# Heterometallic Pt -Au Complexes with $\mu-3 \mathrm{~S}$ Bridging. Syntheses and Structures of $\mathrm{Pt}_{\mathbf{2}}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2} \cdot \mathbf{2 C H} \mathbf{C l}_{2}$ and $\mathrm{Pt}_{\mathbf{2}}\left(\mathbf{P P h}_{3}\right)_{4}-$ $(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right) \mathrm{NO}_{3} \cdot \mathbf{0 . 5 \mathrm { H } _ { 2 } \mathrm { O }}$ 

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## Abstract

From $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})_{2}$ (I) three heterometallic complexes can be prepared: $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2}$ (II), $\left(\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuPPh}_{3}\right)_{2}{ }^{2+}\right.$ (III) and $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}-$ $(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right)^{+}$(IV). Their preparation and properties are described.

The crystal and molecular structures of II and the nitrate of IV has been investigated by X-ray diffraction analysis.

II crystallizes in the monoclinic space group $P 2_{1} / n$, $a=18.359(2) \quad b=13.947(2), c=14.588(2) \AA, \beta=$ $100.982(7)^{\circ}, V=3666.9 \AA^{3}, \quad M_{\mathrm{r}}=2138.28, Z=2$, $D_{\mathrm{c}}=1.94 \mathrm{Mg} / \mathrm{m}^{3}$. Mo $\mathrm{K} \alpha$ radiation (graphite crystal monochromator, $\lambda=0.71069 \AA$ ), $\mu($ Mo K $\alpha$ ) $=85.13$ $\mathrm{cm}^{-1}, F(000)=2032, T=293 \mathrm{~K}$. Final conventional $R$-factor $=0.039, R w=0.050$ for 5084 unique reflections and 155 variables. IV crystallizes in the triclinic space group $P \overline{1}, a=14.605(1), b=15.989(2), c=$ 18.005(2) $\AA, \alpha=101.144(8)^{\circ}, \beta=100.773(7)^{\circ}, \gamma=$ $91.201(2)^{\circ}, \quad V=4045.4 \AA^{3}, \quad M_{\mathrm{r}}=2033.75, \quad Z=2$, $D c=1.66 \mathrm{Mg} / \mathrm{m}^{3} . \mathrm{Cu} \mathrm{K} \alpha$ radiation (graphite crystal monochromator, $\lambda=1.5418 \AA), \mu(\mathrm{Cu} \mathrm{K} \alpha)=116.45$ $\mathrm{cm}^{-1}, F(000)=1986, T=293 \mathrm{~K}$. Final conventional $R$-factor $=0.039 R w=0.051$ for 8631 unique reflections and 297 variables. Both the structures were solved using SHELX84 and DIRDIF.

The hinged square planar geometry of the parent I is kept in IV, where $\mathrm{AuPPh}_{3}$ is bonded to one of the bridging $S$ atoms. In II both bridging $S$ atoms are bonded to AuCl and the hinging geometry is transformed into a nearly planar $\mathrm{P}_{2} \mathrm{PtS}_{2} \mathrm{PtP}_{2}$ frame with the SAuCl vectors nearly perpendicular to it, one on each side of that plane. There are indications for weak $\mathrm{Au}-\mathrm{Pt}$ bonding interactions. In IV and II the three-coordinated S -atoms have bond angles of about $90^{\circ}$. The structure of III is supported to be similar to II. Some reactions and interconversions of II, III and IV are described.

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## Introduction

For the preparation of gold clusters we developed procedures using the evaporation of gold and its subsequent reaction in a cold solution of appropriate ligands. As heterometallic complexes and mixed metal clusters have attracted wide attention in recent years and many compounds containing gold in a varicty of unusual geometries are known now [1-4], we were engaged in the synthesis of mixed metal clusters by the metal evaporation technique.

The ligating properties of $\mathrm{Fe}_{2}(\mu-\mathrm{S})_{2}(\mathrm{CO})_{6}{ }^{2-}$ and $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ are well investigated [5, 6], they act as bidentate ligands towards other metal ions to form heterometallic complexes.

Mingos et al. [6] described the potential and versability of $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ as a bidentate ligand and illustrated this for $\mathrm{Pd}^{2+}$ and $\mathrm{Hg}^{2+}$ compounds.

Our efforts to prepare mixed $\mathrm{Pt}-\mathrm{Au}$ clusters by the reaction of gold gas with cold solutions of $\mathrm{Pt}_{2}$ -$(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ were unsuccessful. However, some heterometallic gold platinum complexes were prepared in this way. The properties and structure of three of these compounds were determined and are reported here.

## Experimental

## Instrumental

$\mathrm{C}, \mathrm{H}$ and N analyses were carried out in the microanalytical department of the University of Nijmegen. The other analyses were measured by Dr. A. Bernhardt, Elbach über Engelskirchen, F.R.G. Molecular weights were determined using a Knauer 11.00 vapour pressure osmometer at $37^{\circ} \mathrm{C}$. Electrical conducting measurements were performed with a Metrohm Konduktoskop and a Philips PR 9510/00 conductivity cell at $25{ }^{\circ} \mathrm{C}$.
${ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR spectra were recorded on a Varian XL 100 FT at 40.5 MHz , infrared spectra on a PerkinElmer 283 spectrophotometer and mass spectra
on a VG 7070 E spectrometer. All materials were of reagent grade.

## Preparations

## I. $P t_{2}(\mu-S)_{2}\left(P P h_{3}\right)_{4}$

Prepared as described by Ugo et al. [7], from $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{3}$ and 2 equivalents of sulfur.

## II. $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-S A u C l)_{2}$

Using the rotary metal evaporation apparatus [8], 100 mg Au was evaporated into 200 ml of toluene containing 100 mg of $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ and 50 mg of $\mathrm{Bu}_{4} \mathrm{NCl}$ at $-100^{\circ} \mathrm{C}$, resulting in a black slurry. After warming up and stirring for 2 h at room temperature a black precipitate is filtered off and the yellow solution is evaporated to about 50 ml . On standing for 24 h yellow crystals are formed. Yield $10 \%$ calculated on $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$. Mass spectrometry: using FAB techniques a parent peak pattern was found around a maximum intensity at 1966 and the isotope ratio was identical with the computer simulation of the formulation $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2}$.

Crystals suitable for X-ray analysis could be obtained by slow diffusion of diethylether into a dichloromethane solution. The crystals are cracked by drying due to loss of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ -$(\mu-\mathrm{SAuCl})_{2}$, molecular weight 1968.32. Anal. Calc. for $\mathrm{C}_{72} \mathrm{H}_{60} \mathrm{Au}_{2} \mathrm{Cl}_{2} \mathrm{Pt}_{2} \mathrm{~S}_{2} \mathrm{P}_{4}$ : $\mathrm{Au}, 20.02$; $\mathrm{Pt}, 19.81$; $\mathrm{S}, 3.25$. Found: $\mathrm{Au}, 19.70 ; \mathrm{Pt}, 19.85 ; \mathrm{S}, 3.07 \%$. The IR spectrum is the same as that of $\mathrm{Pt}_{2}(\mu \cdot \mathrm{~S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ except for a weak $\mathrm{Au}-\mathrm{Cl}$ stretching band at 330 $\mathrm{cm}^{-1},{ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right] \mathrm{NMR}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ relative to TMP 18.98 ppm ${ }^{1} J(\mathrm{PtP}) 3030 \mathrm{~Hz}$.

## III. $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuPPh}_{3}\right)_{2}\left(\mathrm{NO}_{3}\right)_{2}$

To a suspension of 100 mg of $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ in 35 ml THF a solution of 68 mg of $\mathrm{AuPPh}_{3} \mathrm{NO}_{3}$ (molar ratio 1:2) in 5 ml THF is added under stirring.

When nearly 1 equivalent is added the solution becomes clear yellow and by adding more a beige product precipitates. The product is filtered off and washed with THF and diethylether and dried under vacuo (yield $150 \mathrm{mg}, 90 \%$ ). $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuPPh}_{3}\right)_{2}$ $\left(\mathrm{NO}_{3}\right)_{2}$; molecular weight 2546.01. Anal. Calc. for $\mathrm{C}_{108} \mathrm{H}_{90} \mathrm{Au}_{2} \mathrm{Pt}_{2} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{P}_{6} \mathrm{~S}_{2}: \mathrm{C}, 50.95 ; \mathrm{H}, 3.54 ; \mathrm{N}, 1.10$; $\mathrm{Au}, 15.47$; $\mathrm{Pt}, 15.33 ; \mathrm{S}, 2.52$. Found $\mathrm{C}, 49.51 ; \mathrm{H}$, $3.41 ; \mathrm{N}, 0.99$; Au, 15.55; Pt, $15.30 ; \mathrm{S}, 2.49 \%$.) Conductivity $59.2 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$ in DMSO at $25^{\circ} \mathrm{C}$; molecular weight determination $3000 ;{ }^{31} \mathrm{P}$. [ $\left.{ }^{1} \mathrm{H}\right]$ NMR in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ rclative to TMP 18.80 ppm , (4P, $\left.\mathrm{PtPPh}_{3}\right)^{1} J(\mathrm{PtP} 2900 \mathrm{~Hz}, 32.90 \mathrm{ppm}(2 \mathrm{P}, \mathrm{Au}-$ $\mathrm{PPh}_{3}$ ).
IV. $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-S)\left(\mu-S A u P P h_{3}\right) \mathrm{NO}_{3} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$
(a) When a solution of 17.5 mg of $\mathrm{AuPPh}_{3} \mathrm{NO}_{3}$ ( 0.03 mmol ) in 2 ml of THF is added to a suspension
of 50 mg of $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}(0.03 \mathrm{mmol})$ in 8 ml of THF, a clear yellow solution is formed within 15 min and after 24 h yellow crystals are formed. The crystals suitable for an X-ray analysis are filtered off, washed with 2 ml of THF and diethylether and dried in vacuo. Yield $18 \mathrm{mg}, 25 \% \mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ -$(\mu-S)\left(\mu-\mathrm{SAuPPh}_{3}\right) \mathrm{NO}_{3} \cdot 1 / 2 \mathrm{H}_{2} \mathrm{O}$, molecular weight 2033.75. Anal. calc. for $\mathrm{C}_{90} \mathrm{H}_{75} \mathrm{AuPt}_{2} \mathrm{NO}_{3} \mathrm{P}_{5} \mathrm{~S}_{2}$ $1 / 2 \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 53.31 ; \mathrm{H}, 3.77$; N, 0.69 ; Pt, 19.18; Au, 9.69 ; P, 7.61 ; S, 3.15. Found: C, 53.16; H, 3.83; N, $0.71 ; \mathrm{Pt}, 19.20 ; \mathrm{Au}, 9.88 ; \mathbf{P}, 7.55 ; \mathrm{S}, 3.06 \%$.

Conductivity $49.5 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$ in DMSO at $25{ }^{\circ} \mathrm{C},{ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right] \mathrm{NMR}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ relative to TMP, $17.95 \mathrm{ppm}\left(4 \mathrm{P}, \mathrm{PtPPh}_{3}\right),{ }^{1} J(\mathrm{PtP}) 2990 \mathrm{~Hz}, 29.22$ ppm ( $\mathrm{P}, \mathrm{AuPPh}_{3}$ ).

In a similar procedure but using $\mathrm{AuPPh}_{3} \mathrm{Cl}$ instead of $\mathrm{AuPPh}_{3} \mathrm{NO}_{3} \mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right) \mathrm{Cl}$ was obtained. Excess of $\mathrm{AuPPh}_{3} \mathrm{Cl}$ does not yield any other product.
(b) When 50 mg of metallic gold is evaporated in 100 ml toluene containing $100 \mathrm{mg} \mathrm{Pt} 2(\mu-\mathrm{S})\left(\mathrm{PPh}_{3}\right)_{4}$ and $50 \mathrm{mg} \mathrm{PPh}_{3}$ a black brown slurry is formed. To this slurry 100 ml dichloromethane is added and after one hour the dark solid is filtered off and the brown solution is concentrated by evaporation to 50 ml . After one day a red-brown precipitate is formed. The precipitate is filtered off and washed with 50 ml of THF. The ${ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR spectrum of the soluble part of the precipitate in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ shows $\mathrm{Pt}_{2}$. $\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right)^{+}$as the main product.

## Crystal Structure Determination

## II. $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2} \cdot 2 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ and IV. $\mathrm{Pt}_{2^{-}}$ $\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right) \mathrm{NO}_{3} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$

Suitablc yellow crystals of II and IV were used for the measurements. To prevent cracking by loss of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ the crystal of II was mounted in a glass capillary with solvent throughout the experiment. Mo $\mathrm{K} \alpha$ radiation (II) ( $\lambda=0.71069 \AA$ ) and $\mathrm{Cu} \mathrm{K} \alpha$ radiation (IV) $(\lambda=1.5418 \AA)$ were used at 293 K with a graphite crystal monochromator on a Nonius CAD4 single crystal diffractometer. The unit cell dimensions, II: monoclinic, $a=18.359(2), \quad b=$ $13.947(2), c=14.588(2) \AA, \beta=100.982(7)^{\circ}, \quad V=$ $3666.9 \AA^{3}, \quad$ IV: triclinic, $\quad a=14.605(1), \quad b=$ $15.989(2), c=18.005(2) \AA, \alpha=101.144(8)^{\circ}, \beta=$ $100.773(7)^{\circ}, \gamma=91.201(2)^{\circ}, V=4045.4 \AA^{3}$, were determined from the angular settings of 22 reflections with $14^{\circ}<\theta<28^{\circ}$ for II and of 25 reflections with $15^{\circ}<\theta<57^{\circ}$ for IV. The space groups were determined from the systematic absences and the structure determination. II: $\mathrm{P}_{1} / n ; h 0 l, h+l=2 n+$ $1 ; 0 k 0, k=2 n+2$; IV: $P \overline{1}$. The intensity data of 6845 (II) (to $\theta=25^{\circ}$ ) and 14419 reflections (IV) (to $\theta=55^{\circ}$ ) were measured using the $\omega-2 \theta$ scan technique, with a scan angle of $1.00^{\circ}$ and a variable
scan rate with a maximum scan time of 20 s per reflection.

The intensity of the primary beam was checked throughout the data collection by monitoring three reference reflections every 30 min . The final drift correction factors were between 0.95 and 1.03 (II). and 0.96 and 1.04 (IV). A smooth curve based on the reference reflections was used to correct for this drift. On all reflections profile analysis was performed [9, 10]; empirical absorption correction was applied using $\psi$ scans [11]. For II: $\mu(\mathrm{Mo} \mathrm{K} \alpha$ ) $=85.13$ $\mathrm{cm}^{-1}$ (correction factors were in the range 0.70 to 1.00: for IV: $\mu(\mathrm{Cu} \mathrm{K} \alpha)=116.5 \mathrm{~cm}^{-1}$ (correction factors were in the range 0.68 to 1.00 ); Symmetry equivalent reflections were averaged, $R_{\text {int }}=\Sigma(I-$ $\langle I\rangle) / \Sigma I=0.029$ (II) and 0.018 (IV) resulting in 6845 (II) and 10144 (IV) unique reflections of which 5084 (II) and 8631 (IV) were observed with $I>$ $3 \sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $\left|F_{0}\right|$-values.

The gold and platinum atoms were found using SHELX84 [12]. The structures were expanded using DIRDIF [13], thereby establishing the chemical composition. The structures were refined by full-matrix least-squares on $|F|$ values, using SHELX [14]. Scattering factors were taken from International Tables [15]. Two dichloromethane molecules (II) and a half of water molecule (IV) were found from the respectively difference Fourier syntheses and were included in the refinement. Hydrogen atoms were found from difference Fourier syntheses and were included in the refinement. The phenyl type carbon atoms were converted into a regular hexagon with carbon-carbon distances
$1.395 \AA$ and all hydrogen atoms were included in fixed idealized positions $1.08 \AA$ from the carbon atom to which they were bonded. Isotropic refinement converged to $R=0.085$ (II) and 0.063 (IV). At this stage empirical absorption correction was applied [16], resulting in a further decrease of $R$ to 0.072 (II) (correction factors were in the range $0.87-1.13$ ) and to 0.054 (IV) (correction factors were in the range $0.88-1.30$ ). No extinction corrections were applied.

During the final stages of the refinement the positional parameters of the non-phenyl atoms, the anisotropic thermal parameters of gold, platinum, phosphor, sulfur and chlorine (II) and the isotropic thermal parameters of the carbon atoms were refined. The phenyl groups were refined as rigid groups with standard geometry. The hydrogen atoms had fixed isotropic temperature factors of $0.05 \AA$. The final conventional agreement factors were for II: $R=0.039$ and $R_{\mathrm{w}}=0.050$ for the 5084 'observed' reflections and 155 variables, for IV: $R=0.039$ and $R_{\mathrm{w}}=0.051$ for the 8631 'observed' reflections and 297 variables. The function minimized was $\Sigma w\left(F_{\mathrm{o}}-\right.$ $\left.F_{\mathrm{c}}\right)^{2}$ with $w=\sigma\left(F_{\mathrm{o}}+0.0004 F_{\mathrm{o}}\right)^{-2}$ with $\sigma\left(F_{\mathrm{o}}\right)$ from counting statistics. The maximum shift over error ratio in the last full matrix least-squares cycle was for II less than 0.20 except for dichloromethane (up to 1.46) and for IV less than 0.22. The final difference Fourier map showed for II one peak of height $3 \mathrm{e} / \AA^{3}$ at $0.9 \AA$ from Au and several peaks of about $1 \mathrm{e} / \AA^{3}$; and for IV no peaks higher than $0.5 \mathrm{e} / \AA^{3}$. Plots were made with PLUTO [17]. Final positional and thermal parameters are given in Table I. Molecular geometry data are collected in Tables

TABLE I. Fractional Positional and Thermal Parameters (e.s.d. Values in Parentheses): (a) $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuCl}_{2} \cdot \mathbf{2 C H}_{2} \mathrm{Cl}_{2}\right.$. (b) $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuPPh}_{3}\right)(\mu-\mathrm{S})\left(\mathrm{NO}_{3}\right)_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$

| Atom | $x$ | $y$ | $z$ | $U_{\text {eq }}(\times 100)\left(\AA^{2}\right)$ |
| :--- | :--- | :--- | :--- | :---: |
| (a) |  |  |  |  |
| Au1 | $0.11371(2)$ | $0.03719(3)$ | $0.13273(3)$ | $4.59(1)$ |
| Pt1 | $-0.05595(2)$ | $-0.00375(2)$ | $0.08737(2)$ | $2.22(1)$ |
| S1 | $0.04795(11)$ | $-0.08342(14)$ | $0.04903(14)$ | $3.12(6)$ |
| P1 | $-0.05986(11)$ | $-0.12011(14)$ | $0.19668(14)$ | $2.81(6)$ |
| P2 | $-0.14327(11)$ | $0.09878(14)$ | $0.12111(14)$ | $2.68(6)$ |
| C11 | $0.1683(2)$ | $0.1645(3)$ | $0.2185(3)$ | $10.3(2)$ |
| C1 | $0.0323(3)$ | $-0.1514(3)$ | $0.2612(4)$ | $3.5(2)$ |
| C2 | $0.0764(3)$ | $-0.0781(3)$ | $0.3074(4)$ | $4.2(2)$ |
| C3 | $0.1485(3)$ | $-0.0979(3)$ | $0.3540(4)$ | $5.4(3)$ |
| C4 | $0.1764(3)$ | $-0.1909(3)$ | $0.3544(4)$ | $6.1(3)$ |
| C5 | $0.1323(3)$ | $-0.2642(3)$ | $0.3083(4)$ | $6 .(3)$ |
| C6 | $00602(3)$ | $-0.2445(3)$ | $0.2617(4)$ | $4.6(2)$ |
| C7 | $-0.0950(3)$ | $-0.2308(4)$ | $0.1396(3)$ | $3.6(2)$ |
| C8 | $-0.1121(3)$ | $-0.3072(4)$ | $0.1935(3)$ | $4.8(2)$ |
| C9 | $-0.1381(3)$ | $-0.3933(4)$ | $0.1507(3)$ | $6.6(3)$ |
| C10 | $-0.1471(3)$ | $-0.4029(4)$ | $0.0540(3)$ | $6.8(3)$ |
| C11 | $-0.1300(3)$ |  |  | $0.0001(3)$ |
|  |  |  |  | $5.9(3)$ |
|  |  |  |  |  |

TABLE I. (continued)

| Atom | $x$ | $y$ | $z$ | $U_{\text {eq }}(\times 100)\left(\AA^{2}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| C12 | -0.1040(3) | -0.2404(4) | 0.0429(3) | 4.1(2) |
| C13 | -0.1170(2) | -0.1078(5) | 0.2861(4) | 3.4(2) |
| C14 | -0.0861(2) | -0.0835(5) | 0.3780(4) | 4.6(2) |
| C15 | -0.1312(2) | -0.0757(5) | 0.4445 (4) | 6.2(3) |
| C16 | -0.2074(2) | -0.0923(5) | 0.4190(4) | 5.4(3) |
| C17 | -0.2383(2) | -0.1166(5) | 0.3271 (4) | $5.7(3)$ |
| C18 | -0.1931(2) | -0.1244(5) | $0.2606(4)$ | 4.4(2) |
| C19 | -0.2398(3) | 0.0596(4) | 0.0885(4) | $3.5(2)$ |
| C20 | -0.2533(3) | -0.0307(4) | 0.0477(4) | 4.9 (2) |
| C21 | -0.3261(3) | -0.0632(4) | 0.0199(4) | 6.6(3) |
| C22 | -0.3853(3) | -0.0054(4) | 0.0329(4) | 7.0 (3) |
| C23 | -0.3717(3) | 0.0850(4) | $0.0737(4)$ | $7.0(3)$ |
| C24 | -0.2990(3) | $0.1174(4)$ | $0.1015(4)$ | $5.0(2)$ |
| C25 | -0.1421(3) | 0.2110(4) | 0.0575(4) | 3.2 (2) |
| C26 | -0.1883(3) | 0.2203(4) | -0.0298(4) | 4.3(2) |
| C27 | -0.1803(3) | 0.2988(4) | -0.0865(4) | 6.2(3) |
| C28 | -0.1262(3) | 0.3679(4) | -0.0558(4) | 6.3(3) |
| C29 | -0.0801(3) | $0.3585(4)$ | 0.0315(4) | 6.4(3) |
| C30 | -0.0880(3) | $0.2801(4)$ | $0.0881(4)$ | $5.0(2)$ |
| C31 | -0.1233(2) | $0.1332(4)$ | $0.2445(4)$ | 3.1(2) |
| C32 | -0.1778(2) | 0.1445(4) | 0.2984(4) | $4.2(2)$ |
| C33 | -0.1583(2) | $0.1743(4)$ | 0.3911 (4) | 5.4(3) |
| C34 | -0.0842(2) | 0.1929(4) | $0.4300(4)$ | 6.0 (3) |
| C35 | -0.0296(2) | $0.1817(4)$ | 0.3761 (4) | 5.9(3) |
| C36 | -0.0492(2) | 0.1519(4) | $0.2834(4)$ | $4.2(2)$ |
| C 12 | 0.3132(3) | $-0.0480(4)$ | 0.2262(4) | 12.9(2) |
| C13 | 0.4700(3) | 0.9581(5) | 0.2323 (5) | 18.1(3) |
| C37 | 0.391(1) | 0.891(2) | 0.206 (1) | 13.4(7) |
| (b) |  |  |  |  |
| Pt1 | 0.21128(2) | $0.21003(2)$ | 0.32619(2) | 2.265(12) |
| Pt2 | $0.23208(2)$ | 0.26916(2) | $0.16532(2)$ | 1.974(12) |
| Aul | 0.02550(3) | 0.24158(2) | 0.19991 (2) | 3.571 (14) |
| S1 | $0.15119(14)$ | 0.15336(11) | 0.19334(10) | 2.45 (6) |
| S2 | $0.20075(15)$ | 0.33911(11) | 0.28426(11) | 2.64(7) |
| P1 | $0.25742(17)$ | 0.27872 (13) | 0.45070 (12) | 3.23(8) |
| P2 | $0.22231(17)$ | $0.07144(13)$ | 0.34259(12) | 3.23(8) |
| P3 | $0.25272(15)$ | $0.19121(12)$ | 0.05006(11) | 2.57(7) |
| P4 | $0.30829(15)$ | 0.39438(12) | 0.16123 (11) | 2.46(7) |
| P5 | -0.11216(17) | $0.30180(15)$ | $0.19612(14)$ | 3.81 (9) |
| N1 | 0.5561 (9) | $0.7252(7)$ | 0.2111 (7) | 8.8(3) |
| 01 | 0.5551 (8) | $0.7736(7)$ | $0.1647(7)$ | 13.4(4) |
| O2 | $0.4807(8)$ | $0.6811(7)$ | $0.1987(6)$ | 11.9(3) |
| O3 | 0.6262(8) | 0.7058(7) | 0.2530(6) | 12.4(4) |
| O4 | $0.6987(11)$ | 0.8968(9) | $0.2330(8)$ | 6.8(4) |
| C1A | $0.2088(3)$ | 0.2234 (4) | 0.5812(3) | 4.8(3) |
| C2A | 0.1432 (3) | 0.1960(4) | 0.6199(3) | $6.7(3)$ |
| C3A | 0.0484(3) | 0.1892(4) | 0.5864(3) | 6.8(3) |
| C4A | 0.0193(3) | 0.2099(4) | 0.5142(3) | 7.0(3) |
| C5A | 0.0849(3) | 0.2373 (4) | 0.4755 (3) | 5.6(3) |
| C6A | $0.1796(3)$ | 0.2440 (4) | 0.5089(3) | 3.8(2) |
| C7A | $0.4354(4)$ | 0.2232(4) | 0.4473(3) | 4.9(3) |
| C8A | 0.5288(4) | $0.2138(4)$ | 0.4780(3) | 6.4 (3) |
| C9A | $0.5656(4)$ | $0.2492(4)$ | $0.5552(3)$ | 7.2 (3) |
| C10A | 0.5092(4) | 0.2941 (4) | 0.6018(3) | 6.6 (3) |

TABLE I. (continued)

| Atom | $x$ | $y$ | $z$ | $Y_{\text {eq }}(\times 100)\left(\AA^{2}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| C11A | 0.4159(4) | 0.3035(4) | 0.5711(3) | 5.5(3) |
| C12A | 0.3790 (4) | $0.2681(4)$ | 0.4938(3) | 3.7(2) |
| C13A | $0.3230(4)$ | $0.4413(4)$ | $0.4479(4)$ | 5.5(3) |
| C14A | $0.3206(4)$ | 0.5298(4) | 0.4569(4) | 7.1(3) |
| C15A | 0.2485 (4) | 0.5718(4) | $0.4866(4)$ | 7.4(3) |
| C16A | $0.1789(4)$ | 0.5252(4) | $0.5073(4)$ | 7.1(3) |
| C17A | $0.1813(4)$ | 0.4367 (4) | 0.4984(4) | 5.8(3) |
| C18A | 0.2533(4) | $0.3948(4)$ | 0.4687 (4) | 3.9(2) |
| C1B | 0.3431 (5) | -0.0613(4) | $0.3148(4)$ | 6.3(3) |
| C2B | 0.4149(5) | -0.1004(4) | $0.2824(4)$ | 7.8(4) |
| C3B | 0.4628(5) | -0.0583(4) | 0.2390 (4) | 8.0(4) |
| C4B | 0.4390(5) | 0.0231(4) | $0.2279(4)$ | 6.0(3) |
| C5B | $0.3672(5)$ | $0.0623(4)$ | 0.2603(4) | 3.9(2) |
| C6B | $0.3192(5)$ | 0.0201(4) | $0.3037(4)$ | 3.9(2) |
| C7B | $0.1188(4)$ | -0.0743(4) | $0.2474(4)$ | 6.5(3) |
| C8B | $0.0360(4)$ | -0.1236(4) | 0.2146 (4) | 8.9(4) |
| C9B | -0.0493(4) | -0.0917(4) | $0.2266(4)$ | 8.0(4) |
| C10B | -0.0519(4) | -0.0105(4) | $0.2714(4)$ | 7.3(3) |
| C11B | 0.0309(4) | 0.0388(4) | 0.3041 (4) | 5.9(3) |
| C12B | $0.1163(4)$ | $0.0069(4)$ | 0.2921 (4) | 3.9(2) |
| C13B | $0.3289(4)$ | $0.0500(4)$ | $0.4820(4)$ | 6.4(3) |
| C14B | $0.3437(4)$ | $0.0316(4)$ | $0.5558(4)$ | 10.3(5) |
| C15B | $0.2686(4)$ | $0.0044(4)$ | $0.5848(4)$ | 10.4(5) |
| C16B | 0.1788 (4) | -0.0045(4) | $0.5399(4)$ | 9.1 (4) |
| C17B | $0.1640(4)$ | 0.0139(4) | 0.4661(4) | 6.3(3) |
| C18B | $0.2391(4)$ | $0.0412(4)$ | 0.4371(4) | 4.5(2) |
| C1C | $0.3949(4)$ | $0.1191(4)$ | -0.0228(2) | 4.5(2) |
| C2C | $0.4867(4)$ | $0.0975(4)$ | -0.0236(2) | 5.9(3) |
| C3C | $0.5558(4)$ | $0.1237(4)$ | 0.0423(2) | 5.9(3) |
| C4C | $0.5331(4)$ | $0.1716(4)$ | $0.1091(2)$ | 5.4(3) |
| C5C | $0.4412(4)$ | $0.1933(4)$ | $0.1099(2)$ | 3.7(2) |
| C6C | $0.3721(4)$ | 0.1670 (4) | 0.0440(2) | 3.0(2) |
| C7C | 0.2469 (3) | 0.2495(3) | -0.0903(3) | 3.1(2) |
| C8C | $0.2036(3)$ | 0.2900(3) | -0.1484(3) | 4.1 (2) |
| C9C | $0.1174(4)$ | 0.3247 (3) | -0.1446(3) | 4.5(2) |
| $\mathrm{C10C}$ | $0.0744(3)$ | $0.3188(3)$ | $-0.0827(3)$ | 4.6(2) |
| C11C | 0.1176 (3) | $0.2783(3)$ | -0.0246(3) | 3.7(2) |
| C12C | 0.2038(3) | $0.2436(3)$ | -0.0284(3) | 2.6(2) |
| C13C | $0.1163(4)$ | 0.0639(3) | -0.0369(3) | $4.7(2)$ |
| C14C | 0.0758(4) | -0.0192(3) | -0.0574(3) | 6.5(3) |
| C15C | 0.1152(4) | -0.0825(3) | -0.0203(3) | 6.4(3) |
| C16C | $0.1951(4)$ | -0.0628(3) | 0.0374(3) | 5.9(3) |
| C17C | $0.2357(4)$ | $0.0203(3)$ | 0.0579(3) | 4.5(2) |
| C18C | $0.1963(4)$ | 0.0836(3) | $0.0207(3)$ | 3.0(2) |
| C1D | $0.1427(4)$ | 0.4741(3) | $0.1681(3)$ | 3.9(2) |
| C2D | $0.0874(4)$ | 0.5422(3) | $0.1864(3)$ | 5.3(3) |
| C3D | $0.1291(4)$ | $0.6215(3)$ | $0.2265(3)$ | 6.2(3) |
| C4D | 0.2261 (4) | $0.6325(3)$ | 0.2483(3) | 7.1 (3) |
| C5D | $0.2814(4)$ | 0.5644(3) | $0.2300(3)$ | 6.0(3) |
| C6D | $0.2397(4)$ | 0.4851(3) | 0.1900 (3) | 2.9(2) |
| C7d | 0.4436(4) | $0.3708(3)$ | 0.2865 (3) | 3.7(2) |
| C8D | $0.5279(4)$ | $0.3904(3)$ | 0.3393 (3) | 5.1(3) |
| C9D | $0.5895(4)$ | 0.4552(3) | 0.3329 (3) | 5.9(3) |
| C10D | $0.5670(4)$ | 0.5005(3) | $0.2737(3)$ | 4.8(3) |
| C11D | $0.4828(4)$ | $0.4810(3)$ | $0.2209(3)$ | 3.8(2) |
| C12D | 0.4211(4) | 0.4162(3) | 0.2274 (3) | 2.4(2) |
| C13D | 0.2770(3) | 0.4612(3) | 0.0267 (3) | 3.7(2) |
| C14D | 0.1975 (3) | 0.4764(3) | -0.0423(3) | 4.9(3) |

TABLE I. (continued)

| Atom | $x$ | $y$ | $z$ | $U_{\text {eq }}(\times 100)\left(\AA^{2}\right)$ |
| :--- | ---: | :--- | ---: | :--- |
| C15D | $0.3777(3)$ | $0.4453(3)$ | $-0.0668(3)$ | $4.9(3)$ |
| C16D | $0.4374(3)$ | $0.3990(3)$ | $-0.0223(3)$ | $4.9(3)$ |
| C17D | $0.4169(3)$ | $0.3838(3)$ | $0.0467(3)$ | $3.7(2)$ |
| C18D | $0.3367(3)$ | $0.4149(3)$ | $0.0713(3)$ | $2.8(2)$ |
| C1E | $-0.1248(3)$ | $0.3263(4)$ | $0.0464(4)$ | $7.0(3)$ |
| C2E | $-0.1706(3)$ | $0.3282(4)$ | $-0.0285(4)$ | $6.6(3)$ |
| C3E | $-0.2667(3)$ | $0.3093(4)$ | $-0.0502(4)$ | $6.3(3)$ |
| C4E | $-0.3170(3)$ | $0.2884(4)$ | $0.0030(4)$ | $5.5(3)$ |
| C5E | $-0.2712(3)$ | $0.2865(4)$ | $0.0779(4)$ | $3.7(2)$ |
| C6E | $-0.1752(3)$ | $0.3055(4)$ | $0.0996(4)$ | $6.2(3)$ |
| C7E | $-0.2100(5)$ | $0.1555(4)$ | $0.2051(3)$ | $7.0(3)$ |
| C8E | $-0.2709(5)$ | $0.1075(4)$ | $0.2339(3)$ | $8.1(4)$ |
| C9E | $-0.3138(5)$ | $0.1466(4)$ | $0.2936(3)$ | $6.3(4)$ |
| C10E | $-0.2959(5)$ | $0.2337(4)$ | $0.3244(3)$ | $4.4(3)$ |
| C11E | $-0.2350(5)$ | $0.2816(4)$ | $0.2956(3)$ | $5.7(3)$ |
| C12E | $-0.1920(5)$ | $0.2426(4)$ | $0.2359(3)$ | $6.9(3)$ |
| C13E | $-0.0259(4)$ | $0.4419(4)$ | $0.3034(4)$ | $6.1(3)$ |
| C14E | $-0.0190(4)$ | $0.5258(4)$ | $0.3450(4)$ | $5.5(3)$ |
| C15E | $-0.0932(4)$ | $0.5783(4)$ | $0.3328(4)$ | $5.3(3)$ |
| C16E | $-0.1741(4)$ | $0.5470(4)$ | $0.2791(4)$ | $4.2(2)$ |
| C17E | $-0.1810(4)$ | $0.4631(4)$ | $0.2375(4)$ |  |
| C18E | $-0.1069(4)$ | $0.4106(4)$ | $0.2497(4)$ |  |

TABLE II. Atomic Distances (e.s.d. Values in Parentheses) : (a) $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu \mathrm{SAuCl}_{2} \cdot 2 \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$. (b) $\mathrm{Pt}_{2}\left(\mathrm{PPH}_{3}\right)_{4}(\mu-\mathrm{SAu}-$ $\left.\mathrm{PPh})_{3}\right)(\mu-\mathrm{S})\left(\mathrm{NO}_{3}\right)_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$

| (a) |  |  |  |
| :--- | :--- | :--- | :--- |
| Au1-Pt1 | $3.111(1)$ | $\mathrm{Pt} 1-\mathrm{P} 1$ | $2.286(2)$ |
| $\mathrm{Au} 1-\mathrm{Pt} 1^{\prime}$ | $3.218(1)$ | $\mathrm{Pt} 1-\mathrm{P} 2$ | $2.271(2)$ |
| $\mathrm{Au} 1-\mathrm{S} 1$ | $2.284(2)$ |  |  |
| $\mathrm{Au} 1-\mathrm{Cl} 1$ | $2.290(3)$ |  |  |
| $\mathrm{Pt} 1-\mathrm{S} 1$ | $2.365(2)$ |  |  |
| $\mathrm{Pt} 1-\mathrm{S} 1^{\prime}$ | $2.360(2)$ |  |  |
|  |  |  |  |
| $\mathrm{P})$ |  |  |  |
| $\mathrm{Pt} 1-\mathrm{Pt} 2$ | $3.279(1)$ | $\mathrm{Au} 1-\mathrm{S} 1$ | $2.345(2)$ |
| $\mathrm{Pt} 1-\mathrm{Au} 1$ | $3.314(1)$ | $\mathrm{Au} 1-\mathrm{S} 2$ | $2.959(2)$ |
| $\mathrm{Pt} 1-\mathrm{S} 1$ | $2.378(2)$ | $\mathrm{Au} 1-\mathrm{P} 5$ | $2.243(2)$ |
| $\mathrm{Pt} 1-\mathrm{S} 2$ | $2.329(2)$ |  |  |
| $\mathrm{Pt} 1-\mathrm{P} 1$ | $2.267(2)$ |  |  |
| $\mathrm{Pt} 1-\mathrm{P} 2$ | $2.296(2)$ |  |  |
| $\mathrm{Pt} 2-\mathrm{Au} 1$ | $3.231(1)$ |  |  |
| $\mathrm{Pt} 2-\mathrm{S} 1$ | $2.360(2)$ |  |  |
| $\mathrm{Pt} 2-\mathrm{S} 2$ | $2.347(2)$ |  |  |
| $\mathrm{Pt} 2-\mathrm{P} 3$ | $2.280(2)$ |  |  |
| $\mathrm{Pt} 2-\mathrm{P} 4$ | $2.291(2)$ |  |  |

II and III. The molecular contiguration and the crystallographic numbering scheme is given in Fig. 1a and b. No unusual intermolecular contacts are present in both the structures.

## Results and Discussion

The $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2}$ complex is formed when metallic gold is evaporated into a toluene solution containing $\mathrm{Bu}_{4} \mathrm{NCl}$ and $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$. That $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2}$ is formed in the metal evaporation apparatus and not during the recrystallization in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ can be concluded from mass spectral data of the products precipitated from the toluene solution. Using FAB techniques a parent peak pattern was found around a maximum intensity at 1966, and the isotope ratio was identical with the computer simulation of the formulation $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2}$. The reaction path in the metal evaporation experiment is unknown. The oxidation of the gold to $\mathrm{Au}(\mathrm{I})$ may be due to traces of air or water in the apparatus [8, 19]. Interestingly we found that neither AuCl nor $\mathrm{Au}(\mathrm{CO}) \mathrm{Cl}$ reacts with $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4} \mathrm{~S}_{2}$ to form $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu$ $\mathrm{AuCl})_{2}$. The $\mathrm{Au}-\mathrm{Pt}$ compounds described in this paper are in general inert to $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, which is noteworthy as the parent $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4} \mathrm{~S}_{2}$ reacts with $\mathrm{CH}_{2}$ $\mathrm{Cl}_{2}$ to form the S -methylated $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})$ -$\left(\mu-\mathrm{SCH}_{2} \mathrm{Cl}\right)^{+}$[18].

The crystal structure determination shows $\mathrm{Pt}_{2^{-}}$ $\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2}$ to have in good approximation $C_{2 h}$ symmetry with the $\mathrm{Pt}-\mathrm{Pt}$ vector as the local twofold axis. The hinged squares present in the parent compound $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4} \mathrm{~S}_{2}$ are bent to a flat structure

(a)

(b)

Fig. 1. Molecular configuration and atomic numbering scheme for (a) $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuCl}_{2} \cdot 2 \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$; (b) $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-$ $\mathrm{SAuPPh} h_{3}(\mu-\mathrm{S})\left(\mathrm{NO}_{3}\right)_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$.

TABLE III. Bond Angles (e.s.d. Values in Parentheses); (a) $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2} \cdot 2 \mathrm{CH}_{2} \mathrm{Cl}_{2}$. (b) $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-$ $\left.\mathrm{SAuPPh}_{3}\right)(\mu-\mathrm{S})\left(\mathrm{NO}_{3}\right)_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$

| (a) |  |  |  |
| :---: | :---: | :---: | :---: |
| Pt1-Au1-Pt1 ${ }^{\prime}$ | 68.6(1) | $\mathrm{Au} 1^{\prime}-\mathrm{Pt} 1-\mathrm{Pl}$ | 123.0(1) |
| P11-Au1-S1 | 49.1(1) | Au1'-Pt1-P2 | 101.3(1) |
| Pt1'-Au1-S1 | 47.1(1) | S1-Pt1-S1' | 82.0(1) |
| Pt1-Au1-Cl1 | 125.1(1) | S1-Pt1-P1 | 88.0(1) |
| Pt1'-Au1-Cll | 133.2(1) | $\mathrm{S} 1-\mathrm{Pt1}$-P2 | 169.0(2) |
| S1-Au1-Cl1 | 174.2(1) | S1'-Pt1-P1 | 165.7(1) |
| Aul-Pt1-Aul' | 111.4(1) | S1'-Pt1-P2 | $91.0(1)$ |
| Au1-Pt1-S1 | 46.9(1) | P1-Pt1-P2 | 100.3(1) |
| Aul-Pt1-S1' | 82.0(1) | Au1-S1-Pt1 | 84.0(1) |
| Au1'-Pt1-S1 | 79.8(1) | Au1-S1-Pi1 | 87.7(1) |
| Aul'-Ptl-S1' | 45.2(1) | Pt1-S1-Ptl | 98.0(1) |
| Au1-Pt1-P1 | 98.3(1) |  |  |
| Au1-Pt1-P2 | 123.9(1) |  |  |
| (b) |  |  |  |
| Pt2-Pt1-Aul | 58.7(1) | S1-Pt2-P4 | 169.1(1) |
| Pt2- Pt 1 -S1 | 46.0(1) | S2-Pt2-P4 | 86.8(1) |
| Au1-Pt1-S1 | 45.0(1) | P3-Pt2-P4 | 98.5(1) |
| Pt2-Ft1-S2 | 45.7(1) | Pt1-Au1-Pt2 | 60.1(1) |
| Au1-Pt1-S2 | 60.3(1) | Pt1-Au1-S1 | 45.9(1) |
| S1-Pt1-S2 | 82.4(1) | $\mathrm{Pt} 2-\mathrm{Au} 1-\mathrm{S} 1$ | 46.8(1) |
| $\mathrm{Pt} 2-\mathrm{Pt} 1-\mathrm{P} 1$ | 130.5(1) | Pt1-Au1-S2 | 43.1(1) |
| Au1-Pt1-P1 | 128.0(1) | Pt2-Au1-S2 | 44.3(1) |
| S1-Ptl-P1 | 172.6(1) | S1-Au1-S2 | 70.5(1) |
| S2-Pt1-P1 | 91.4(1) | Pt1-Au1-P5 | 140.2(1) |
| Pt2-Pt1-P2 | 123.1(1) | Pt 2 -Au1-P5 | 142.1(1) |
| Au1-Pt1-P2 | 114.4(1) | S1-Au1-P5 | 168.6(1) |
| S1-Ptl-P2 | 87.2(1) | S2-Au1-P5 | 120.8(1) |
| S2-Ptl-P2 | 168.7(1) | $\mathrm{Pt} 1-\mathrm{S} 1-\mathrm{Pt} 2$ | 87.6(1) |
| P1-Pt1-P2 | 99.3(1) | Pt1-S1-Au1 | 89.1(1) |
| $\mathrm{Pt} 1-\mathrm{Pt} 2-\mathrm{Au} 1$ | 61.2(1) | Pt2-S1-Au1 | 86.7(1) |
| Pt1-Pt2-S1 | 46.4(1) | Pt1-S2-Pt2 | 89.0(1) |
| Au1-Pt2-S1 | 46.4(1) | Pt1-S2-Au1 | 76.6(1) |
| $\mathrm{Pt} 1-\mathrm{Pt} 2-\mathrm{S} 2$ | 45.3(1) | $\mathrm{Pt} 2-\mathrm{S} 2-\mathrm{Au} 1$ | 74.0(1) |
| Au1-Pt2-S2 | 61.7(1) |  |  |
| $\mathrm{S} 1-\mathrm{Pt} 2-\mathrm{S} 2$ | 82.4(1) |  |  |
| Pt1 -Pt2 P3 | 130.8(1) |  |  |
| Au1-Pt2-P3 | 113.7(1) |  |  |
| S1-Pt2-P3 | 92.4(1) |  |  |
| S2-Pt2-P3 | 174.6(1) |  |  |
| Pt1-Pt2-P4 | 123.5(1) |  |  |
| Au1-Pt2-P4 | 128.1(1) |  |  |

with a planar $\mathrm{P}_{2} \mathrm{PtS}_{2} \mathrm{PtP}_{2}$ frame. The Pt atoms are $0.015 \AA$ out of the least-squares plane through the 4 P and the 2 S atoms, one Pt below and the other above that plane. Au is linearly coordinated ( $\mathrm{S}-\mathrm{Au}$ Cl is $174.2^{\circ}$ ). The angle $\mathrm{Au}-\mathrm{S}-\mathrm{Pt}$ is $84.0^{\circ}$ and $\mathrm{Au}-$ $\mathrm{S}-\mathrm{Pt}^{1}$ is $87.7^{\circ}$, the lowest angle of $84.0^{\circ}$ corresponds with the Pt atom that comes up from the $\mathrm{P}_{4} \mathrm{~S}_{2}$ plane in the direction of the Au atom, the $\mathrm{Au}-\mathrm{Pt}$ distance is $3.111 \AA$ as compared with $3.28 \AA$ for the $\mathrm{Au}-\mathrm{Pt}^{1}$ distance. This interesting detail in the molecular structure indicates a weak $\mathrm{Pt}-\mathrm{Au}$ bonding interaction (Fig. 2). The bis-S-alkylated compounds $\mathrm{Pt}_{2}\left(\mathrm{PProp}_{3}\right)_{4}(\mu-\mathrm{SEt})_{2}{ }^{2+}[20]$ and $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{2}\left(\mathrm{NO}_{2}\right)_{2}-$ ( $\mu$-SMe) $)_{2}$ [18] both have a hinged square-planar geometry with hinge angles of $130^{\circ}$ and $140^{\circ}$ respectively. The $\mathrm{Pt}-\mathrm{S}-\mathrm{C}$ angles are in the range $110-140^{\circ}$, bending the alkyl groups away from the hinge. In the Pt -Au compound described here the bond angles on the $S$ atoms are close to $90^{\circ}$. MO calculations [21] have shown that the energy involved in the hinging of coordination squares is relatively small and that subtile electronic and crystal packing effects determine the actual hinge angle.


Fig. 2. The $\mathrm{Pt}-\mathrm{Au}$ interactions indicated in a schematic figure of the molecular structure of $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2}$.

When a suspension of $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ in THF is treated with 1 equivalent of $\mathrm{AuPPh}_{3} \mathrm{NO}_{3}, \mathrm{Pt}_{2}$ -$\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right) \mathrm{NO}_{3} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ is obtained as yellow crystals. Conductivity measurements in DMSO ( $\Lambda_{\mathrm{o}}=49.5 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$ at $25^{\circ} \mathrm{C}$ ) and the infrared spectrum (free nitrate at $1360 \mathrm{~cm}^{-1}$ ) are in agreement with the results of a single-crystal X-ray analysis. This shows $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})(\mu$-SAu$\left.\mathrm{PPh}_{3}\right)^{+}$to have a hinged square-planar geometry with the hinge angle, that is the dihedral angle between the local coordination planes, of $135^{\circ}$. The Au-S distances $2.345 \AA$ and $2.959 \AA$ indicate that Au is coordinated to only one of the S -atoms. In these respects it resembles the methylated $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ ( $\mu$-S $)(\mu \text {-SMe })^{+}$, which has a hinge angle of $138^{\circ}$ [9]. In the Pd and Hg compounds both S atoms are coordinated, making $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4} \mathrm{~S}_{2}$ a bidentate ligand [6]. The rather long $\mathrm{Pt}-\mathrm{Pt}$ ( $3.279 \AA$ ) and $\mathrm{Pt}-\mathrm{Au}$ ( 3.314 and $3.231 \AA$ ) distances give no evidence for metal-metal bonding. The gold atom is linear coordinated ( $\mathrm{S}-\mathrm{Au}-\mathrm{P}$ angle is $168.6^{\circ}$ ). The $\mathrm{Pt}_{1}-\mathrm{S}-\mathrm{Pt}_{2}$ angle is $87.6^{\circ}$, quite near to that in the forementioned methylated compound ( $88.9^{\circ}$ ). That methyl group is bended away from the hinge; $\mathrm{Pt}-\mathrm{S}-\mathrm{C}$ angles being $104.0^{\circ}$ and $100.2^{\circ}$ [6]. However, the $\mathrm{S}-\mathrm{Au}$ vector is nearly perpendicular to the $\mathrm{Pt}-\mathrm{S}-\mathrm{Pt}$ plane, the Pt-S-Au angles are $86.7^{\circ}$ and $89.1^{\circ}$.
$\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuPPh}_{3}\right)_{2}\left(\mathrm{NO}_{3}\right)_{2}$ is formed when a suspension of $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ in THF is treated with 2 equivalents of $\mathrm{Au} \mathrm{PPh}_{3} \mathrm{NO}_{3}$. The composition was established by analyses, conductivity measurements ( $\Lambda=59.2 \mathrm{ohm}^{-1} \mathrm{~cm}^{-2} \mathrm{~mol}^{-1}$ in DMSO, $25^{\circ} \mathrm{C}$ ) which agrees with a 1:2 electrolyte and the molar weight determination. We suggest that this complex is built up in the same way as $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{SAuCl})_{2}$ with a planar $\mathrm{P}_{2} \mathrm{PtS}_{2} \mathrm{PtP}_{2}$ frame and a linear coordinated gold atom on each side of that plane. Comparing the chemical shifts of the ${ }^{31} \mathrm{P}$ [ $\left.{ }^{1} \mathrm{H}\right]$ NMR spectra of the three complexes: $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right)$ IV: $17.95 \mathrm{ppm}\left(\mathrm{P}_{\mathrm{P}} \mathrm{PPPh}_{3}\right), 29.22 \mathrm{ppm}\left(\mathrm{P}, \mathrm{AuPPh}_{3}\right)$; $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuCl}_{2}: 18.88 \mathrm{ppm}\left(\mathrm{P}, \mathrm{Pt}_{2} \mathrm{PPh}_{3}\right) ; \mathrm{Pt}_{2}\right.$ $\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuPPh}_{3}\right)_{2}\left(\mathrm{NO}_{3}\right)_{2}$ III: 18.80 ppm (P, $\left.\mathrm{PtPPh}_{3}\right), 32.90 \mathrm{ppm}\left(\mathrm{P}_{\mathrm{Au}} \mathrm{APPh}_{3}\right)$ (all shifts downfield relative to TMP in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ), the suggestion of the structure of $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuPPh}_{3}\right)_{2}\left(\mathrm{NO}_{3}\right)_{2}$ is underlined.

In the reaction of onc equivalent or an excess of $\mathrm{AuPPh}{ }_{3} \mathrm{Cl}$ with $\mathrm{Pt}_{2}(\mu-\mathrm{S})_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ only $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}$ -$(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right)^{+}$is formed, while the reaction of $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\left(\mu-\mathrm{SAuPPh}_{3}\right)_{2}\left(\mathrm{NO}_{3}\right)_{2}$ with $\mathrm{Cl}^{-}$ions yields $\mathrm{Pt}_{2}\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right)^{+}$and $\mathrm{AuPPh}_{3} \mathrm{Cl}$. Obviously $\mathrm{Cl}^{-}$is successful in competing with $\mathrm{Pt}_{2}$ -$\left(\mathrm{PPh}_{3}\right)_{4}(\mu-\mathrm{S})\left(\mu-\mathrm{SAuPPh}_{3}\right)^{+}$for $\mathrm{AuPPh}_{3}$ while $\mathrm{NO}_{3}{ }^{-}$ is not.

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