Gold(0) and Gold(III) Reactivity towards the Tetraphenyldithioimidodiphosphinic Acid, [$Ph_2P(S)NHP(S)Ph_2$]

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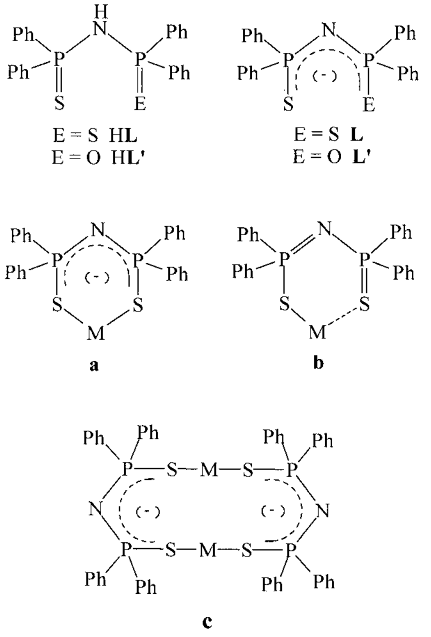
The reaction of gold powder with the iodine adduct of $Ph_2P(S)NHP(S)Ph_2$ (H**L**) in Et_2O gave the complex [Au(**L**)I_2] under mild reaction conditions. Its crystal structure is comprised of discrete, monomeric molecules with a central Au^{III} ion bonded to two sulfur atoms by an anionic ligand **L** and two iodide anions in a slightly distorted square-planar coordination geometry. From the reaction of [$AuCl_3$(tht)] with H**L** in CH_2Cl_2 it is possible, besides the main complex [Au(**L**)]$_2$, to separate the neutral Au^I complex [Au(**L**′$_2$H)], **L**′ = [$Ph_2P(S)NP(O)Ph_2$]$^-$, the crystal structure of which features a Au^I ion linearly coordinated to two sulfur atoms and a proton bridging two oxygen atoms of the PO groups. ^{31}P NMR CP MAS spectroscopy is in accordance with the nature of the ligands in the complex. The reaction chemistry of [Au(**L**′$_2$H)] in CH_2Cl_2 towards the acid CF_3COOH and the organic base 1,8-bis(dimethylamino)naphthalene is reported.

Introduction

The transition metal chemistry of tetraphenyldithioimidodiphosphinic acid, $Ph_2P(S)NHP(S)Ph_2$ (H**L**), has received great attention during the past years[1] and continues to remain an area of interest since the ligand H**L** has found applications as a selective extraction agent for metals,[2] as a lanthanide NMR shift reagent[3] and more recently in catalysis.[4] The reaction of H**L** with metal ions usually leads to deprotonation of the NH group and concomitant formation of the anionic tetraphenyldithioimidodiphosphinate ligand [$Ph_2P(S)NP(S)Ph_2$]$^-$ (**L**) which features the negative charge delocalised throughout the SPNPS skeleton.[1] A vast body of results show that **L** commonly coordinates to the metal atom through both sulfur atoms, either symmetrically or asymmetrically,[1] resulting in chelate structures (see **a** and **b** in Scheme 1). Alternatively, supramolecular polymeric structures and bridging modes such as **c** (Scheme 1) with formation of homobimetallic compounds are possible.[1]



Scheme 1

The chemistry of H**L** with gold(I) and gold(III) ions has yielded only two X-ray characterised complexes, i.e. [Au(**L**)Cl_2] (**1**), in which the Au^{III} centre is tetracoordinated in a square-planar fashion[5] and [(Ph_3P)Au(**L**)] which con-

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tains a three-coordinate Au^I atom.[6] A few other complexes obtained from the reaction of **HL** with [RAu(tht)], [AuCl(tht)] or $[R_2AuCl]_2$ (R = C_6F_5; tht = tetrahydrothiophene) and containing the ligand in its deprotonated form were only partially characterised.[7,8] As part of an ongoing study on the coordination ability of **HL**,[9−12] we have further explored its reactivity towards the complex $[Au^{III}Cl_3(tht)]$ in CH_2Cl_2 and tested the oxidation in diethyl ether at room temperature of Au^0 metal powder with I_2 in the presence of **HL**. In addition, the structures of the neutral complexes $[Au^{III}(\mathbf{L})I_2]$ (**2**) and $[Au^I(\mathbf{L'}_2H)]$ (**3**) {**L′** = $[Ph_2P(S)NP(O)Ph_2]^-$}, the latter being obtained as a byproduct from the reaction of **HL** with $[AuCl_3(tht)]$, have been determined by single-crystal X-ray diffraction studies.

Results and Discussion

Oxidation of Gold Powder by the Adduct HL·I₂

The oxidation/complexation reaction of metal powders by the iodine adducts of phosphane,[13] thiophosphane[9−12] and polyfunctional thione donors[14−17] has been well documented in recent years. The numerous papers on the subject have shown this synthetic route to be a useful tool in obtaining coordination compounds with unusual geometries, stoichiometries and oxidation numbers at the metal centre. In particular, the I_2 and IBr adducts of *N*,*N′*-dimethyl-perhydro-diazepine-2,3-dithione[15−17] have been applied successfully to noble metals such as gold and platinum for the recovery of these precious metals from waste materials.

The reaction between the adduct $\mathbf{HL}\cdot I_2$, generated in situ, and Au metal powder (1:1 molar ratio; **HL** = 2.22×10^{-3} $mol\cdot dm^{-3}$, 25 °C) in anhydrous Et_2O yielded a dark-red solution from which air-stable dark-red crystals of formula $[Au(\mathbf{L})I_2]$ (**2**) could be separated (yield 20% based upon Au). Concentration of the filtrate solution to dryness yielded a sticky red oil, the FT-Raman spectrum of which showed intense peaks in the low frequency region at 169, 144 and 112 cm^{-1}. The peaks at 112 and 144 cm^{-1} indicate the presence of asymmetric I_3^-, while the peak at 169 cm^{-1} is due to weakly perturbed I_2 molecules.[18] The course of the reaction was also monitored by ^{31}P NMR spectroscopy over a three-week period. As the adduct $\mathbf{HL}\cdot I_2$ in Et_2O (δ = 57.4 ppm) reacts with the gold powder, a new species appears which shows a signal at δ = 37.4 ppm. The assignment of this signal to complex **2** is straightforward and supported by a comparison with the spectrum of the neat compound recorded in $CDCl_3$, δ = 36.4 ppm. During the course of the reaction the signal related to $\mathbf{HL}\cdot I_2$ decreases in intensity and, since complex **2** has a low solubility in Et_2O, the separation of a dark-red fine powder can be observed during this time. Though the synthesis of complex **2** occurs in low yield (Equation 1), the mixture of **HL** with I_2 can oxidise Au^0 to Au^{III} (Equation 1). The influence of this mixture on the process of oxidation is not yet fully understood, though there is no doubt that the reaction of gold powder with either **HL** or I_2 alone leaves the gold unchanged.

$$\mathbf{HL} + 1.5I_2 + Au \xrightarrow[\text{r.t.}]{Et_2O} Au(\mathbf{L})I_2 + HI + \text{other products} \qquad (1)$$

On the basis of cyclic voltammetry (CV) measurements, presented in a previous paper,[10] we have shown that neither iodine ($I_2/2I^-$, $E_{pc} = -0.05$ V) nor the adduct $\mathbf{HL}\cdot I_2$ ($\mathbf{HL}\cdot I_2/2I^-$, $E_{pc} = -0.19$ V) have reduction potentials capable of matching those of noble metals such as Pd, Pt, or Au. Presumably, however, the simultaneous presence of **HL** and I_2 lowers the oxidation potentials of the metals allowing their oxidation, dissolution and complexation. Similar conclusions have also been reached by other researchers employing iodine adducts of sulfur-containing ligands on metal(0) powders or thin sheets.[17] Although complex **2** is known in the literature,[5] its crystal structure has not yet been reported. The results of our single-crystal X-ray structural analysis are reported in Figure 1 as an ORTEP plot, while crystal data and selected geometric parameters of the compound are listed in Table 1 and Table 2, respectively.[19−24] Complex **2** shows a molecular structure similar to that of **1** reported by Laguna et al.,[5] despite showing marked differences in unit cell parameters. It consists of a central Au^{III} ion bonded to two sulfur atoms from an anionic ligand **L** and two iodide anions in a slightly distorted square-planar coordination geometry, showing a maximum deviation from the Au(1)S(1)S(2)I(1)I(2) mean plane of 0.0769(4) Å and a dihedral angle between the I(1)Au(1)I(2) and S(1)Au(1)S(2) planes of 4.70(5)°. A comparison of the structures of **1** and **2** shows some differences, mainly due to the arrangement of the bulky iodide ions around the central Au^{III} ion (Table 3). As already observed in **1**, as well as in various other metal-dichalcogenoimidodiphosphinate complexes,[1] the anionic ligand **L** adopts a pseudo-boat conformation where S(1) and P(2) act as "bow" and "stern", with deviations of 1.1839(12) and 0.6131(3) Å, respectively, from the mean Au(1)P(1)N(1)S(2)

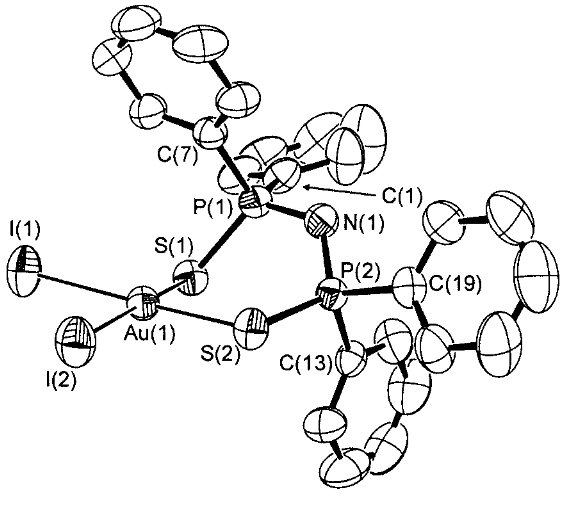

Figure 1. ORTEP plot of **2** showing the atom labelling scheme and 50% probability thermal ellipsoids; hydrogen atoms have been omitted for clarity

Table 1. Crystal data and experimental parameters for **2** and **3**

	2	**3**
Chemical formula	$C_{24}H_{20}AuI_2NP_2S_2$	$C_{48}H_{41}AuN_2O_2P_4S_2$
M	899.24	1062.79
Crystal system	monoclinic	monoclinic
a (Å)	10.5624(3)	9.557(4)
b (Å)	16.1600(5)	26.007(3)
c (Å)	16.4393(5)	19.453(4)
β (°)	99.9250(10)	91.54(2)
U (Å^3)	2764.00(14)	4833(2)
Space group (no.)[24]	$P2_1/n$ (14)	$P2_1/n$ (14)
Z	4	4
μ (mm^{-1})	7.837	3.301
Collected reflections	39937	10515
Unique reflections	9953[a]	8424[b]
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0327$	$R_1 = 0.0820$
	$wR_2 = 0.0735$	$wR_2 = 0.2034$
R indices (all data)	$R_1 = 0.0591$	$R_1 = 0.1553$
	$wR_2 = 0.0820$	$wR_2 = 0.2506$

[a] R(int.) = 0.0537. [b] R(int.) = 0.0662.

Table 2. Selected interatomic distances (Å) and angles (°) for complex **2**

Au(1)–S(2)	2.3509(10)	Au(1)–S(1)	2.3575(10)
Au(1)–I(1)	2.6104(3)	Au(1)–I(2)	2.6207(3)
S(1)–P(1)	2.0456(14)	S(2)–P(2)	2.0603(13)
P(1)–N(1)	1.593(3)	N(1)–P(2)	1.584(3)
S(1)···S(2)	3.5677(13)	I(1)···I(2)	3.7109(5)
I(1)···S(1)	3.4194(11)	I(2)···S(2)	3.3480(10)
S(2)–Au(1)–S(1)	98.53(3)	I(1)–Au(1)–I(2)	90.368(11)
S(2)–Au(1)–I(2)	84.48(2)	S(1)–Au(1)–I(1)	86.83(3)
S(1)–Au(1)–I(2)	175.51(2)	S(2)–Au(1)–I(1)	173.70(3)
P(1)–S(1)–Au(1)	100.35(5)	P(2)–S(2)–Au(1)	108.46(5)
N(1)–P(1)–S(1)	115.48(13)	N(1)–P(2)–S(2)	116.88(14)
P(2)–N(1)–P(1)	123.9(2)		
C(1)–P(1)–S(1)	104.81(17)	C(7)–P(1)–S(1)	109.33(13)
N(1)–P(1)–C(1)	109.1(2)	N(1)–P(1)–C(7)	108.68(18)
C(1)–P(1)–C(7)	109.27(19)		
C(13)–P(2)–S(2)	110.47(14)	C(19)–P(2)–S(2)	102.37(13)
N(1)–P(2)–C(13)	111.99(19)	N(1)–P(2)–C(19)	107.45(19)
C(19)–P(2)–C(13)	106.71(18)		

Table 3. Selected structural data [inter-atomic distances (Å) and angles (°)] for **1**[5] and **2**

	2	**1**[5]
Au–S(1)	2.3575(10)	2.314(2)
Au–S(2)	2.3509(10)	2.303(2)
Au–X(1)[a]	2.6104(3)	2.307(2)
Au–X(2)[a]	2.6207(3)	2.314(2)
S(1)–P(1)	2.0456(14)	2.052(2)
S(2)–P(2)	2.0603(13)	2.055(2)
X(1)–Au–X(2)	90.368(11)	91.0(1)
S(1)–Au–S(2)	98.53(3)	99.9(1)
S(1)–Au–X(1)	86.83(3)	85.6(1)
S(2)–Au–X(2)	84.48(2)	83.5(1)
S(1)–P(1)–N(1)	115.48(5)	116.1(1)
S(2)–P(2)–N(1)	116.88(5)	109.9(1)
P(1)–N(1)–P(2)	123.9(2)	122.6(3)

[a] X = I and Cl for **1** and **2**, respectively.

plane and dihedral angles between the Au(1)P(1)N(1)S(2) and Au(1)S(1)P(1) [S(2)P(2)N(1)] planes of 57.46(3) [41.33(10)]°. Some extent of π-electron delocalisation can be observed over the whole nonplanar $[Au(SP)_2N]$ ring, as indicated by the shorter P–N and longer P–S bond lengths observed in **2** [1.593(3)–1.584(3) and 2.0456(14)–2.0603(13) Å, respectively] with respect to those in the free ligand **HL** [1.672(2)–1.683(2) and 1.937(1)–1.950(1) Å, respectively].[25] The presence of a metal-bonded iodide acting as a terminal ligand is not very common among gold(III) compounds containing a sulfur-bonded metal ion, as observed in **2**. To the best of our knowledge, a similar feature has been observed only in the square-planar cation $[Au(\mathbf{D})I_2]^+$ (**D** = *N,N′*-dimethylperhydrodiazepine-2,3-dithione), obtained by oxidation of gold powder employing a $\mathbf{D}{\cdot}2I_2$ adduct[15,17] and in $[Au_2^{I,III}I_2(C_6H_3\text{-}2\text{-}PPh_2\text{-}5\text{-}Me)(S_2CN\textit{n}Bu_2)]$ which is a mixed-valence complex featuring a square-planar, iodide-bound Au^{III} ion bridged by the C_6H_3-2-PPh_2-5-Me group to a linear $[Au^I{-}I]$ moiety.[26]

Gold(III) Reactivity towards HL, Crystal Structure of [Au(L′$_2$H)]

The reaction between $[Au^{III}Cl_3(tht)]$ and **HL** in CH_2Cl_2 has been partly studied by Laguna et al.[5] who were able to separate the complexes $[Au^{III}(\mathbf{L})Cl_2]$ (**1**) and $[Au^I(\mathbf{L})]_2$ (**4**) using reagent molar ratios of 1:1 and 1:2, respectively. In order to further investigate the reduction reaction of Au^{III} during the formation of complex **4**, we have reconsidered the reaction between $[Au^{III}Cl_3(tht)]$ and **HL** in CH_2Cl_2 using a 1:2 molar ratio. The red colour of the reaction mixture disappeared after a few hours with concomitant formation of buff-coloured fine powder which proved to be elemental sulfur. The subsequently formed insoluble white powder proved to be the expected gold(I) complex **4**. The ^{31}P NMR spectrum of the filtered solution revealed the presence of further phosphorus-containing species besides very small amounts of **4**. In fact, the solvent was slowly evaporated to firstly give a white powder which, on the basis of elemental analysis and ^{31}P NMR spectroscopy [δ = 57.5 and 21.6 ppm; d, $^2J_{P,P}$ = 16.5 Hz, CH_2Cl_2], was identified as the unsymmetrical oxygen/sulfur containing ligand $Ph_2P(S)NHP(O)Ph_2$, (**HL′**).[27,28] Secondly, white stable crystals of a new compound (**3**) were formed which, on the basis of elemental analysis, were tentatively assigned as the neutral Au^I complex [Au(**L′**)(**HL′**)] containing the ligand **HL′** (Scheme 1) in both the protonated and deprotonated forms. In the Au^{III} to Au^I redox reaction the ligand **HL** has, therefore, a double role acting firstly as a reducing agent with production of the oxidised species **HL′** and elemental sulfur and consequently as a complexing agent towards the Au^I ion. However, the solid state ^{31}P CP MAS spectrum of **3** which shows peaks at δ = 33.6 ($\Delta\nu_{1/2}$ = 143 Hz), 25.6

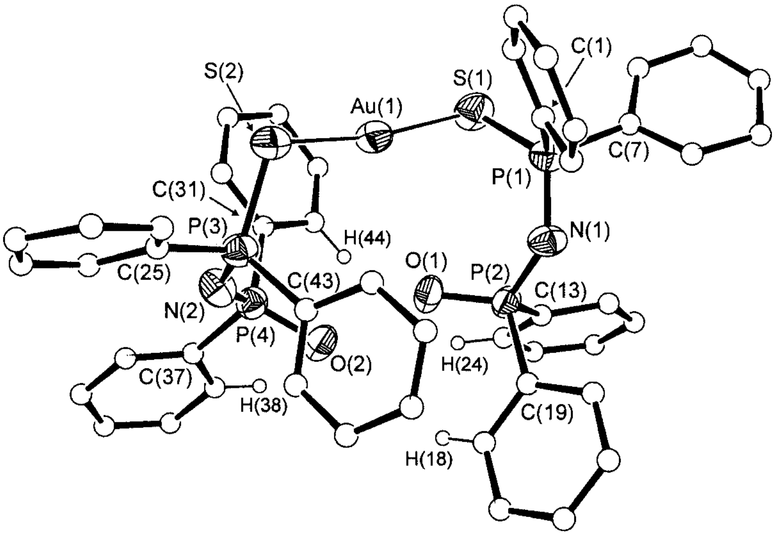

Figure 2. ORTEP plot of **3** showing the atom labelling scheme and 40% probability thermal ellipsoids for the Au, S, O, P and N atoms; C atoms are represented as spheres with arbitrary radii; hydrogen atoms have partly been omitted for clarity

($\Delta\nu_{1/2}$ = 180 Hz) and 18.4 ppm ($\Delta\nu_{1/2}$ = 212 Hz) with a relative intensity ratio of 1:1:2 does not support the presence of **HL′** in its neutral form in the complex since no signal in the 50−60 ppm range was detected (**HL′**, ^{31}P CP MAS: δ = 57.9 and 20.0). Fortunately, we have obtained good quality crystals of **3** for a single-crystal X-ray diffraction study. The molecular structure of **3** is shown in Figure 2, while selected structural parameters are listed in Table 4. The crystal lattice is made up of an Au^{I} complex featuring a quite distorted linear coordination geometry with the sulfur atoms of two ligand molecules [S−Au−S angle 170.24(12)°; average Au−S bond length 2.286(7) Å; nonbonding Au···O distances of 3.212(10) and 4.321(11) Å, for O(1) and O(2), respectively]. Both ligand molecules show a *syn* conformation of the sulfur and oxygen atoms with respect to the PNP fragment, with dihedral angles S(1)P(1)N(1)[O(1)P(2)N(1)]−P(1)N(1)P(2) and S(2)P(3)-N(2)[O(2)P(4)N(2)]−P(3)N(2)P(4) of 9(2) [49.8(12)] and 59.7(11) [55.4(15)]°, respectively, and deviations from the corresponding PNP basal planes in the ranges 0.27(4)−1.52(3) Å for sulfur [S(1) and S(2), respectively] and 1.02(3)−1.12(2) Å for the oxygen atoms [O(1) and O(2), respectively]. This arrangement of ligand moieties gives rise to a nonplanar Au[SO(P$_2$N)]$_2$ ring [deviations from the average atom plane ±1.479(5) Å] which can also be regarded as the connection of two almost planar fragments, namely S(1)Au(1)S(2)P(3) and P(4)O(2)O(1)P(2)N(1) (deviations from the mean plane of ±0.023(2) and ±0.062(7) Å, respectively) by the N(2) and P(1) ′bridging′ atoms. The absence of any counterion in the lattice is the most intriguing feature of the structure since it requires the simultaneous presence, in the molecule, of the ligand both in its neutral (**HL′**) and anionic (**L′**) forms to achieve electroneutrality. In the chemistry of metal tetraorganodichalcogenoimidodiphosphinate complexes, the presence of differentially protonated ligands in the same molecule is quite uncommon and, to the best of our knowledge, only two examples have been reported so far, namely the cationic complex [Pd{*i*Pr$_2$P(S)NHP(S)*i*Pr$_2$}{*i*Pr$_2$P(S)NP-(S)*i*Pr$_2$}]$^+$ [29] and [Au{Ph$_2$P(S)NP(O)Ph$_2$-*S*}{Ph$_2$PNHP-(O)Ph$_2$-*P*}] (**5**)[30] which shows a phosphorus-coordinated Au^{I} ion. Interestingly, in both complexes, the neutral ligands feature an N−H group and effectively retain the hy-

Table 4. Selected interatomic distances (Å) and angles (°) for complex **3**

Au(1)−S(1)	2.297(5)	Au(1)−S(2)	2.274(5)
S(1)−P(1)	2.025(6)	S(2)−P(3)	2.023(6)
O(1)−P(2)	1.496(10)	O(2)−P(4)	1.542(11)
P(1)−N(1)	1.581(12)	P(3)−N(2)	1.579(13)
P(2)−N(1)	1.579(12)	P(4)−N(2)	1.553(14)
Au(1)···O(1)	3.212(10)	Au(1)···O(2)	4.321(11)
S(1)···S(2)	4.554(7)	O(1)···O(2)	2.399(15)
O(1)···H(18)[a]	2.7123	O(1)···H(24)[a]	2.7596
O(2)···H(38)[a]	2.6907	O(2)···H(44)[a]	2.6347
S(2)−Au(1)−S(1)	170.24(16)		
P(1)−S(1)−Au(1)	97.6(2)	P(3)−S(2)−Au(1)	108.2(2)
N(1)−P(1)−S(1)	118.6(5)	N(2)−P(3)−S(2)	119.4(5)
P(2)−N(1)−P(1)	134.0(8)	P(4)−N(2)−P(3)	138.1(9)
O(1)−P(2)−N(1)	116.5(7)	O(2)−P(4)−N(2)	117.8(7)
C(7)−P(1)−S(1)	104.6(7)	C(1)−P(1)−S(1)	110.8(6)
N(1)−P(1)−C(1)	106.3(7)	N(1)−P(1)−C(7)	111.6(8)
C(7)−P(1)−C(1)	104.2(8)		
O(1)−P(2)−C(13)	109.0(7)	O(1)−P(2)−C(19)	110.0(7)
N(1)−P(2)−C(13)	111.9(7)	N(1)−P(2)−C(19)	105.0(6)
C(13)−P(2)−C(19)	103.6(6)		
C(25)−P(3)−S(2)	101.4(6)	C(31)−P(3)−S(2)	112.5(6)
N(2)−P(3)−C(25)	108.3(8)	N(2)−P(3)−C(31)	108.2(7)
C(31)−P(3)−C(25)	105.9(7)		
O(2)−P(4)−C(37)	105.0(7)	O(2)−P(4)−C(43)	108.1(8)
N(2)−P(4)−C(37)	107.8(7)	N(2)−P(4)−C(43)	111.4(8)
C(43)−P(4)−C(37)	105.9(7)		

[a] Hydrogen atoms in calculated positions.

drogen atom topology shown by the corresponding free molecules.[27,31] This seems not to be true in the case of **3**. Although the metric parameters of the two ligands are substantially equivalent and do not allow the identification of a protonated molecule, they do indeed reveal a surprisingly short O(1)···O(2) distance of 2.399(15) Å which strongly suggests the presence of an *intramolecular* hydrogen bond between the two oxygen atoms. Though experimental detection of a bridging hydrogen atom is not possible due to the quality of the solid-state structural determination, such a feature would be reasonable. The presence of a strong negative-Charge Assisted Hydrogen Bond[32] would in fact involve a negative charge-sharing between the two oxygen atoms and explain the equivalence, to within 3σ, of the P−O and N−P bond lengths in the ligands as well as the presence of P−O bonds significantly longer [1.496(10)−1.542(11) Å] than the usual P=O distances [1.47−1.50 Å][25,33,34] observed in *both* ligand fragments of the molecule of **3**. The latter bond length, in particular, could not be ascribed to other intramolecular interactions since the oxygen atoms show only weak nonbonding C−H···O interactions at distances of about 2.7 Å. On the basis of these structural data it is therefore possible to explain the solid state ^{31}P NMR spectroscopic data. The values at δ 33.6 and 25.6 reflect the different phosphorus environments of the *P*S groups in the complex, whereas the broad band at δ = 18.4 ppm reflects the similarity of the two *P*O groups.

It is worthy of note that the presence of strong *intramolecular* hydrogen bonds is not unusual in phosphane-derived compounds. Some examples reported in the literature include complex **5**[30] which features a (N−H···O$^-$) bridge, the chloro-bridged platinum(III) dimer $[PtCl(Ph_2PO)_2H]_2$ [35] and $[(Ph_2PO)_2H(Ph_3PO)]^+I_3^-$ in which an *intramolecular* hydrogen bond drives the cation conformation[36a] and the salts $[(Ph_3PO)H(Ph_3PO)]^+[AuCl_4]^-$[36b] and $[(Ph_3PO)H(Ph_3PO)]^+[ICl_4]^-$.[36c]

Further support of the structural data of **3** and of the stabilisation exerted by the *intramolecular* hydrogen bond between O(1)···O(2) comes from DFT calculations. Starting from the structural data of **3**, the geometry of the model complex $[Au(\mathbf{L}'')_2]^-$ was optimised, {[H$\mathbf{L}''$ = $H_2P(S)NHP(O)H_2$; $\mathbf{L}''$ = $H_2P(S)NP(O)H_2]^-$}. Subsequently, a hydrogen atom was positioned on the nitrogen or on the oxygen atom of an $\mathbf{L}''$ unit so as to form the model complexes $[Au(H\mathbf{L}'')(\mathbf{L}'')]$ and $[Au(\mathbf{L}''_2H)]$, respectively, and these complexes were then optimised. While the calculated structure of $[Au(H\mathbf{L}'')(\mathbf{L}'')]$ is markedly different from that of **3**, the one related to $[Au(\mathbf{L}''_2H)]$ features a P−O···H···O−P bridge with a calculated O−O bond length of 2.401 Å which agrees well with the experimental value of 2.399(15) Å found in **3**. Moreover, the energy of the model complex $[Au(\mathbf{L}''_2H)]$ was found to be 20 kcal/mol more stable than that of $[Au(H\mathbf{L}'')(\mathbf{L}'')]$. An NBO analysis of $[Au(\mathbf{L}''_2H)]$ showed that the two ligand units $\mathbf{L}''$ feature a similar charge distribution (differing by 0.09 e) and that the bridging hydrogen has a strong positive charge (0.539 e); see also Supplementary Information.

Acid/Base Behaviour of Complex 3

The protonation and deprotonation reactions of complex **3** were investigated by ^{31}P NMR spectroscopy. The solution ^{31}P NMR spectrum of **3** (CH_2Cl_2)[37] features a pair of doublets with the same integrated intensity at δ(*P*S) 32.8 ppm and δ(*P*O) 18.4 ppm (Table 5). The similarity of these values to those reported for the solid-state sample indicates that the structure of **3** is retained in solution with the proton bridging the two oxygen atoms. Treatment of complex **3** dissolved in CH_2Cl_2 with increasing amounts of a very strong base, 1,8-bis(dimethylamino)naphthalene (DMAN), produced the broadening and lowering of peaks related to **3** and the concomitant formation of two new peaks at δ = 29.0 ppm and 12.7 ppm. Notably, these values are similar to those previously observed for the $\mathbf{L}'$ moiety in [Au{Ph$_2$P(O)NP(S)Ph$_2$−*S*}{Ph$_2$P(O)NHPPh$_2$−*P*}] [δ(*P*S) 28.5 ppm, δ(*P*O) 14.0 ppm, $CDCl_3$] in which $\mathbf{L}'$ coordinates to the gold ion *via* the sulfur atom only, leaving the PO group pendant. This indicates that DMAN is able to deprotonate complex **3** with formation of the anionic complex $[Au(\mathbf{L}')_2]^-$ in which the metal ion is coordinated only by the sulfur atoms of two $\mathbf{L}'$ ligands leaving, in this case also, the PO groups as pendants. This also agrees very well with the fact that the variation of the chemical shifts of (*P*O) is more pronounced with respect to that observed for (*P*S).

Table 5. ^{31}P NMR spectroscopic data for complex **3**, H$\mathbf{L}'$ and related reactions

Compound/reaction[a]	δ(*P*S) / ppm	δ(*P*O) / ppm	$^2J(P_SP_O)$ / Hz
3 (solid state)	33.6 25.6	18.4	
3 (CH_2Cl_2)	32.8	18.4	2.5
3 + DMAN[b][c] (CH_2Cl_2)	29.0	12.7	
3 + CF_3COOH[b][d] (CH_2Cl_2)	56.4	26.8	14
H$\mathbf{L}'$ (CH_2Cl_2)	57.5	21.6	16.5
H$\mathbf{L}'$ + CF_3COOH[b][e] (CH_2Cl_2)	57.4	28.8	15.9

[a] All measurements carried out at 25 °C. [b] In situ reaction. [c] **3**/DMAN 1:2 molar ratio; **3** = 5×10^{-2} mol·dm^{-3}. [d] **3**/CF_3COOH 1:1 molar ratio; **3** = 5×10^{-2} mol·dm^{-3}. [e] H$\mathbf{L}'$/CF_3COOH 1:1 molar ratio; H$\mathbf{L}'$ = 5×10^{-2} mol·dm^{-3}.

The addition of an equivalent of CF_3COOH to a solution of **3** in CH_2Cl_2 resulted in a considerable change in the ^{31}P NMR spectrum of the complex with both the (*P*S) and (*P*O) resonance signals shifted to higher values of δ = 56.4 ppm and 26.8 ppm, respectively. The value of δ(*P*S) at 56.4 ppm, which is strongly indicative of *N*-protonation of the ligands in the complex, agrees well with the signal observed for the neutral complexes $[Pd(H\mathbf{L})I_2]$[10] [δ(*P*S) 56.5 ppm, $CHCl_3/CH_3CN$, v:v, 1:1] and $[Hg(H\mathbf{L})I_2]$[38] [δ(*P*S) 57.8 ppm, CH_2Cl_2] and for *cis*-[Pd{Ph$_2$P(O)NHP(S)Ph$_2$−*O*,*S*}$_2$][BF$_4$]$_2$ [δ(*P*S) 57.6 ppm, δ(*P*O) 45.9 ppm, d,

$^{2}J_{P,P}$ = 7.0 Hz), $CDCl_3$] in which the ligand acts in an *O,S*-bidentate manner thus forming a six-membered Pd−O−P−N−P−S ring. It is interesting to note that the (*P*O) signal for the protonated complex **3** is very different from that observed for the palladium complex *cis*-[Pd{$Ph_2P(O)NHP(S)Ph_2$-*O,S*}$_2$][BF_4]$_2$, while it is comparable with that measured for an acidic solution of H**L**′′ [δ(*P*O) 28.8 ppm, CH_2Cl_2] (Table 5). Hence it is reasonable to hypothesise that in acidic media the PO groups in **3** remain uncoordinated to the metal and protonated, and that the variation observed at the δ(*P*O) depends on the *N*-protonation of the ligands.

Conclusion

It has been demonstrated that the adduct H**L**·I_2 in Et_2O can oxidise Au^0 powder to produce the complex [Au^{III}(**L**)I_2] under mild conditions in a single step. This reaction indicates that the oxidation of Au^0 by charge transfer adducts of iodine can be accomplished using very different donor molecules and, consequently, it may be of some importance in the gold-based technology of semiconductor devices since it avoids the use of unattractive reagents in the etching process. As a result of an interest in the reactions between [$Au^{III}Cl_3$(tht)] with H**L**, it has been shown that the reducing agent is the ligand HL and the products are the complex [Au^I(**L**)]$_2$, sulfur, the free ligand $Ph_2P(S)NHP(O)Ph_2$ (H**L**′) and a very small amount of its Au^I complex. The nature of this unusual complex has been investigated by X-ray crystallography and ^{31}P CP MAS spectroscopy. Interestingly, this complex shows a structure similar to that depicted in Scheme 1 (see **c**), with an Au^I ion bridging two sulfur atoms of two anionic ligands **L**′ and a proton bridging two oxygen atoms of the PO groups. The nature of this complex is also supported by DFT calculations. The protonation and deprotonation reactions of [Au(**L**′$_2$H)] leave the coordination environment of the Au^I centre unaffected. ^{31}P NMR spectroscopic data suggest that in the case of protonation, both ligands are protonated at the nitrogen atoms.

Experimental Section

Materials and Instrumentation: Reagents were used as purchased from Aldrich. Diethyl ether was distilled form $LiAlH_4$ shortly before use.

$^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity 400 MHz spectrometer. Chemical shift values were referenced to an external standard of 85% H_3PO_4 (δ_{31P} = 0.0) inserted in a sealed co-axial tube. All solution NMR experiments were carried out in NMR tubes with PTFE valves (Aldrich). ^{31}P NMR CP MAS spectra were calibrated indirectly through the 85% H_3PO_4 peak (δ_{31P} = 0.0). IR spectra were measured as KBr (4000−400 cm^{-1}) and polyethylene pellets (400−50 cm^{-1}) on a Bruker Equinox 55 FT-IR spectrometer. FT-Raman spectra were recorded on a Bruker FRS 100/S Fourier transform Raman spectrometer operating with a diode-pumped Nd:YAG exciting laser emitting at 1064 nm.

Syntheses: Compounds [$Ph_2P(S)NHP(S)Ph_2$] (H**L**) and Cs[$Ph_2P(S)NP(S)Ph_2$] (Cs**L**) were prepared according to ref.[39] and ref.[11], respectively. Complexes [AuCl(tht)] and [$AuCl_3$(tht)] were prepared according to ref.[7]; complex [Au(**L**)Cl_2] was prepared according to ref.[5]

[Au(L)I$_2$] (2): A mixture of H**L** (0.100 g, 0.222 mmol) and I_2 (0.084 g, 0.333 mmol) in diethyl ether (200 mL) was stirred at 25 °C under N_2 until the reagents were completely dissolved. Gold metal powder (100 mesh) (0.044 g, 0.222 mmol) was added with stirring. Stirring was continued at room temperature for ca. 3 weeks. The resultant red-black solid and crystals were collected by suction filtration, washed with a mixture of CH_2Cl_2 and *n*-hexane (1:5, v:v) and dried in vacuo. Yield 0.040 g, 20%. m.p. 230−232 °C. Elemental analysis for $C_{24}H_{20}AuI_2NP_2S_2$ (899.24): calcd. C 32.06, H 2.24, N 1.56, S 7.13; found C 32.5, H 2.4, N 1.8, S 7.6. ^{31}P NMR ($CDCl_3$): δ = 36.4 ppm. IR (KBr): $\tilde{\nu}$ = 3051 w, 1476 w, 1436 s, 1308 w, 1187 s, 1172 vs, 1108 vs, 1026 w, 997 w, 923 w, 827 m, 746 s, 721 s, 700 vs, 690 vs, 567 vs, 554 vs, 523 m, 511 s, 491 m cm^{-1}.

[Au(L′$_2$H)] (3): $Ph_2P(S)NHP(S)Ph_2$ (0.233 g, 0.520 mmol) was added to a solution of $AuCl_3$(tht) (0.100 g, 0.260 mmol) in dichloromethane (50 mL) and the mixture was stirred for 2 h at room temperature. The cloudy mixture was then filtered to separate a fine buff-coloured powder (sulfur) and, after 48 hours, filtration was again carried out to separate complex **4**. The filtrate was reduced by two-thirds to give the white compound $Ph_2P(S)NHP(O)Ph_2$. Further evaporation of the solvent to almost dryness yielded white crystals of **3**, yield 5%, m.p. 208−210 °C. Elemental analysis for $C_{48}H_{41}AuN_2O_2P_4S_2$ (1062.79): calcd. C 54.24, H 3.89, N 2.64, S 6.03; found C 54.6, H 4.0, N 2.8, S 6.5. ^{31}P NMR (CH_2Cl_2): δ(*P*S) 32.8, δ(*P*O) 18.4 ppm, $^{2}JP_{S}P_{O}$ = 2.5 Hz. IR (KBr): $\tilde{\nu}$ = 3055 m, 1591 w, 1481 m, 1436 s, 1253 br, 1179 m 1124 s, 1110 s, 1067 m, 1027 m, 1000 m, 889 br, 746 ms, 722 s, 691 vs, 618 w, 579 s, 565 s, 546 s, 509 s cm^{-1}.

X-ray Crystallography: X-ray quality crystals of **2** and **3** were obtained directly as described above. The structures were solved by direct methods (SIR-97[20] and SHELXS-97[21] for **2** and **3**, respectively) and refined using the SHELXL-97 program[21] implemented in the WINGX suite.[22] Details of the crystal data and structural refinements are reported in Table 1. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were treated as idealised contributors in calculated positions and refined isotropically. Selected interatomic distances and angles can be found in Table 2 and Table 4. CCDC-233084 (for **2**) and -233085 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Complex 2: Diffraction data were collected at room temperature on an Bruker SMART-CCD system automatic diffractometer equipped with a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) in the range 3.6 < 2θ < 66.6°. Refinement of 290 parameters on 9953 independent reflections gave *R1* [*wR2*] = 0.0327 [0.0819] on $I > 2\sigma(I)$ [all data]. The maximum and minimum residual electron densities on the final Δ*F* map were 0.95 and −1.06 e·Å^{-3}.

Complex 3: A 0.58 × 0.22 × 0.10 mm crystal was mounted at room temperature on a Siemens P4-RA automatic diffractometer equipped with graphite-monochromated Mo-K_α radiation (α = 0.71073 Å). A total of 10515 reflections (8424 unique) were collected in the range $3.8 < 2\theta < 50.1°$. Intensities were corrected for Lorentz-polarisation effects and an empirical absorption correction was applied (ψ-scan).[23] Refinement of 532 parameters gave $R1$ [$wR2$] = 0.0820 [0.2506] on $I > 2\sigma(I)$ [all data]. The maximum and minimum residual electron densities on the final ΔF map were 1.59 and -0.83 e·Å^{-3}.

Computations: Density Functional Calculations (DFT) were carried out on the model complexes $[\mathrm{Au}(\mathbf{L}'')_2]^-$, $[\mathrm{Au}(\mathrm{H}\mathbf{L}'')(\mathbf{L}'')]$ and $[\mathrm{Au}(\mathbf{L}''_2\mathrm{H})]$ using the Gaussian 98 suite of programs (Rev. A11)[40] with the hybrid Becke3LYP functional[41–43] and the LanL2DZ basis set for C, H, N, O, P, S and Au. The NBO charge distribution[44] was calculated for all the examined compounds. The results were examined with the Molden 3.9 program.[45]

Supporting Information Available (see also footnote on the first page of this article): Table S1, Optimised geometry calculated for the complex $[\mathrm{Au}(\mathbf{L}''_2\mathrm{H})]$ in the orthogonal Cartesian coordinate format; Table S2, Mulliken atomic charges at the optimised geometry calculated for the complex $[\mathrm{Au}(\mathbf{L}''_2\mathrm{H})]$; Table S3, Summary of natural population analysis at the optimised geometry calculated for the complex $[\mathrm{Au}(\mathbf{L}''_2\mathrm{H})]$.

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