chem Soc Dallon Trans 1997;221.
[25] Feng DF, Tang SS, Liu CW, Lin IJB. Organometallics 1997;16:901.
[26] Tang SS, Chang CP, Lin IJB, Liou LS, Wang JC. Inorg. Chem 1997;36:2294.
[27] Vincente J, Chicote MT, Abrisqueta MD, Guerrero R, Jones PG. Angew. Chem Int. Ed. Engl 1997;36:1203.
[28] Mansour MA, Connick WB, Lachicoue RJ, Gysling HJ, Eisenberg R. J Am Chem Soc 1998;120:1329.
[29] Schmidbaur H, Graf W, Müller G. Angew. Chem Int Ed Engl 1988;27:417.
[30] Dziwok K, Lachmann J, Wilkinson DL, Müller G, Schmidbaur H. Chem Ber 1990;123:423.
[31] Raptis RG, Fackler Jr JP, Murray HH, Porter LC. Inorg Chem 1989;28:4057.
[32] Pyykkö P. Chem Rev 1988;88:563.
[33] Pitzer KS. Acc Chem Res 1979;12:271.
[34] Pyykkö P, Desclaux JP. Acc Chem Res 1979;12:276.
[35] Pyykkö P, Zhao Y. Angew. Chem Int Ed Engl 1991;30:604.
[36] Li J, Pyykkö P. Chem Phys Lett 1992;197:586.
[37] Dilworth JR, Hu J. Adv Inorg Chem 1994;40:411.
[38] Krebs B, Henkel G. Angew Chem Int. Ed. Engl 1991;30:769.
[39] Newman MS, Karnes HA. J Org Chem 1966;31:3980.
[40] Huntress EH, Autenrieth JS. J Am Chem Soc 1941;63:3446.
[41] Blower PJ, Dilworth JR, Hutchinson J, Nicholson T, Zubieta JA. J Chem Soc Dalton Trans 1985;2639.
[42] Nakamoto M, Hiller W, Schmidbaur H. Chem Ber 1993;126:605.
[43] Jones AG, Powell DB. Spectrochim. Acta Part A 1974;30:563.
[44] Chuchani G, Frohlich A. J Chem Soc B 1971;1417.
[45] Kuliev AM, Kyazim-Zade AK, Guseinov KZ. Zh Org Khim 1970;6:1813 Chem Abstr 1970, 73, 120236k.
[46] Leonardi A, Rossi S, Palmeri C, Nardi D, Subissi A. Boll Chim Farm 1979;118:286; Chem Abstr 1980;92:69460s.
[47] Perrin DD, Armarego WLF. Purification of Laboratory Chemicals, 3rd ed. Oxford: Pergamon, 1988.
[48] Brewster RQ, Schroeder W. Org Synth 1939;19:79.
[49] Brewster RQ, Schroeder W. Org Synth, 2nd Coll. Vol., 574.
[50] DePamphilis BV, Averill BA, Herskovitz T, Que L Jr, Holm RH. J Am Chem Soc 1974;96:4159.
[51] Davies DA. B.Sc. dissertation, University of Essex 1994.

[52] Adams R, Reifschneider W, Ferretti A. Org Synth 1962;42:22.
[53] Adams R, Reifschneider W, Ferretti A. 5th Coll. Vol., 107.
[54] Adams R, Ferretti A. J Am Chem Soc 1959;81:4927.
[56] Fair CK. MOLEN, An Interactive Structure Solution Procedure. Enraf-Nonius, Delft 1990.
[55] Clegg W. Acta Crystallogr Sect A 1981;37:22.
[56] SHELXTL (version 5). Siemans Analytical X-ray Instruments, Madison, WI 1995.
[58] Banfield JE. J Chem Soc 1960;456.
[59] Adams R, Ferretti A. J Am Chem Soc 1959;81:4939.
[60] Ferretti A. Org Synth 1962;42:54.
[61] Ferretti A. Org Synth, 5th Coll. Vol. 419.
[62] Raasch MS. J Org Chem 1979;44:2629.
[63] Smith LI, Dobrovolny FJ. J Am Chem Soc 1926;48:1420.
[64] Conant JB, Fieser LF. J Am Chem Soc 1923;45:2194.
[65] Forward JM, Bohmann D, Fackler JP, Staples RJ. Inorg Chem 1995;34:6330.
[66] Coates GE, Kowala C, Swan JM. Aust J Chem 1966;19:539.
[67] Kowala C, Swan JM. Aust J Chem 1966;19:547.
[68] Hoskins BF, Lu Z, Tiekink ERT. Inorg Chim Acta 1989;158:7.
[69] Kuz'mina LG, Smislova EI, Grandberg KI. Zh Neorg Khim 1993;38:1009.
[70] Narayanaswamy R, Young MA, Parlhurst E, Ouellette M, Kerr ME, Ho DM, Elder RC, Bruce AE, Bruce MRM. Inorg Chem 1993;32:2506.
[71] Tong YY, Pombeiro AJL, Hughes DL, Richards RL. Transition Met. Chem (London) 1995;20:372.
[72] Sladek A, Schmidbaur H. Chem Ber 1995;128:907.
[73] Viotte M, Gautheron B, Nifantev I, Kuz'mina LG. Inorg Chim Acta 1996;253:71.
[74] Schneider W, Bauer A, Schmidbaur H. Organometallics 1996;15:5445.
[75] Sladek A, Schmidbaur H. Inorg Chem 1996;35:3268.
[76] Sladek A, Schneider W, Angermeier K, Bauer A, Schmidbaur H. Z. Naturforsch. B Chem Sci 1996;51:765.
[77] Bishop P, Marsh P, Brisdon AK, Brisdon BJ, Mahon MF. J Chem Soc Dalton Trans 1998;675.
[78] Onaka S, Katsukawa Y, Yamashita M. Chem Lett 1998;525.
[79] Fackler JP, Staples RJ, Elduque A, Grant T. Acta Crystallogr. Sect. C 1989;45:520.
[80] Schmidbaur H, Weidenhiller G, Steigelmann O, Müller G. Chem Ber 1990;123:285.
[81] Pyykkö P, Li J, Runeberg N. Chem Phys Lett 1994;218:133.
[82] Abraham SP, Samuelson AG. Proc Indian Acad Sci 1996;108:131.
[83] Adams H-N, Hiller W, Strähle J. Z Anorg Allg Chem 1982;485:81.
[84] Conzelmann W, Hiller W, Strähle J, Sheldrick GM. Z Anorg Allg Chem 1984;512:169.
[85] Ahrland S, Norén B, Oskarsson Å. Inorg Chem 1985;24:1330.
[86] Wang S, Fackler Jr JP. Inorg Chem 1990;29:4404.
[87] Bauer A, Schmidbaur H. J Am Chem Soc 1996;118:5324.
[88] Pyykkö P, Schneider W, Bauer A, Bayler A, Schmidbaur H. Chem Commun 1997;1111.
[89] Angermaier K, Schmidbaur H. Chem Ber 1994;127:2387.
[90] Bauer A, Schneider W, Angermaier K, Schier A, Schmidbaur H. Inorg Chim Acta 1996;251:249.