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Polyhedron 19 (2000) 743–749



POLYHEDRON

Synthesis, spectroscopic and structural characterisation of copper, silver and gold complexes of the mixed P/O-donor ligand $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{PPh}_2$

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Received 8 September 1999; accepted 3 January 2000

Abstract

Reaction of L^1 ($\text{L}^1 = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{PPh}_2$) with $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ or AgBF_4 in CH_2Cl_2 solution yields the complexes $[\text{Cu}(\text{L}^1)]\text{PF}_6$ and $[\text{Ag}(\text{L}^1)]\text{BF}_4$ respectively as white solids. Spectroscopic measurements are consistent with coordination via the P-donors and the crystal structure of $[\text{Ag}(\text{L}^1)]\text{BF}_4$ confirms that L^1 acts as a *trans*-chelate giving an unusual example of approximately linear P_2 -coordination at Ag(I) ($\angle \text{P}-\text{Ag}-\text{P} = 164.66(4)^\circ$) and, despite the availability and proximity of the ether O atoms, these remain essentially uncoordinated ($\text{Ag}\cdots\text{O} = 2.95 \text{ \AA}$), thus reflecting the low affinity of the soft Ag(I) ion for hard O-donor ligands. $[\text{AuCl}(\text{tht})]$, L^1 and TiPF_6 react in a 1:1:1 molar ratio in MeCN solution to yield the analogous Au(I) species $[\text{Au}(\text{L}^1)]\text{PF}_6$, the structure of which also shows linear P_2 -coordination and once again the O-donors are non-coordinating, at a distance of ca. 3.16 \AA from Au(I). The neutral dinuclear species $[(\text{AuCl})_2(\text{L}^1)]$ is readily formed by reaction of $[\text{AuCl}(\text{tht})]$ with L^1 in a 2:1 molar ratio in MeCN. Confirmation of the coordinated Cl ligands comes from IR spectroscopy, $\nu(\text{Au}-\text{Cl}) = 324 \text{ cm}^{-1}$, and $\delta(^{31}\text{P})$ which is indicative of a PCl donor set at Au(I). This arrangement is confirmed in the solid state from the crystal structure. The related phosphathia complex $[(\text{AuBr})_2(\text{L}^2)]$ ($\text{L}^2 = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{S}(o\text{-C}_6\text{H}_4)\text{S}(\text{CH}_2)_2\text{PPh}_2$) is prepared similarly from $[\text{AuBr}(\text{tht})]$ and L^2 in MeCN solution and its structure reveals the AuBr units each coordinated to one P-donor and directed to the same side as the *o*- C_6H_4 unit. ©2000 Elsevier Science Ltd All rights reserved.

Keywords: Copper complexes; Silver complexes; Gold complexes

1. Introduction

Our interest in multidentate mixed P/S-, P/N- and P/O-donor ligands, in which the phosphine functions are located at the termini, stems mainly from the fact that complexes of these ligands offer a wide structural diversity, and incorporation of two different donor types within a single ligand may lead to unusual properties. Phosphine ligation may enhance the binding properties of the poorer thioether functions or of the hard amine or ether functions or, alternatively, these functions may simply act as spacers between the phosphines. To date, our work has mainly focused on the phosphathia ligands and we have shown, for example, that $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{PPh}_2$ (L^3) coordinates to Pt(II) and Pt(IV) via both the P and the S donor atoms in $[\text{Pt}(\text{L}^3)]^{2+}$ and $[\text{PtX}_2(\text{L}^3)]^{2+}$, generating square planar and octahedral species respectively [1]. In contrast, in the Au(I) species $[\text{Au}(\text{L}^3)]\text{PF}_6$ we observe primary P_2 -coordination, with

weak interactions to the thioether donors at ca. 3.0 \AA . L^3 can also act as a bridging ligand, e.g. in $[\text{Au}_2(\text{L}^3)_2]\text{Cl}_2$, which adopts a helical metallocyclic cavity which hosts one of the Cl^- anions [2–4]. In view of the unusual structures adopted by these phosphathia ligand complexes we were interested to investigate the effect of substituting the thioether functions for the much harder ether functions, since the combination of hard and soft donors may lead to other unusual characteristics. A variety of transition metal complexes of the mixed P/O-donor ligand $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{PPh}_2$ (L^1) are known, including *cis*- and *trans*- $[\text{MX}_2(\text{L}^1)]$ ($\text{M} = \text{Ni}, \text{Pd}$ or Pt , $\text{X} = \text{Cl}, \text{Br}$ or I) [5–7], and the Rh(I) species $[\text{Rh}(\text{L}^1)(\text{EtOH})(\text{CO})]\text{PF}_6$ [8]. Gray and co-workers have also investigated metallocyclic species containing the related P_2O_n -donor ligands L ($\text{L} = \text{Ph}_2\text{P}\{(\text{CH}_2)_2\text{O}\}_n(\text{CH}_2)_2\text{PPh}_2$, $n = 3\text{--}5$), e.g. *cis*- $[\text{Mo}(\text{CO})_4(\text{L})]$ [9], which involve bidentate P_2 -coordination with the O-donors non-coordinating. The Pt(II) species $[\text{PtX}_2(\text{L})]$ also show P_2 -coordination and treatment of these species with a halide abstractor affords the species $[\text{Pt}(\text{H}_2\text{O})(\text{L})]^{2+}$, which involve coordination of L

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to Pt(II) via both P-donor atoms and one ether O-donor [10]. The closely related metallocrown ether complex $[\text{PdX}_2\{\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{CH}_2\text{PPh}_2\text{-P,P'}\}]_n$ ($\text{X} = \text{Cl}$ or I) shows a unique and reversible mode of molecular recognition in which PdX_2 units are incorporated into the metallocrown ether ring via a ring-expansion [11].

We describe herein the preparation and characterisation of a series of transition metal complexes incorporating the mixed P/O-donor ligand L^1 , including the crystal structures of $[\text{Ag}(\text{L}^1)]\text{BF}_4$, $[\text{Au}(\text{L}^1)]\text{PF}_6$ and $[(\text{AuCl})_2(\text{L}^1)]$. The crystal structure of the phosphathia ligand complex $[(\text{AuBr})_2(\text{L}^2)]$ is also included.

2. Results and discussion

The ligand L^1 was prepared using a modification of the literature procedure [6]. LiPPh_2 was generated in situ by reaction of Li metal with PPh_3 in thf solution. The LiPh byproduct was then destroyed by addition of $^t\text{BuCl}$ and $\text{Cl}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{Cl}$ was added. The resulting mixture was refluxed for 1 h. After work-up and recrystallisation of the product from CH_2Cl_2 /hexane, L^1 was obtained in good yield. When the reaction was attempted without refluxing, $^{31}\text{P}\{^1\text{H}\}$ NMR studies showed considerable amounts of starting material, along with some mono-substituted product and traces of L^1 .

Treatment of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ with one molar equivalent of L^1 in CH_2Cl_2 solution, followed by precipitation with Et_2O , yields a white solid. Electrospray mass spectrometry shows peaks at 549 and 551 indicative of $[\text{Cu}(\text{L}^1)]^+$, with no significant peaks at higher m/z . The IR spectrum shows no evidence for any remaining coordinated MeCN, but peaks corresponding to coordinated L^1 and free PF_6^- are clearly evident. ^1H NMR spectroscopy and microanalyses are consistent with the formulation $[\text{Cu}(\text{L}^1)]\text{PF}_6$ for the product. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at -16.2 ppm (broadened owing to direct bonding to quadrupolar $^{63/65}\text{Cu}$) arising owing to the coordinated L^1 and a septet due to the PF_6^- anion centred at -146 ppm. The NMR spectra were recorded using thoroughly degassed solvents, since upon the introduction of air to the solution the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also shows a resonance at $+29.5$ due to oxidised phosphine. These data indicate the formulation $[\text{Cu}(\text{L}^1)]\text{PF}_6$ for the product, and suggest that coordination to Cu(I) is via the P-donors.

The corresponding Ag(I) species, $[\text{Ag}(\text{L}^1)]\text{BF}_4$, was obtained as a white, light-sensitive solid by reaction of AgBF_4 with L^1 in MeCN in a foil-wrapped flask, followed by concentration of the solution and addition of Et_2O . The IR spectrum shows peaks indicative of coordinated L^1 as well as peaks at ca. 1053 and 525 cm^{-1} , corresponding to free BF_4^- anion. The APCI mass spectrum shows peaks at m/z 593 and 595, corresponding to $[\text{Ag}(\text{P}_2\text{O}_2)]^+$. These data, together with ^1H NMR spectroscopic and microanalytical data, indicate the formulation $[\text{Ag}(\text{L}^1)]\text{BF}_4$ for the product.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this species shows (Fig. 1) two doublets at -3.4 ppm with $^1J(^{109}\text{Ag-P}) = 601$ Hz and $^1J(^{107}\text{Ag-P}) = 523$ Hz. These data are consistent with coordination of L^1 to Ag(I) via the two P-donor atoms [12]. The coupling constants for this species are larger than those observed for the phosphathia ligand analogues, e.g. $[\text{Ag}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{PPh}_2\}]^+$ which gave $^1J(^{109}\text{Ag-P}) = 510$ Hz and $^1J(^{107}\text{Ag-P}) = 445$ Hz [2–4], although the $^1J(^{107}\text{Ag-P}):^1J(^{109}\text{Ag-P})$ ratio of 0.87 is the same, and this is consistent with the ratio expected from the respective nuclear magnetic moments of the two nuclei. $^1J(^{107}\text{Ag-P})$ for the two-coordinate species $[\text{Ag}\{\text{P}(\text{tol})_3\}]_2\text{PF}_6$ and $[\text{Ag}(\text{P}^t\text{Bu}_3)_2]\text{BF}_4$ are reported as 496 and 444 Hz respectively [12,13], while the crystallographically authenticated two-coordinate $[\text{Ag}\{\text{P}(\text{NMe}_2)_3\}]_2\text{-BPh}_4$ shows $^1J(^{107}\text{Ag-P}) = 610$ Hz [14].

In order to confirm the 1:1 Ag: L^1 stoichiometry and to establish unequivocally the coordination mode of L^1 to Ag(I), a single crystal structure determination was undertaken. The crystal structure of $[\text{Ag}(\text{L}^1)]\text{BF}_4$ confirms (Fig. 2, Table 1) that L^1 functions essentially as a *trans*-chelating ligand, giving an approximately linear arrangement at Ag(I) with $d(\text{Ag-P}) = 2.402(1)$ Å, and with a P–Ag–P angle of $164.66(4)^\circ$. The Ag \cdots O distances of ca. 2.95 Å are possibly indicative of very weak interactions, but are probably simply a consequence of the bite angle of the diphosphine unit in L^1 . Both the large P–Ag–P angle and the observation that the P, O and Ag atoms are approximately co-planar, provide strong evidence that the O-donor atoms are not coordinating. L^1 is expected to be sufficiently flexible to accommodate a distortion towards the tetrahedral geometry usually favoured by four coordinate Ag(I). Both the cation and the BF_4^- anion have crystallographic two-fold symmetry, with the Ag and B atoms sitting on two-fold axes. Although Ag(I) has a much greater affinity for soft donor atoms such as phosphines rather

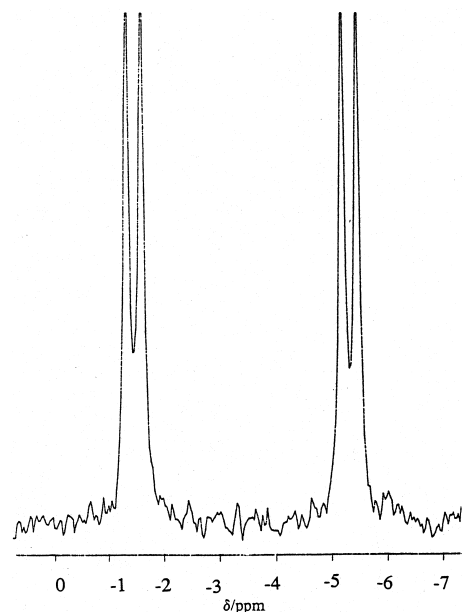


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ (145.8 MHz, CDCl_3) NMR spectrum of $[\text{Ag}(\text{L}^1)]\text{BF}_4$.

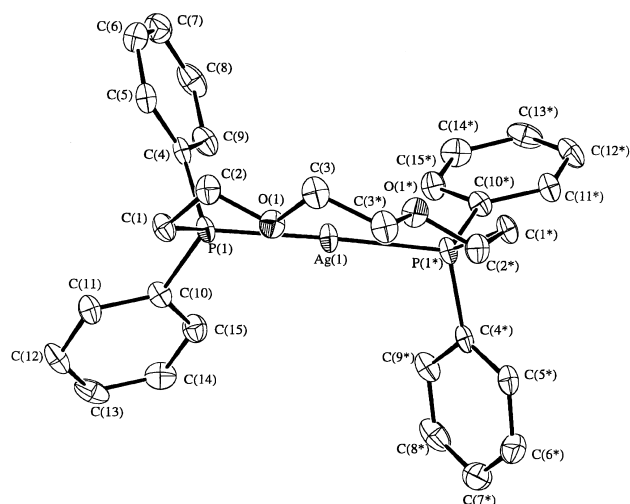


Fig. 2. View of the structure of $[\text{Ag}(\text{L}^1)]^+$ with the numbering scheme adopted. Atoms marked * are related by a crystallographic two-fold axis. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for $[\text{Ag}(\text{L}^1)]\text{BF}_4$

Ag(1)–P(1)	2.402(1)
P(1)–Ag(1)–P(1*)	164.66(4)
Ag(1)–P(1)–C(1)	113.9(1)
Ag(1)–P(1)–C(4)	109.0(1)
Ag(1)–P(1)–C(10)	116.8(1)

than hard ether functions, significant Ag–O(ether) interactions have been observed, for example, in the mixed thia/oxa macrocyclic species $[\text{Ag}_n(\text{[15]aneS}_2\text{O}_3)_n](\text{PF}_6)_n$ ([15]ane- $\text{S}_2\text{O}_3 = 1,4,7$ -trioxa-10,13-dithiacyclopentadecane) (Ag–O = 2.492(4)–2.690(4) Å [15] and $[\text{Ag}_2(\text{[18]aneS}_2\text{O}_4)_2](\text{PF}_6)_4$ ([18]ane- $\text{S}_2\text{O}_4 = 1,4,7,10$ -tetraoxa-13,16-dithiacyclohexadecane) (Ag–O = 2.458(7)–2.661(6) Å [16], hence there is no inherent reason for the O-donors not interacting with the Ag(I) ion. Only two mononuclear Ag(I) complexes involving genuine P_2 -coordination have been structurally characterised previously, $[\text{Ag}(\text{trimesitylphosphine})_2]\text{PF}_6$ (P–Ag–P = 179.4(5)°, Ag–P = 2.461(6) Å [17,18] and $[\text{Ag}\{\text{P}(\text{NMe}_2)_3\}_2]\text{BPh}_4$ (P–Ag–P = 166.9(1)°, Ag–P = 2.395(2), 2.393(2) Å [14]. Several bis(phosphine)–silver(I) species involving ClO_4^- or NO_3^- are known, although these also involve coordination via the O-donors of the anions and this results in a much smaller P–Ag–P angle, e.g. $[\text{Ag}\{\text{PPh}_2(\text{C}_5\text{H}_9)\}_2]\text{ClO}_4$, Ag–P = 2.397(2)–2.432(2) Å, Ag⋯O = 2.662(5), 2.709(5) Å, $\angle \text{P–Ag–P} = 145.1(1), 153.0(1)^\circ$ [19], $[\text{Ag}(\text{PCy}_3)_2](\text{NO}_3)]$, Ag–P = 2.440(3), 2.445(3) Å, Ag–O = 2.45(1), 2.73(1) Å, $\angle \text{P–Ag–P} = 139.04(9)^\circ$ [20], $[\text{Ag}(\text{PCy}_3)_2]\text{ClO}_4$, Ag–P = 2.429(1), 2.432(1) Å, Ag⋯O = 2.720(7) Å, $\angle \text{P–Ag–P} = 147.34(3)^\circ$ [20].

Reaction of L^1 with $[\text{AuCl}(\text{tht})]$ in a 2:1 molar ratio in MeCN gave the neutral dinuclear species $[(\text{AuCl})_2(\text{L}^1)]$ which was isolated by precipitation with Et_2O from a con-

centrated solution. The IR spectrum confirms the presence of L^1 and a peak at 327 cm^{-1} is attributed to $\nu(\text{Au–Cl})$. This compares with 324 cm^{-1} for $[(\text{AuCl})_2(\text{L}^2)]$ [2–4]. The APCI mass spectrum shows peaks with the correct isotopic distribution at m/z 915, corresponding to $[\text{Au}_2(\text{L}^1)\text{Cl}]^+$. Further peaks at lower m/z correspond to loss of Cl or Au from the complex. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a single resonance at +23.3 ppm, which is comparable with $\delta(^{31}\text{P})$ for the previously synthesised $[(\text{AuCl})_2(\text{L}^2)]$ (25.3 ppm) [2–4].

The crystal structure of $[(\text{AuCl})_2(\text{L}^1)]$ shows (Fig. 3, Table 2) each gold atom coordinated to one P-donor from L^1 and one Cl ligand, giving essentially linear coordination, with no interaction between the Au centres and the O-donor atoms. The Cl–Au–P angles are $174.2(2)$ and $174.1(3)^\circ$. The L^1 backbone adopts a twisted conformation with the AuCl units pointing in the same direction.

We have reported previously the preparation and spectroscopic characterisation of the species $[(\text{AuCl})_2(\text{L})]$ ($\text{L} = \text{L}^2, \text{L}^3$ or L^4) ($\text{L}^4 = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{PPh}_2$) although their structures were not authenticated crystallographically [2–4]. In order to provide a comparison with

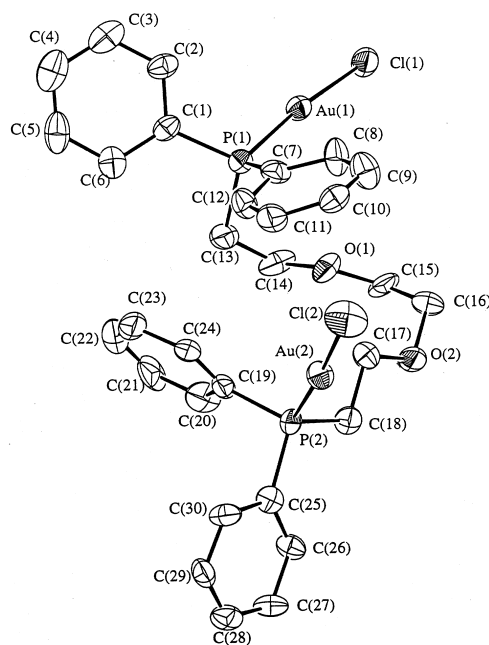


Fig. 3. View of the structure of $[(\text{AuCl})_2(\text{L}^1)]$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability and H atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for $[(\text{AuCl})_2(\text{L}^1)]$

Au(1)–Cl(1)	2.295(5)	Au(1)–P(1)	2.231(5)
Au(2)–Cl(2)	2.279(5)	Au(2)–P(2)	2.219(5)
Cl(1)–Au(1)–P(1)	174.2(2)	Cl(2)–Au(2)–P(2)	174.1(3)
Au(1)–P(1)–C(1)	113.7(6)	Au(1)–P(1)–C(7)	112.9(8)
Au(1)–P(1)–C(13)	110.8(8)	Au(2)–P(2)–C(19)	110.7(7)
Au(2)–P(2)–C(18)	113.4(7)		
Au(2)–P(2)–C(25)	115.5(6)		

$[(\text{AuCl})_2(\text{L}^1)]$ above, we have prepared the species $[(\text{AuBr})_2(\text{L}^2)]$ similarly from L^2 and $[\text{AuBr}(\text{tht})]$ in MeCN. The Au–Br stretching vibration occurs at 315 cm^{-1} for this species and $\delta(^{31}\text{P})$ occurs as a singlet at 28.0 ppm, consistent with coordination of an AuBr fragment to each P-donor of L^2 . A single crystal X-ray structure determination was also undertaken on a weakly diffracting crystal of $[(\text{AuBr})_2(\text{L}^2)]$. The structure shows (Fig. 4) a dinuclear molecule with each Au(I) ion coordinated linearly to one P-donor from L^2 and one Br atom, with the S-donor atoms remaining non-coordinating. The molecule has crystallographic C_2 symmetry and the Au–P distances of $2.16(1)\text{ \AA}$ are slightly shorter than those in $[(\text{AuCl})_2(\text{L}^1)]$ above, although since the structure quality is rather poor, geometric parameters should be treated with caution. The P–Au–Br angle is $177.5(4)^\circ$. The L^2 backbone adopts an approximately planar arrangement and the AuBr units lie on the same side of the backbone as the *o*-phenylene unit.

The 1:1 Au: L^1 complex, $[\text{Au}(\text{L}^1)]\text{PF}_6$ was prepared readily by treatment of $[\text{AuCl}(\text{tht})]$ with one molar equivalent of L^1 and TiPF_6 in MeCN to give a white precipitate (TICl) and a colourless solution. Following removal of the TICl by filtration through Celite, concentration of the solution and addition of Et_2O , a white precipitate was obtained. The IR spectrum of this product provides evidence for the presence of L^1 and PF_6^- ($840, 555\text{ cm}^{-1}$), and there is no evidence for an Au–Cl stretching vibration. The highest mass peak in the APCI mass spectrum appears at m/z 683, corresponding to $[\text{Au}(\text{L}^1)]^+$. These data, together with ^1H NMR spectroscopic and microanalytical data, suggest the formulation $[\text{Au}(\text{L}^1)]\text{PF}_6$ for the product. The $^{31}\text{P}\{^1\text{H}\}$ NMR resonance due to the coordinated L^1 occurs at 32.5 ppm, i.e. a higher frequency than that for $[(\text{AuCl})_2(\text{L}^1)]$, and is indicative of a P_2 -donor set at Au(I). The septet due to the PF_6^- anion occurs at -146.0 ppm .

This crystal structure of $[\text{Au}(\text{L}^1)]\text{PF}_6$ shows (Fig. 5, Table 3) L^1 acting as a *trans*-chelating ligand, bonded to Au(I) by the two P-donors ($\text{Au–P} = 2.308(2), 2.311(2)\text{ \AA}$), with the $\text{Au}\cdots\text{O}$ distances ca. 3.15 \AA indicating no interaction, and demonstrating the indifference of Au(I) towards the hard O-donor atoms. Thus, this geometry is similar to that observed for $[\text{Ag}(\text{L}^1)]^+$ above. The Au–P distances in this cation are slightly shorter than the Ag–P distances in $[\text{Ag}(\text{L}^1)]^+$ and the P–Au–P angle of $171.85(9)^\circ$ is larger than the corresponding P–Ag–P angle in the analogous Ag(I) species. Schmidbaur and co-workers have previously demonstrated that for the isomorphous species $[\text{Ag}(\text{trimesitylphosphine})_2]\text{BF}_4$ and $[\text{Au}(\text{trimesitylphosphine})_2]\text{BF}_4$, $d(\text{Ag–P}) > d(\text{Au–P})$ by almost 0.1 \AA [18]; a similar trend is observed here. The structure of the analogous phosphathia complex $[\text{Au}(\text{L}^2)]\text{PF}_6$ shows similar primary Au–P interactions of $2.284(7)$ and $2.302(7)\text{ \AA}$, although in this case long-range, weak $\text{Au}\cdots\text{S}$ interactions of ca. 3.0 \AA are also observed in the solid state [2–4].

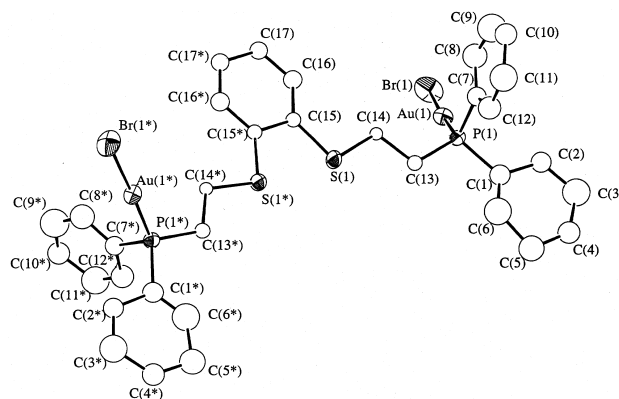


Fig. 4. View of the structure of $[(\text{AuBr})_2(\text{L}^2)]$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability. Atoms marked * are related by a crystallographic two-fold axis and H atoms are omitted for clarity. $\text{Au}(1)\text{--P}(1) = 2.16(1)\text{ \AA}$, $\angle \text{P}(1)\text{--Au}(1)\text{--Br}(1) = 177.5(4)^\circ$.

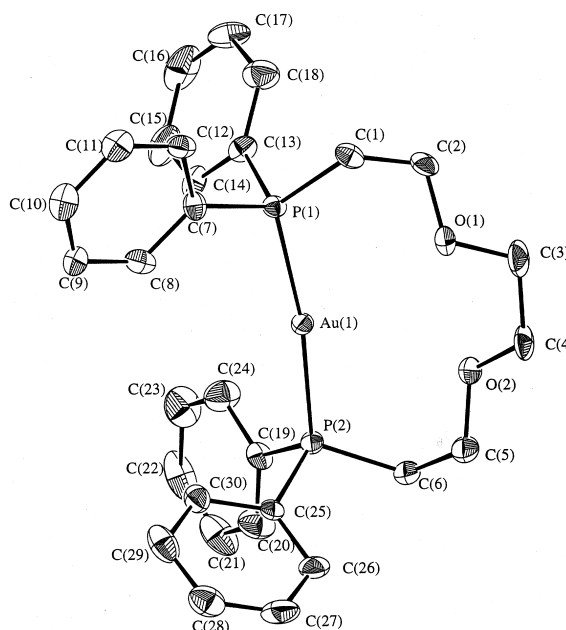


Fig. 5. View of the structure of $[\text{Au}(\text{L}^1)]^+$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability and H atoms are omitted for clarity.

Table 3

Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{Au}(\text{L}^1)]\text{PF}_6$

$\text{Au}(1)\text{--P}(1)$	2.308(2)	$\text{Au}(1)\text{--P}(2)$	2.311(2)
$\text{P}(1)\text{--Au}(1)\text{--P}(2)$	171.85(9)	$\text{Au}(1)\text{--P}(1)\text{--C}(1)$	117.4(3)
$\text{Au}(1)\text{--P}(1)\text{--C}(7)$	113.5(3)	$\text{Au}(1)\text{--P}(1)\text{--C}(13)$	107.9(3)
$\text{Au}(1)\text{--P}(2)\text{--C}(6)$	115.5(3)	$\text{Au}(1)\text{--P}(2)\text{--C}(19)$	114.3(3)
$\text{Au}(1)\text{--P}(2)\text{--C}(25)$	109.2(3)		

3. Experimental

Infrared spectra were recorded as KBr or CsI disks using a Perkin-Elmer 983 spectrometer over the range $4000\text{--}200\text{ cm}^{-1}$. Mass spectra were run by positive electrospray or by APCI (atmospheric pressure chemical ionisation) in MeCN solution using a VG Biotech platform. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 using a Bruker AM300 spec-

trometer. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded in CH_2Cl_2 containing ca. 10–15% CDCl_3 using a Bruker AM360 spectrometer operating at 145.8 MHz and are referenced to 85% H_3PO_4 . Microanalyses were performed by the University of Strathclyde microanalytical service. L^2 was prepared according to the literature procedure [6].

3.1. Preparations

L^1 : PPh_3 (30 g, 114 mmol) was dissolved in dry, degassed thf (300 cm^3) and freshly crushed Li (3 g, 432 mmol) was added in small pieces at room temperature. This reaction mixture was stirred for 12 h, before the remaining pieces of lithium were filtered off. $^t\text{BuCl}$ (9.9 cm^3 , 91 mmol) was added dropwise and the mixture was stirred for 1 h at room temperature. $\text{Cl}((\text{CH}_2)_2\text{O})_2(\text{CH}_2)_2\text{Cl}$ (7.5 cm^3 , 0.4 equiv., 46 mmol) was added slowly and the mixture was heated to reflux for 1 h until it decolourised and a white precipitate formed. After cooling, degassed water (30 cm^3) was added dropwise. The organic layer was separated, the aqueous layer was washed with Et_2O and the combined organic extracts were dried over MgSO_4 . The MgSO_4 was filtered off under nitrogen and the solvent was removed in vacuo. The residue was taken up in a small amount of CH_2Cl_2 , then hexane was added. The mixture was stirred for a few minutes and subsequent cooling yielded a white precipitate which was filtered and dried in vacuo. Yield 10.7 g, 39%. *Anal.* Calc. for $\text{C}_{30}\text{H}_{32}\text{O}_2\text{P}_2$: C, 74.1; H, 6.6. Found: C, 73.7; H, 6.9%. ^1H NMR: δ 7.41–7.52 (m, 20H, Ph), 3.58 (m, 4H, OCH_2), 3.51 (s, 4H, OCH_2), 2.40 (m, 4H, CH_2P) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 28.9 (CH_2P), 68.7 ($\text{CH}_2\text{CH}_2\text{P}$), 70.2 ($\text{OCH}_2\text{CH}_2\text{O}$), 128.6 (*para*-C), 128.8 (*meta*-C), 132.8 (*ortho*-C), 138.5 (*ipso*-C) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ –21.3.

$[\text{Cu}(\text{L}^1)]\text{PF}_6$: L^1 (0.100 g, 0.206 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (0.077 g, 0.206 mmol) was added in one portion. The mixture was stirred for 1 h and the volume was reduced to ca. 2 cm^3 in vacuo. Et_2O was then added to afford a white solid which was collected by filtration and dried in vacuo. Yield 0.085 g, 60%. *Anal.* Calc. for $\text{C}_{30}\text{H}_{32}\text{O}_2\text{P}_3\text{F}_6\text{Cu}$: C, 51.8; H, 4.6. Found: C, 52.4; H, 4.6%. ^1H NMR: δ 7.17–7.49 (m, 20H, Ph), 3.62–3.77 (m, 8H, CH_2), 2.59 (m, 4H, CH_2) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ –16.2 (s, L^1), –146.2 (spt, PF_6^-) ppm. APCI mass spectrum: found m/z 551, 549, 487; calc. for $[\text{Cu}(\text{L}^1)]^+ m/z$ 551, $[\text{Cu}(\text{L}^1)]^+ 549$, $[\text{L}^1]^+ 486$. IR spectrum (CsI disk): 3058w, 2985w, 2922w, 2873w, 1574w, 1485m, 1438s, 1403w 1360m, 1310w, 1161m, 1133s, 1101s, 999m, 841vs, 744s, 696s, 558m, 508m, 478m cm^{-1} .

$[\text{Ag}(\text{L}^1)]\text{BF}_4$: To a degassed solution of L^1 (0.100 g, 0.206 mmol) in MeCN (20 cm^3) at 0°C was added AgBF_4 (0.040 g, 0.206 mmol) and the resulting mixture was stirred for 1 h at room temperature in a foil-wrapped flask. The solution was then concentrated in vacuo to ca. 5 cm^3 and Et_2O was added to afford a white solid which was filtered, washed with Et_2O and dried in vacuo. Yield 0.096 g, 69%. *Anal.* Calc. for $[\text{C}_{30}\text{H}_{32}\text{AgBF}_4\text{O}_2\text{P}_2]$: C, 52.9; H, 4.7. Found: C, 52.6; H,

4.4%. Electrospray mass spectrum (MeCN): found m/z 595, 593, 487; calc. for $[\text{Ag}(\text{L}^1)]^+ m/z$ 595, $[\text{Ag}(\text{L}^1)]^+ 593$, $[\text{L}^1]^+ 486$. ^1H NMR: δ 7.4–7.7 (m, Ph, 20H), 3.7 (m, CH_2O , 8H), 2.8 (m, CH_2P , 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ –3.4 (d, $^1J^{109}(\text{Ag}-^{31}\text{P}) = 601$ Hz, d, $^1J^{107}(\text{Ag}-^{31}\text{P}) = 523$ Hz). IR spectrum (CsI disk): 3055w, 2960w, 2917w, 2869w, 1572w, 1481m, 1461w, 1434m, 1410w, 1365m, 1350m, 1309w, 1284w, 1099s, 1053s, 1005s, 998s, 976w, 885m, 856m, 790w, 760s, 746s, 712m, 698s, 692s, 673w, 525m cm^{-1} .

$[\text{Au}(\text{L}^1)]\text{PF}_6$: To a solution of L^1 (0.100 g, 0.206 mmol) in degassed MeCN (20 cm^3) was added $[\text{AuCl}(\text{tht})]$ (0.066 g, 0.206 mmol). After stirring this mixture for 15 min, TIPF_6 (0.072 g, 0.206 mmol) was added and the reaction mixture was stirred for ca. 12 h. The resulting white precipitate (TICl) was removed by filtration and the filtrate was concentrated in vacuo. Addition of Et_2O gave a white precipitate which was filtered, washed with Et_2O and dried in vacuo. Yield 0.054 g, 32%. *Anal.* Calc. for $[\text{C}_{30}\text{H}_{32}\text{AuF}_6\text{O}_2\text{P}_3]$: C, 43.5; H, 3.9. Found: C, 43.5; H, 3.6%. Electrospray mass spectrum (MeCN): found m/z 683, 487; calc. for $[\text{Au}(\text{L}^1)]^+ m/z$ 683, $[\text{L}^1]^+ 486$. ^1H NMR: δ 7.5–7.8 (m, Ph, 20H), 3.8 (m, CH_2O , 4H), 3.6 (s, CH_2O , 4H), 2.9 (m, CH_2P , 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 32.5 (s, L^1), –146.0 (spt, PF_6^-). IR spectrum (CsI disk): 3061w, 2980w, 2925w, 2866w, 1560w, 1482m, 1458w, 1435s, 1406w, 1362m, 1227w, 1186w, 1134s, 1114m, 1104s, 1063m, 1012m, 836vs, 789m, 744m, 713s, 696s, 690s, 558s, 529m, 509m 463m, 438w cm^{-1} .

$[(\text{AuCl})_2(\text{L}^1)]$: To a solution of L^1 (0.100 g, 0.206 mmol) in degassed MeCN (30 cm^3) was added $[\text{AuCl}(\text{tht})]$ (0.130 g, 0.411 mmol). The mixture was stirred for 1 h before being concentrated in vacuo. Et_2O was then added to yield a white solid which was filtered, washed with Et_2O and dried in vacuo. Yield 0.060 g, 31%. *Anal.* Calc. for $[\text{C}_{30}\text{H}_{32}\text{Au}_2\text{Cl}_2\text{O}_2\text{P}_2]$: C, 37.9; H, 3.4. Found: C, 38.0; H, 3.4%. Electrospray mass spectrum (MeCN): found m/z 915, 683, 487; calc. for $[\text{Au}_2^{35}\text{Cl}(\text{L}^1)]^+ m/z$ 915, $[\text{Au}(\text{L}^1)]^+ 683$, $[\text{L}^1]^+ 486$. ^1H NMR: δ 7.4–7.8 (m, Ph, 20H), 3.8 (m, CH_2O , 4H), 3.5 (s, CH_2O , 4H), 2.8 (m, CH_2P , 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ +23.3 (s, L^1). IR spectrum (CsI disk): 3049w, 2945w, 2911w, 2857w, 1560w, 1482m, 1433s, 1395w, 1368m, 1351m, 1289w, 1158w, 1129s, 1100s, 1009m, 998w, 980m, 905w, 864w, 763m, 744s, 698s, 690s, 544m, 525m, 487m, 476w, 327m cm^{-1} .

$[(\text{AuBr})_2(\text{L}^2)]$: To a solution of L^2 (0.08 g, 0.0141 mmol) in degassed MeCN (30 cm^3) was added $[\text{AuBr}(\text{tht})]$ (0.103 g, 0.242 mmol). The resulting mixture was stirred for 1 h. The reaction volume was concentrated to 2 cm^3 in vacuo and Et_2O was added to give a white solid. Yield 0.115 g, 73%. *Anal.* Calc. for $[\text{C}_{34}\text{H}_{32}\text{Au}_2\text{Br}_2\text{P}_2\text{S}_2] \cdot \text{Et}_2\text{O}$: C, 38.1; H, 3.3. Found: C, 37.8; H, 3.0%. Electrospray mass spectrum (MeCN): found m/z 763, 566; calc. for $[\text{Au}(\text{L}^2)]^+ m/z$ 763, $[\text{L}^2]^+ 566$. ^1H NMR: δ 7.1–7.7 (m, aromatic H, 24H), 2.6–3.2 (m, CH_2S , 8H). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 28.0 (s, L^1). IR spectrum (Nujol mull): 315 cm^{-1} .

Table 4
Crystallographic data

	[Ag(L ¹)]BF ₄	[Au(L ¹)]PF ₆	[(AuCl) ₂ (L ¹)]	[(AuBr) ₂ (L ²)] · 2CH ₂ Cl ₂
Formula	C ₃₀ H ₃₂ AgBF ₄ O ₂ P ₂	C ₃₀ H ₃₂ AuF ₆ O ₂ P ₃	C ₃₀ H ₃₂ Au ₂ Cl ₂ O ₂ P ₂	C ₃₆ H ₃₂ Au ₂ Br ₂ Cl ₄ P ₂ S ₂
<i>M</i>	681.20	828.46	951.37	1286.27
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>P</i> -1	<i>Pn</i>	<i>C2</i>
<i>a</i> (Å)	15.822(7)	10.670(3)	9.285(2)	13.203(5)
<i>b</i> (Å)	13.157(7)	15.458(4)	11.905(2)	13.038(4)
<i>c</i> (Å)	15.76(1)	10.135(3)	14.276(1)	12.250(6)
α (°)	90	107.97(2)	90	90
β (°)	118.11(5)	97.75(3)	96.54(1)	95.02(3)
γ (°)	90	75.39(2)	90	90
<i>U</i> (Å ³)	2894(3)	1535.6(8)	1567.8(5)	2100(1)
<i>Z</i>	4	2	2	2
μ (Mo K α) (cm ⁻¹)	8.58	50.27	96.16	93.64
Transmission factors (max. and min.)	1.000, 0.850	1.000, 0.667	1.000, 0.490	1.000, 0.499
Unique observed reflections	5112	5400	2917	3973
<i>R</i> _{int} (based on <i>F</i> ²)	0.075	0.050	0.064	0.170
Observed reflections with <i>I</i> _o > <i>n</i> σ (<i>I</i> _o)	4469, <i>n</i> = 2	4191, <i>n</i> = 2	2169, <i>n</i> = 2	1118, <i>n</i> = 2
No. of parameters	182	379	343	117
<i>R</i> ^a	0.053	0.045	0.035	0.063
<i>R</i> _w ^b	0.073	0.057	0.040	0.069

^a $R = \sum (|F_{\text{obs}}|_i - |F_{\text{calc}}|_i) / \sum |F_{\text{obs}}|_i$.

^b $R_w = \sqrt{[\sum w_i (|F_{\text{obs}}|_i - |F_{\text{calc}}|_i)^2 / \sum w_i |F_{\text{obs}}|_i^2]}$.

3.2. X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 4. The crystals were grown by vapour diffusion of diethyl ether onto solutions of the complexes in CH₂Cl₂ at ca. -15°C or by slow evaporation from a solution of the complex in CH₂Cl₂/EtOH ([Ag(L¹)]BF₄). Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems open-flow cryostat operating at 150 K, using graphite-monochromated Mo K α X-radiation ($\lambda = 0.71073$ Å). The structures were solved by heavy atom methods [21] and developed by iterative cycles of full-matrix least-squares and difference Fourier synthesis [22]. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses.

[Ag(L¹)]BF₄: During data collection an 8.2% decrease in the intensity of the standard reflections was observed and hence a linear decay correction was applied. The initial cell was triclinic, and was solved to reveal one [Ag(L¹)]⁺ cation and one BF₄⁻ anion occupying general positions. However, further analysis suggested a C-centred monoclinic cell, which was solved to reveal a half [Ag(L¹)]⁺ cation and half BF₄⁻ anion, both with crystallographic two-fold symmetry. Although the final residuals for the monoclinic version are slightly higher (*R* = 0.053 versus 0.045) than for the triclinic solution, it does appear that the correct solution is as monoclinic C-centred. All non-H atoms were refined anisotropically while H-atoms were placed in fixed, calculated positions. Selected bond lengths and angles are given in Table 1.

[Au(L¹)]PF₆: All non-H atoms were refined anisotropically while H-atoms were placed in fixed, calculated positions. Selected bond lengths and angles are given in Table 3.

[(AuCl)₂(L¹)]⁺: All non-H atoms were refined anisotropically and H atoms were included in fixed, calculated positions. Selected bond lengths and angles are given in Table 2.

[(AuBr)₂(L²)] · 2CH₂Cl₂: The data were collected from a weakly diffracting crystal, hence the structure quality is not as high as normal. The molecule possesses crystallographic C₂ symmetry and hence only half the molecule is present in the asymmetric unit. A CH₂Cl₂ solvent molecule was also identified in the asymmetric unit. At isotropic convergence a DIFABS [23] absorption correction was applied. In view of the weak data, only the Au, Br, S and P atoms were refined anisotropically. The H atoms were included in fixed, calculated positions.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition numbers 134142–134145.

Acknowledgements

We thank the EPSRC and the University of Southampton for support and Johnson Matthey plc for generous loans of gold salts. We also thank the crystallographic referee for suggesting the higher symmetry cell for [Ag(L¹)]BF₄.

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