

# Moderating the nucleophilicity of the sulfide ligands in the dinuclear {Pt<sub>2</sub>S<sub>2</sub>} metalloligand system using triphenylarsine

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## Abstract

Reaction of *cis*-[PtCl<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>] with excess sodium sulfide in benzene gave the triphenylarsine analogue of the well-known metalloligand [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] as an orange solid. The compound was characterised by detailed mass spectrometry studies, and by conversion to various alkylated and metallated derivatives. The sulfide ligands in [Pt<sub>2</sub>(μ-S)<sub>2</sub>(AsPh<sub>3</sub>)<sub>4</sub>] are less basic than the triphenylphosphine analogue, and the complex gives a relatively weak [M+H]<sup>+</sup> ion in the positive-ion electrospray (ESI) mass spectrum, compared with the phosphine analogue. Methylation of an equimolar mixture of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] and [Pt<sub>2</sub>(μ-S)<sub>2</sub>(AsPh<sub>3</sub>)<sub>4</sub>] with MeI gave the species [Pt<sub>2</sub>(μ-S)(μ-SMe)(AsPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup> and [Pt<sub>2</sub>(μ-SMe)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>I]<sup>+</sup>, indicating a reduced tendency for the sulfide of [Pt<sub>2</sub>(μ-S)(μ-SMe)(AsPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup> to undergo alkylation. The lability of the arsine ligands is confirmed by the reaction of an equimolar mixture of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] and [Pt<sub>2</sub>(μ-S)<sub>2</sub>(AsPh<sub>3</sub>)<sub>4</sub>] with *n*-butyl chloride, giving [Pt<sub>2</sub>(μ-S)(μ-SBu)(EPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup> (E = P, As), which with Me<sub>2</sub>SO<sub>4</sub> gave a mixture of [Pt<sub>2</sub>(μ-SMe)(μ-SBu)(PPh<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and [Pt<sub>2</sub>(μ-SMe)(μ-SBu)(AsPh<sub>3</sub>)<sub>3</sub>Cl]<sup>+</sup>. Reactivity towards 1,2-dichloroethane follows a similar pattern. The formation and ESI MS detection of mixed phosphine–arsine {Pt<sub>2</sub>S<sub>2</sub>} species of the type [Pt<sub>2</sub>(μ-S)<sub>2</sub>(AsPh<sub>3</sub>)<sub>*n*</sub>(PPh<sub>3</sub>)<sub>4-*n*</sub>] is also discussed. Coordination chemistry of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(AsPh<sub>3</sub>)<sub>4</sub>] towards a range of metal-chloride substrates, forming sulfide-bridged trinuclear aggregates, has also been probed using ESI MS, and found to be similar to the phosphine analogue. The X-ray crystal structure of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(AsPh<sub>3</sub>)<sub>4</sub>Pt(cod)](PF<sub>6</sub>)<sub>2</sub> (cod = 1,5-cyclo-octadiene) has been determined for comparison with the (previously reported) triphenylphosphine analogue. ESI MS is a powerful tool in exploring the chemistry of this system; in some cases the derivatising agent *p*-bromobenzyl bromide is used to convert sparingly soluble and/or poorly ionising {Pt<sub>2</sub>S<sub>2</sub>} species into soluble, charged derivatives for MS analysis.

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**Keywords:** Arsine ligands; Sulfide ligands; Platinum complexes; Electrospray mass spectrometry

## 1. Introduction

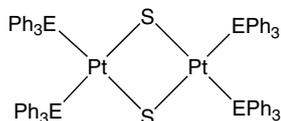
Complexes containing the {Pt<sub>2</sub>S<sub>2</sub>} core have a rich and diverse chemistry. The sulfide ligands are highly nucleophilic, and can undergo protonation and alkylation, as well as acting as donor ligands towards a range of main group, transition metal and actinide centres. The chemistry of this system has been the subject of several reviews [1–3]. The

most widely studied complex of this type is the triphenylphosphine derivative [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (1), probably because of its accessibility from air-stable starting materials, and its tendency to produce crystalline derivatives. However, recent studies have shown that the chemistry of the {Pt<sub>2</sub>S<sub>2</sub>} core can be modified by changing the ancillary phosphine ligands from PPh<sub>3</sub> to a diphosphine such as Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>*n*</sub>PPh<sub>2</sub> (*n* = 2, 3) [4,5]. Other studies have focused on derivatives containing phosphines such as PhPMe<sub>2</sub> [6,7] and P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub> [8] (which provide greater solubility in organic solvents), chiral phosphines such as DIOP (to investigate the applicability of {Pt<sub>2</sub>S<sub>2</sub>} complexes

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in enantioselective reactions) [9], redox active 1,1'-bis(diphenylphosphino)ferrocene (dppf) [10] and the pyridyl phosphine  $\text{Ph}_2\text{Ppy}$  [11] (which can be used to assemble large multimetallic sulfide aggregates) [12].



1, E = P  
2, E = As

In contrast to the abundance of studies that use ancillary phosphine ligands on the  $\{\text{Pt}_2\text{S}_2\}$  core, systems with other ancillary ligands are scarcely known. In very early work, Chatt and Mingos attempted the preparation of derivatives containing thioether ligands ( $\text{SEt}_2$  or  $\text{EtSC}_2\text{H}_4\text{SEt}$ ) but obtained brown, insoluble polymeric products that analysed as  $[\text{Pt}_4\text{S}_3(\text{SEt}_2)_3]_n$  and  $[\text{Pt}_2\text{S}_2(\text{EtSC}_2\text{H}_4\text{SEt})]_n$  [7]. Arsine ligands attracted our attention, because of their overall similarity, but generally poorer ligand properties, when compared to the corresponding phosphines. During the course of this work, González-Duarte and co-workers reported a detailed study on the synthesis of the arsine complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)_2]$ , including an X-ray structure on the parent complex, and the synthesis and characterisation of a number of trinuclear sulfide-bridged aggregates containing  $\{\text{Pt}_2\text{MS}_2\}$  cores (M = Pt, Cu, Zn, Cd, Hg) [13]. In this work, it was found, from X-ray crystallographic and electrochemical studies that the more weakly electron-donating and lower *trans*-influence [14] arsine ligand moderates the basicity of the sulfides of the  $\{\text{Pt}_2\text{S}_2\}$  core.

Some other arsine-containing platinum-sulfide species are also known; trinuclear sulfido derivatives  $[\text{Pt}_3(\mu\text{-S})_2(\text{PMe}_2\text{Ph})_4(\text{AsMe}_2\text{Ph})_2]^{2+}$  were reported in early work by Chatt and Mingos, by reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PMe}_2\text{Ph})_4]$  with *cis*- $[\text{PtCl}_2(\text{AsMe}_2\text{Ph})_2]$  [7] and compounds containing dinuclear thiolate-bridged cores  $\{\text{Pt}_2(\mu\text{-SMe})_2\}$  with ancillary  $\text{AsMe}_3$  ligands have been prepared [15].

Our recent methodology, employing electrospray ionisation mass spectrometry (ESI MS) as a powerful tool for monitoring reaction chemistry of  $\{\text{Pt}_2\text{S}_2\}$  systems [2,16–18] is ideal for studying the chemistry of  $\text{Ph}_3\text{As}$  derivatives. Here NMR spectroscopy will be of little use compared to the related triphenylphosphine system, or the system containing  $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{AsPh}_2$  ligands, where the  $\text{CH}_2$  resonances are readily accessible, and permit reaction monitoring [13]. In this paper, we describe the synthesis of the triphenylarsine analogue  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ , together with a preliminary investigation into its properties in comparison with the phosphine analogue  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ , using ESI MS to further define the characteristics of the arsine-substituted  $\{\text{Pt}_2\text{S}_2\}$  core.

## 2. Results and discussion

### 2.1. Synthesis and initial characterisation of $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$

The reaction of *cis*- $[\text{PtCl}_2(\text{AsPh}_3)_2]$  with solid sodium sulfide hydrate, using analogous conditions used to prepare  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ , gave a bright orange suspension, from which the arsine analogue  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  (**2**) was isolated as an orange solid by filtration, followed by washing with benzene and water. The yield of product was typically rather low (ca. 20%), and the reaction filtrate was an orange-brown colour, indicating that significant material remained in solution. An ESI mass spectrum of the reaction filtrate showed a major unidentified platinum-containing species at *m/z* 1963, together with ions assigned as  $[\text{Ph}_3\text{AsO}+\text{Na}]^+$  (*m/z* 345),  $[\text{Ph}_3\text{AsO}+\text{K}]^+$  (*m/z* 361) and  $[2\text{Ph}_3\text{AsO}+\text{Na}]^+$  (*m/z* 667); no ions were observed in negative-ion mode.

The reaction appears to proceed more slowly than the analogous synthesis of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ ; an improved yield and higher purity product (as evidenced by microanalysis) was obtained when the reaction time was increased from 24 to 48 h. However, the product could not be obtained analytically pure; analysis of three independently prepared samples all showed low carbon and hydrogen percentages. SEM-EDAX analysis of samples prepared with 24 and 48 h reaction times showed similar heavy element compositions, but the shorter reaction time sample showed greater traces of sodium and chlorine.

Suspecting that the lability of triphenylarsine was the key cause of the low yield in the synthesis, addition of free  $\text{AsPh}_3$  ligand to the reaction mixture gave a nominally improved yield (62%) of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  after a 48 h reaction period, though the elemental microanalytical data for this material still showed an impure material with low carbon and hydrogen percentages. It is noteworthy that the recent synthesis of the analogous bidentate-arsine complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)_2]$  was not plagued by such problems, and a good yield of 80% was obtained for this complex, which could be recrystallised from benzene [13]. In contrast, complex **2** appeared to be essentially insoluble in benzene.

The  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  was analysed by detailed mass spectrometry studies described hereafter, and subsequently converted to alkylated and metal complex derivatives which have been characterised by NMR spectroscopy, elemental analysis and in one case by an X-ray crystal structure determination.

### 2.2. Protonation and alkylation reactions of $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$

$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  qualitatively shows a lower solubility in methanol compared to  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ . Thus, when a small quantity of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  is added to methanol, a clear pale yellow solution is obtained; such solutions have

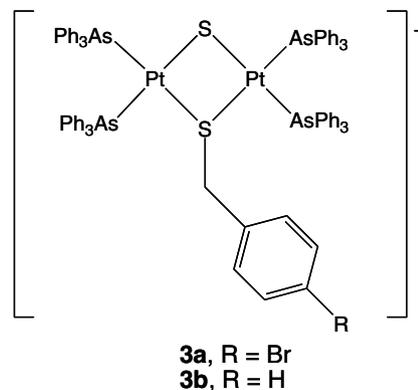
been found by ESI MS to yield the  $[M+H]^+$  ion [18], and this species is much more soluble than neutral  $[Pt_2(\mu-S)_2(PPh_3)_4]$  in methanol. However, for  $[Pt_2(\mu-S)_2(AsPh_3)_4]$  little dissolution appears to take place and the complex gives a weak  $[M+H]^+$  ion at  $m/z$  1679 in the positive-ion ESI mass spectrum. The mass spectrum of a dilute equimolar mixture of  $[Pt_2(\mu-S)_2(AsPh_3)_4]$  and  $[Pt_2(\mu-S)_2(PPh_3)_4]$  in methanol is thus dominated by the protonated ion of the phosphine complex, with some undissolved solid (presumably the arsine complex) remaining. The phosphine complex is expected to have a greater basicity than the arsine complex, as a result of the better electron-donating properties of the phosphines, which makes the sulfide ligands more electron-rich [13]. This will effect a higher degree of protonation, producing a more soluble  $[M+H]^+$  complex and concomitantly a more intense signal thereof in the ESI mass spectrum. These observations are in accord with results from alkylation studies discussed hereafter, as well as results from the  $Ph_2AsCH_2CH_2AsPh_2-\{Pt_2S_2\}$  system [13].

Alkylation reactions of  $[Pt_2(\mu-S)_2(AsPh_3)_4]$  have also been studied in order to provide comparative data with  $[Pt_2(\mu-S)_2(PPh_3)_4]$ , which is known to undergo both mono- and dialkylation reactions, depending on the nature of the alkylating agent. We have recently carried out an extensive mass spectrometry-based survey of alkylation reactions of  $[Pt_2(\mu-S)_2(PPh_3)_4]$  [19], which provide a benchmark for the present study. Several alkylation systems have been studied using ESI MS, in order to build up a picture of reactivity of the arsine complex.

The reaction with an excess of a simple alkylating agent, benzyl chloride, was initially studied. This reagent was chosen because benzyl halides give selective and rapid mono-alkylation with  $[Pt_2(\mu-S)_2(PPh_3)_4]$ , as reported previously [7,19,20]. By using an equimolar mixture of  $[Pt_2(\mu-S)_2(PPh_3)_4]$  and  $[Pt_2(\mu-S)_2(AsPh_3)_4]$ , information on the purity of the latter can be obtained, together with the relative rates of product formation. Although the starting  $[Pt_2(\mu-S)_2(AsPh_3)_4]$  gives only a weak ion in the ESI mass spectrum, the product species  $[Pt_2(\mu-S)(\mu-SCH_2Ph)(EPh_3)_4]^+$  ( $E = P, As$ ) are cationic and would be expected to have high ionisation efficiencies. The mono-benzylated derivatives  $[Pt_2(\mu-S)(\mu-SCH_2Ph)(PPh_3)_4]^+$  ( $m/z$  1593) and  $[Pt_2(\mu-S)(\mu-SCH_2Ph)(AsPh_3)_4]^+$  ( $m/z$  1770) are formed at approximately the same rate, and at the conclusion of the reaction, the  $[M+H]^+$  ion of  $[Pt_2(\mu-S)_2(PPh_3)_4]$  had disappeared, giving the two benzylated products in equal proportions. Similar results were observed in the analogous reaction with excess butyl chloride (refer Fig. 2a). These observations indicate that the  $[Pt_2(\mu-S)_2(AsPh_3)_4]$ , which does not give a satisfactory elemental microanalysis, is of sufficient purity to enable further comparative studies by MS.

Reaction of  $[Pt_2(\mu-S)_2(AsPh_3)_4]$  with excess 4-bromobenzyl bromide or benzyl bromide in methanol on the macroscopic scale gave  $[Pt_2(\mu-S)(\mu-SCH_2C_6H_4Br)(AsPh_3)_4]^+$  **3a** and  $[Pt_2(\mu-S)(\mu-SCH_2C_6H_5)(AsPh_3)_4]^+$  **3b**, isolated as their  $PF_6^-$  salts as yellow solids. The complexes show the

expected  $[M]^+$  ion in the positive-ion ESI mass spectrum at a cone voltage of 20 V, and successive loss of two  $AsPh_3$  ligands as the cone voltage is raised to 70 V. The  $^1H$  NMR spectrum of the arsine complex **3b** showed the  $CH_2$  protons as a single resonance at  $\delta$  3.99; three-bond coupling to  $^{195}Pt$  effected broadening of the peak baseline, but could not be resolved. By comparison, the analogous phosphine complex showed a  $CH_2$  resonance at  $\delta$  3.70. These chemical shifts are consistent with reduced electron density at the sulfur centres in the arsine system.



In an experiment to investigate possible exchange reactions between alkylated phosphine and arsine systems, an equimolar solution of  $[Pt_2(\mu-S)(\mu-SCH_2C_6H_4Br)(AsPh_3)_4]^+$  and  $[Pt_2(\mu-S)(\mu-SCH_2Ph)(PPh_3)_4]^+$  in dichloromethane was analysed by ESI MS. The expected parent ions were observed, but on allowing the solution to stand for several days, there was a gradual loss in intensity of the  $[Pt_2(\mu-S)(\mu-SCH_2C_6H_4Br)(AsPh_3)_4]^+$  ion (which disappeared after 1 week), and formation of a low intensity, unidentified ion at  $m/z$  2307. These observations again suggest different behaviour for the arsine system, where even a monoalkylated derivative appears to be unstable in dichloromethane. Attempts at growing crystals of the parent alkylated derivative or decomposition product(s) suitable for an X-ray crystallographic study were unsuccessful.

In order to access dialkylation and subsequent reactions, an equimolar mixture of  $[Pt_2(\mu-S)_2(AsPh_3)_4]$  and  $[Pt_2(\mu-S)_2(PPh_3)_4]$  was reacted with excess MeI. Spectra recorded after reaction times of 15 min and 2.5 h are shown in Fig. 1. Rapid monomethylation of both complexes occurs, giving the monocationic derivatives  $[Pt_2(\mu-S)(\mu-SMe)(EPh_3)_4]^+$  ( $E = P, m/z$  1518;  $E = As, m/z$  1694), Fig. 1a. Upon further reaction, the pathways for the two complexes diverge. With  $[Pt_2(\mu-S)_2(PPh_3)_4]$ , as we have described previously [19], monomethylation is followed by dimethylation, with the resulting  $[Pt_2(\mu-SMe)_2(PPh_3)_4]^{2+}$  cation being subject to nucleophilic attack by the generated iodide, giving  $[Pt_2(\mu-SMe)_2(PPh_3)_3I]^+$  ( $m/z$  1397) as the major phosphine species after 2.5 h, Fig. 1b. In contrast, however, the arsine complex remains predominantly as the monomethylated derivative, indicating a significantly lower tendency to undergo

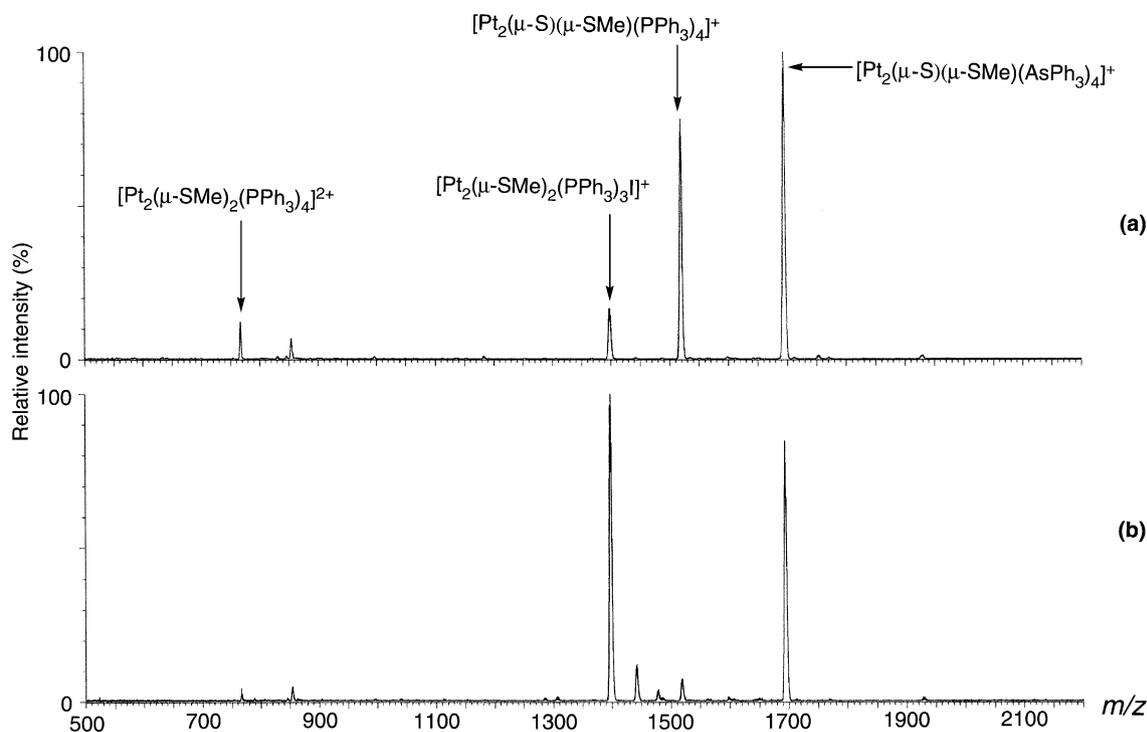


Fig. 1. Positive-ion ESI mass spectra comparing the reactivity of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  with MeI in methanol solution (cone voltage 20 V), (a) recorded after 15 min and (b) after ca. 2.5 h.

the second methylation step. After standing the reaction mixture for 24 h, the major peak in the spectrum was due to  $[\text{Pt}_2(\mu\text{-SMe})_2(\text{PPh}_3)_3\text{I}]^+$ , with small amounts of other unidentified species at  $m/z$  1442 and 1478; no arsine species were positively identified. This again appears to indicate that alkylated triphenylarsine  $\{\text{Pt}_2\text{S}_2\}$  derivatives are unstable compared to their phosphine counterparts.

To investigate the dialkylation step as an isolated process, it was necessary to avoid the presence of good nucleophiles, which attack the dications  $[\text{Pt}_2(\mu\text{-SR})_2(\text{EPh}_3)_4]^{2+}$ . Therefore, an equimolar mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  was reacted with excess *n*-butyl chloride, giving  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SBu})(\text{EPh}_3)_4]^+$  ( $\text{E} = \text{P}$ ,  $m/z$  1560;  $\text{E} = \text{As}$ ,  $m/z$  1737) as their chloride salts. The positive-ion ESI mass spectrum, Fig. 2(a) shows predominantly the two ions in equal intensities. Upon addition of dimethyl sulfate (a potent methylating agent which does not furnish a good nucleophilic anion), the ESI mass spectrum after 1 h, Fig. 2(b), showed two main species,  $[\text{Pt}_2(\mu\text{-SMe})(\mu\text{-SBu})(\text{PPh}_3)_4]^{2+}$  ( $m/z$  787.5), and  $[\text{Pt}_2(\mu\text{-SMe})(\mu\text{-SBu})(\text{AsPh}_3)_3\text{Cl}]^+$  ( $m/z$  1480). In the phosphine case, simple methylation of the second sulfur occurs, with formation of a stable dication, as we have reported previously [19]. However, the arsine ligand is more labile, and can be displaced by the chloride ion. Palladium(II) analogues also represent labile systems that show loss of even a coordinated phosphine ligand, for example reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with  $[\text{PdCl}_2(\text{PPh}_3)_2]$  gives  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{PdCl}(\text{PPh}_3)]^+$  [17].

Alternatively, the rate of dialkylation can be explored using the reaction with  $\text{ClCH}_2\text{CH}_2\text{Cl}$ . The reactivity of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  towards this reagent has been previously

explored [19,21], and gives the dialkylated product  $[\text{Pt}_2(\mu\text{-SCH}_2\text{CH}_2\text{S})(\text{PPh}_3)_4]^{2+}$ . The relative reactivities of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  were again explored by means of ESI MS of an equimolar mixture. Spectra recorded after 40 and 90 min are shown in Fig. 3, and demonstrate the differing reactivities of the two complexes. After 40 min, the arsine complex has formed predominantly monoalkylated  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CH}_2\text{Cl})(\text{AsPh}_3)_4]^+$  ( $m/z$  1742), while the phosphine complex formed the expected  $[\text{Pt}_2(\mu\text{-SCH}_2\text{CH}_2\text{S})(\text{PPh}_3)_4]^{2+}$  ( $m/z$  765). Only a trace of the arsine analogue  $[\text{Pt}_2(\mu\text{-SCH}_2\text{CH}_2\text{S})(\text{AsPh}_3)_4]^{2+}$  ( $m/z$  853.5) is seen, confirming the lesser reactivity of the arsine complex. Furthermore, an ion at  $m/z$  1436 is assigned as the arsine-displaced species  $[\text{Pt}_2(\mu\text{-SCH}_2\text{CH}_2\text{S})(\text{AsPh}_3)_3\text{Cl}]^+$ , formed by dissociation of a more weakly bound arsine ligand and replacement by chloride. On standing the reaction mixture further (spectrum b), the total intensity of ions from the arsine system has decreased, especially for  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CH}_2\text{Cl})(\text{AsPh}_3)_4]^+$ , presumably again due to dialkylation and the subsequent instability of arsine-containing products in the presence of chlorinated solvents.

The results of the investigations into the alkylation chemistry of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  with three different alkylating systems (MeI, BuCl +  $\text{Me}_2\text{SO}_4$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ) are in overall agreement. The second alkylation step is considerably slower for the arsine system, and the resulting dication is prone to displacement of an arsine ligand by even a weak nucleophilic anion (generated from the alkylating agent), such as chloride.

Overall, the initial data from ESI MS monitored alkylation of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  confirm the conclusions of

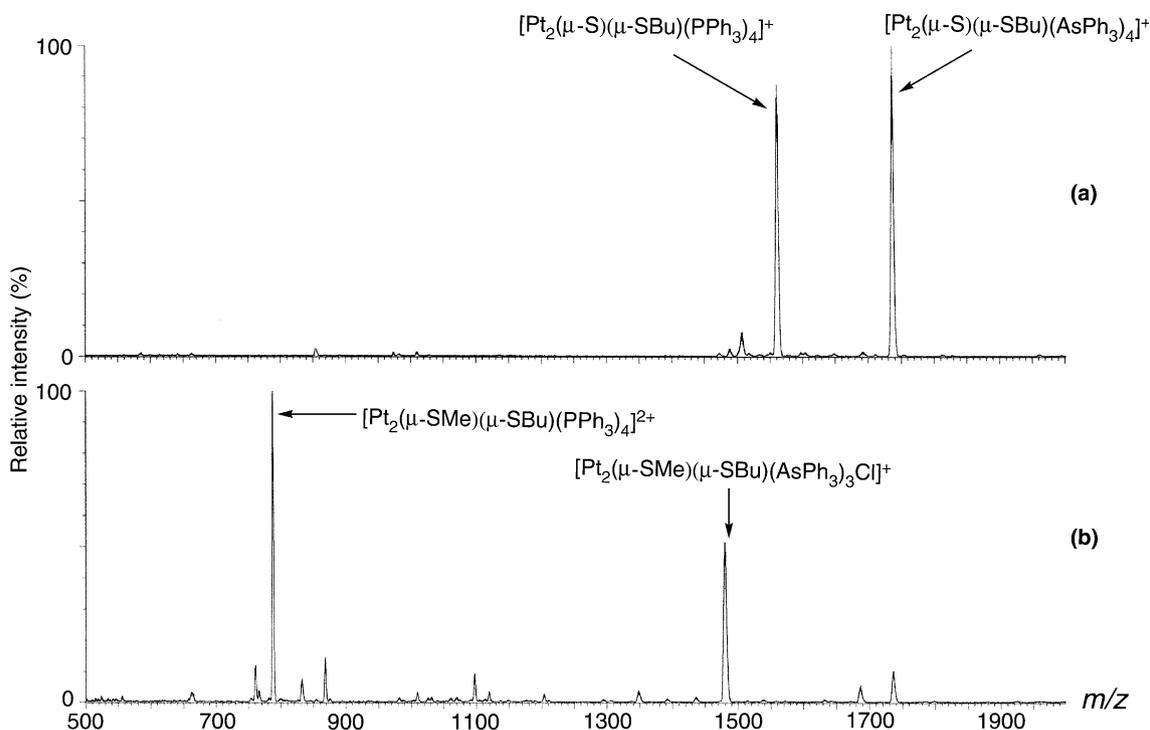


Fig. 2. Successive alkylation of an equimolar mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  in methanol; positive-ion ESI mass spectra recorded at a cone voltage of 20 V; (a) with excess *n*-butyl chloride after 1 week, showing formation of the monobutyl derivatives  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SBu})(\text{PPh}_3)_4]^+$  and (b) 1 h after subsequent addition of excess dimethyl sulfate. The spectra clearly show the different reaction pathways for the phosphine and arsine systems.

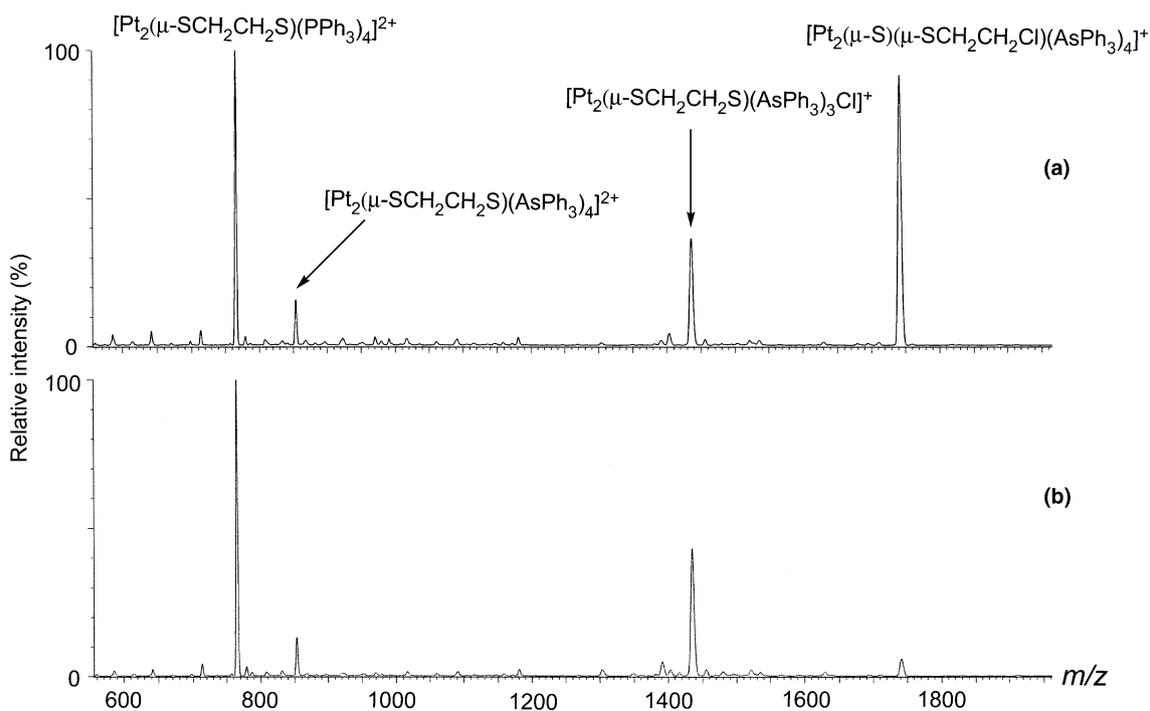


Fig. 3. Parallel reaction of equimolar quantities of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  with excess  $\text{ClCH}_2\text{CH}_2\text{Cl}$  in methanol: (a) after ca. 40 min and (b) after ca. 90 min, showing the divergent reactions of the two complexes.

González-Duarte and co-workers that the  $\{\text{As}_4\text{Pt}_2\text{S}_2\}$  system contains less reactive sulfide groups compared to phosphine analogues [13].

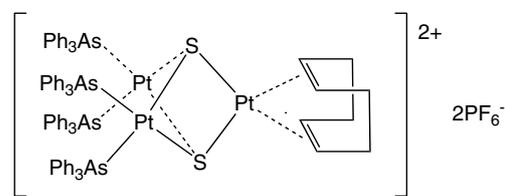
### 2.3. Formation of trinuclear metal complexes from $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$

We wished to extend the comparison of triphenylphosphine and triphenylarsine  $\{\text{Pt}_2\text{S}_2\}$  systems to the formation of metal derivatives. In their study, González-Duarte et al. prepared a number of trinuclear adducts containing  $\{\text{Pt}_2\text{MS}_2\}$  cores, and by means of X-ray structure determinations showed that the M–S bond distances were longer than in the corresponding phosphine analogues, indicating that the  $\{\text{As}_4\text{Pt}_2\text{S}_2\}$  system has reduced coordinating ability [13].  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  is known to form adducts with a diverse range of metal substrates, including examples from main group, transition and actinide metals [1–3,16–18].

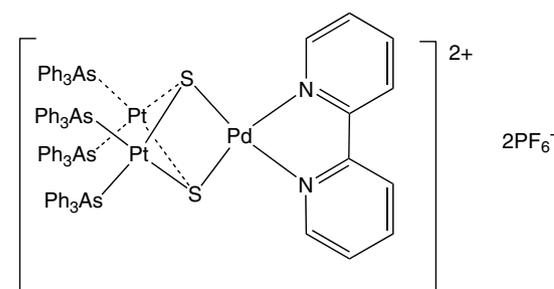
Reactions of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  with a range of metal-halide complexes were carried out, using ESI MS to screen products of reaction, following the methodology that we have previously developed [16–18]. A summary of the major observed ions is given in Table 1. In these examples, the cationic metal fragment formed by halide loss is coordinated to the  $\{\text{Pt}_2\text{S}_2\}$  moiety, giving mono- or di-cationic product species. In all cases, excellent agreement was observed between experimental and calculated isotope distribution patterns, with the dications showing the expected 0.5  $m/z$  separation of adjacent peaks. The species observed correlate very closely with those previously reported for the corresponding  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  systems [16–18]. As an illustrative example, reaction with  $[\text{RhCl}_2\text{Cp}^*]_2$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) gave exclusively the adduct  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{RhCp}^*]^{2+}$  as illustrated in Fig. 4.

The syntheses of two metal complex derivatives,  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pt}(\text{cod})](\text{PF}_6)_2$  **4** and  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pd}(\text{bipy})](\text{PF}_6)_2$  **5**, were carried out on the macroscopic scale by reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  with  $[\text{PtCl}_2(\text{cod})]$  and  $[\text{PdCl}_2(\text{bipy})]$ , respectively. The reactions proceed by dissolution of the starting materials, giving slightly cloudy solutions. Some dark orange insoluble matter is probably

impurity material present in the  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ . The complexes were isolated as their hexafluorophosphate salts by addition of excess  $\text{NH}_4\text{PF}_6$  to the filtered reaction solutions.



4



5

A positive-ion ESI mass spectral study on the palladium complex was carried out, and show ions highly dependent on the cone voltage. At a low cone voltage (5 V), the parent dication  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pd}(\text{bipy})]^{2+}$  ( $m/z$  970) dominates the spectrum, while at 80 V, the ion pair  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pd}(\text{bipy})+\text{PF}_6]^+$  ( $m/z$  2086) was the base peak. It is noteworthy that ion pair formation allows the complex cation to remain intact at elevated cone voltages; other derivatives such as the alkylated complexes  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SR})(\text{AsPh}_3)_4]^+$  ( $\text{R} = \text{tBu}, \text{CH}_2\text{Ph}$ ) undergo loss of  $\text{AsPh}_3$  at these higher cone voltages. The platinum-cod complex also shows a dominant  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pt}(\text{cod})]^{2+}$  ion at  $m/z$  991, together with a minor ion-pair  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pt}(\text{cod})+\text{PF}_6]^+$  ion at  $m/z$  2127.

In order to examine the effect of the arsine donor ligands on the steric and electronic properties of the  $\{\text{Pt}_2\text{S}_2\}$  core, and to fully characterise one derivative of the  $\{\text{Pt}_2\text{S}_2\text{As}_4\}$  core, an X-ray structure determination was carried out on the platinum(II)-cyclo-octadiene (cod) derivative **4**. The cation (illustrated in Fig. 5) has a very similar conformation to that of the  $\text{Ph}_3\text{P}$  analogue, although only **4** has crystallographically imposed  $C_2$  symmetry. In each case the  $\text{Pt}(\text{cod})$  group is coordinated to the  $\{\text{Pt}_2\text{S}_2\}$  metalloligand via the S atoms with the cod group in the usual twisted boat form.

Several other  $\text{Pt}(\text{cod})$  derivatives of  $[\text{Pt}_2(\mu\text{-E})_2(\text{PPh}_3)_4]$  compounds have been structurally characterised previously, namely the phosphine analogue of **4**,  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{Pt}(\text{cod})]^{2+}$  [17], as well as the selenide derivatives  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4\text{Pt}(\text{cod})]^{2+}$  and  $[\text{Pt}(\mu\text{-Se})_2(\text{PPh}_3)_2\{\text{Pt}(\text{cod})\}_2]^{2+}$  [22]. Deprotonation of a coordinated cod ligand

Table 1

Major ions observed in the positive-ion ESI MS spectra (cone voltage 20 V) for reactions of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  with a selection of metal-halide complexes<sup>a</sup>

Substrate	Observed ions ( $m/z$ )
$[\text{RhCl}(\text{cod})]_2$	$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Rh}(\text{cod})]^{2+}$ (1890)
$[\text{IrCl}(\text{cod})]_2$	$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Ir}(\text{cod})]^{2+}$ (1979)
$[\text{PtCl}_2(\text{cod})]$	$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pt}(\text{cod})]^{2+}$ (991)
$[\text{PdCl}_2(\text{bipy})]$	$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pd}(\text{bipy})]^{2+}$ (974)
$[\text{RhCl}_2\text{Cp}^*]_2$	$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{RhCp}^*]^{2+}$ (958)
$[\text{IrCl}_2\text{Cp}^*]_2$	$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{IrCp}^*]^{2+}$ (1003)
$[\text{RuCl}_2(\eta^6\text{-p-cymene})]_2$	$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Ru}(\eta^6\text{-p-cymene})]^{2+}$ (957)
$\text{PhHgCl}$	$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{HgPh}]^+$ (1957)

<sup>a</sup> Abbreviations used: cod = 1,5-cyclo-octadiene; bipy = 2,2'-bipyridine;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ .

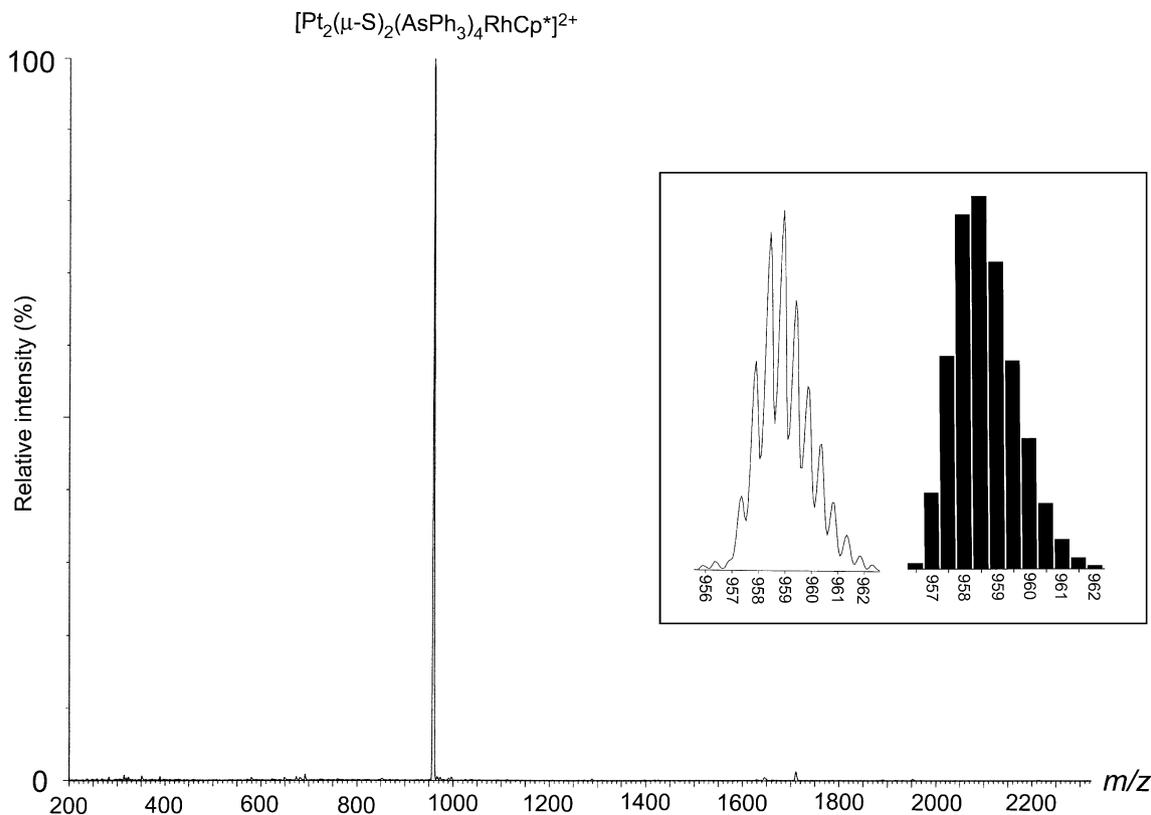


Fig. 4. Positive-ion ESI mass spectrum of the micro scale reaction mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  and  $[\text{RhCl}_2\text{Cp}^*]_2$  in methanol at a cone voltage of 20 V, showing exclusive formation of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{RhCp}^*]^{2+}$ . The inset shows a comparison of the observed (left) and calculated (right) isotope distribution patterns for the parent dication.

in the derivative  $[\text{Pt}_2(\mu\text{-S})_2(\text{dppp})_2\text{Pt}(\text{cod})]^{2+}$  [dppp =  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ ] has also been described [23]. Detailed bond parameters for **4** are compared with those of the  $\text{Ph}_3\text{P}$  analogue in Table 2, and show some significant differences. All of the Pt–S bond lengths of **4** are significantly longer, suggesting a less tightly bound  $\text{Pt}_2\text{S}_2$  core. While this might have been expected for the bonds to the  $\text{Pt}(\text{cod})$  moiety as a consequence of the reduced basicity of the S-donor atoms, it is surprising for the Pt–S bonds *trans* to the  $\text{Ph}_3\text{As}$  groups since these should have a lesser *trans* influence than  $\text{PPh}_3$  groups. In this case, it may arise from the wider fold angle between the two  $\text{As}_2\text{PtS}_2$  groups ( $138.8^\circ$ ) compared with that between the two  $\text{P}_2\text{PtS}_2$  planes ( $133.9^\circ$ ), which in turn is presumably allowed by lesser interactions between the  $\text{Ph}_3\text{As}$  groups and the  $\text{Pt}(\text{cod})$  unit as a consequence of longer Pt–As and As–C bonds. The Pt–S bonds of **4** are significantly longer than those of a series of  $\{\text{Pt}_2\text{S}_2\text{M}\}$  derivatives containing  $\text{Ph}_2\text{AsCH}_2\text{-CH}_2\text{AsPh}_2$  ligands recently described by González-Duarte et al. [13].

Interestingly, few structures of platinum complexes containing tertiary arsine ligands *trans* to sulfur donor ligands have been carried out, however, As–Pt bond distances of 2.361(1) Å and 2.3293(6) Å are observed in the complexes  $[\text{Pt}\{\text{S}_2\text{P}(\text{OEt})_2\}_2\{\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{CH}_2\text{AsPh}_2\}]$  and  $[\text{Pt}\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}(\text{CH}_3)(\text{AsPh}_3)]$ , respectively, where the arsine ligands are *trans* to a chelated dithiophosphate ligand [24].

#### 2.4. Generation of mixed phosphine–arsine complexes $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_n(\text{PPh}_3)_{4-n}]$

Having demonstrated the utility of ESI MS in probing the chemistry of the arsine complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ , the methodology has been extended to an investigation into the synthesis of mixed phosphine–arsine derivatives of the  $\{\text{Pt}_2\text{S}_2\}$  core. Reaction of equimolar quantities of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  and *cis*- $[\text{PtCl}_2(\text{AsPh}_3)_2]$  with excess  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  for 24 h in the usual manner gave an orange solid in low yield. Because of the significantly different ionisation efficiencies of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ , small samples of product were derivatised using an alkylating agent, either *n*-butyl chloride or 4-bromobenzyl bromide, in order to form soluble, cationic derivatives and thus obtain an accurate product distribution. 4-Bromobenzyl bromide was the reagent of choice, because it is a good (but not too powerful) alkylating agent that rapidly and selectively forms a monoalkylated product, is a conveniently handled solid, and avoids ion overlaps which would occur with  $\text{PhCH}_2\text{Br}$  itself. The resulting cationic benzylated species are soluble in methanol, and the peak intensity should closely reflect the abundance of the  $\{\text{Pt}_2\text{S}_2\}$  species in the isolated product. Comparable results were obtained for both alkylation methods, though the reaction with *n*-butyl chloride was expectedly much slower, and showed some underderivatised  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  as its protonated ion at  $m/z$  1503.

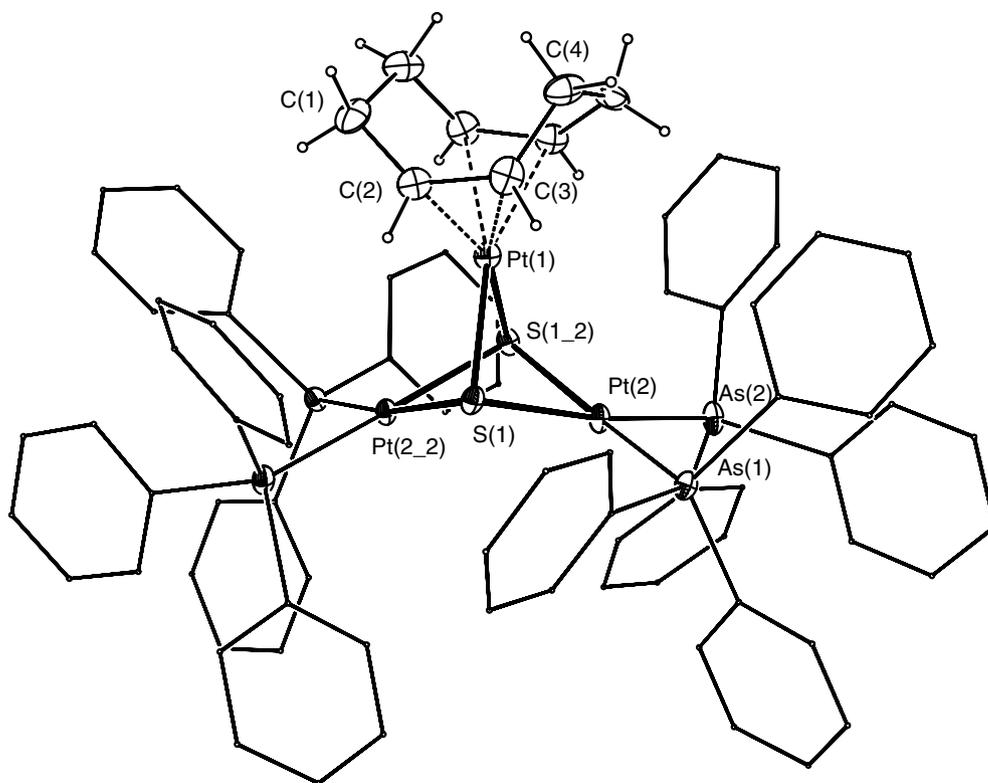


Fig. 5. X-ray structure of the cation  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4\text{Pt}(\text{cod})]^{2+}$ , with selected atom labels. The  $\text{PF}_6^-$  counter ions and dichloromethane of crystallisation are not shown.

Table 2  
Selected bond parameters for  $[\text{Pt}_2(\mu\text{-S})_2(\text{EPh}_3)_4\text{Pt}(\text{cod})]^{2+}$  (E = As, P)

	E = As (4)	E = P <sup>a,b</sup>
<i>Bond lengths</i> (Å)		
Pt(1)–S(1)	2.418(3)	2.336(2)
Pt(2)–S(1)	2.424(3)	2.368(2)
Pt(2)–S(1)′	2.427(3)	2.367(2)
Pt(2)–E(1)	2.467(2)	2.299(2)
Pt(2)–E(2)	2.486(2)	2.283(2)
Pt(2)··Pt(2)′	3.406(2)	3.323(2)
Pt(1)··Pt(2)	3.101(2)	3.053(2)
<i>Bond angles</i> (°)		
S(1)–Pt(1)–S(1)′	80.3(2)	79.9(1)
S(1)–Pt(2)–S(1)′	80.0(2)	78.7(1)
E(1)–Pt(2)–E(2)	96.7(1)	98.6(1)
<i>Dihedral angles</i> (°)		
E <sub>2</sub> Pt(2)S <sub>2</sub> /E′ <sub>2</sub> Pt(2)′S <sub>2</sub>	138.8	133.9
E <sub>2</sub> Pt(2)S <sub>2</sub> /Pt(1)S <sub>2</sub>	110.5	113.1

<sup>a</sup> From Ref. [17], renumbered to correspond to that of 4.

<sup>b</sup> Averaged over chemically equivalent bonds where appropriate.

The spectrum for the 4-bromobenzyl bromide system is illustrated in Fig. 6; no dialkylated species were observed in the reaction timescale used (20 min). The main species are  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{Br})(\text{PPh}_3)_4]^{2+}$  ( $m/z$  1674),  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{Br})(\text{AsPh}_3)_4]^{2+}$  ( $m/z$  1849), and the expected mixed phosphine–arsine derivative  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{Br})(\text{PPh}_3)_2(\text{AsPh}_3)_2]^{2+}$  ( $m/z$  1761). In addition to these species, low intensity ions at  $m/z$  1717 and 1805 are attributed to the tris-phosphine  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{Br})(\text{PPh}_3)_3\text{-}$

$(\text{AsPh}_3)]^{2+}$  and the tris-arsine  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{Br})(\text{PPh}_3)(\text{AsPh}_3)_3]^{2+}$ , respectively, indicating that the isolated product is actually a mixture of all possible  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_n(\text{PPh}_3)_{4-n}]$  species. No attempt was made to increase the amounts of mixed species formed in this reaction. Exchange of phosphine and arsine ligands was not observed when an equimolar mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  was refluxed in methanol for 6 h, and the reaction mixture analysed after 4-bromobenzyl bromide derivatisation.

Mixed phosphine–arsine species are also accessible from ligand substitution reactions that utilise the lability of  $\text{AsPh}_3$ . A mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  and excess  $\text{PPh}_3$  in methanol was stirred at room temperature, and aliquots of the reaction mixture derivatised with 4-bromobenzyl bromide for analysis by ESI MS, as above. Slow ligand substitution was found to occur, giving a mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_n(\text{PPh}_3)_{4-n}]$  species as their bromobenzyl derivatives, as illustrated in Fig. 7. It is worth commenting that the intensity of the  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  species was greater than those of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_n(\text{PPh}_3)_{4-n}]$  ( $n = 1\text{--}3$ ), possibly because substitution of one arsine ligand produces a derivative that is more basic and more soluble, which then undergoes further substitution steps more readily. Solubility of the final product is not a factor in the ESI MS analysis, because the derivatisation step employed produces a soluble, charged species. Such ligand substitution might provide an alternative pathway to new phosphine-containing  $\{\text{Pt}_2\text{S}_2\}$  systems.

### 3. Conclusions

The triphenylarsine  $\{\text{Pt}_2\text{S}_2\}$  system has been synthesised for the first time, and the reactivity of this complex towards alkylating agents indicates that the reactivity of the sulfide ligands has been moderated by the more poorly electron-donating arsines, which are also more labile than the phosphine ligands. The results support the conclusions previously made by González-Duarte and co-workers on the corresponding system with  $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$  ligands [13]. The decreased lability of the bidentate arsine ligands suggests that this is a more workable system than the labile  $\text{AsPh}_3$  system. The use of other neutral ancillary ligands on the  $\{\text{Pt}_2\text{S}_2\}$  core could furnish further interesting developments in the chemistry of this enigmatic system.

### 4. Experimental

#### 4.1. General methods and materials

General instrumental details were as described in recent papers from these laboratories [16–18]. Benzene was AR grade, and used as supplied. Products were recrystallised from dichloromethane and diethyl ether that were dried and distilled (from  $\text{CaH}_2$  and sodium-benzophenone ketyl, respectively) under a nitrogen atmosphere prior to use. Petroleum spirits refers to the fraction of boiling range 40–60 °C.

Electrospray mass spectra were recorded using positive-ion mode on a VG Platform II instrument, using methanol as the mobile phase and solvent. Assignment of ions was aided by use of the ISOTOPE simulation program [25].

Sodium sulfide nonahydrate (Ajax Chemicals, Sydney, Australia), ammonium hexafluorophosphate (Aldrich), benzyl chloride (BDH), butyl chloride (Riedel de Hæn), iodomethane (Aldrich), 4-bromobenzyl bromide (Aldrich), benzyl bromide (BDH), triphenylarsine (Fluka) and phenyl mercury chloride (Aldrich) were used as supplied.

The complexes  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  [20], *cis*- $[\text{PtCl}_2(\text{AsPh}_3)_2]$  [26], *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  [27],  $[\text{RhCl}(\text{cod})_2]$  [28],  $[\text{IrCl}(\text{cod})_2]$  [29],  $[\text{PtCl}_2(\text{cod})]$  [30],  $[\text{PdCl}_2(\text{bipy})]$  [31],  $[\text{RhCl}_2\text{Cp}^*]_2$  [32],  $[\text{IrCl}_2\text{Cp}^*]_2$  [32], and  $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})_2]$  [33] were synthesised by the literature procedures. The complex  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{Ph})(\text{PPh}_3)_4]\text{PF}_6$  was prepared from  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  and  $\text{PhCH}_2\text{Br}$  in methanol [20], and precipitated by addition of excess  $\text{NH}_4\text{PF}_6$ .

#### 4.2. Synthesis of $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ (2)

A suspension of the complex *cis*- $[\text{PtCl}_2(\text{AsPh}_3)_2]$  (1.00 g, 1.139 mmol) and powdered  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (1.60 g, 6.66 mmol) in benzene (40 mL) was stirred vigorously for 48 h, giving an orange suspension. The solid was filtered off, washed with benzene ( $2 \times 10$  mL) and copious quantities of distilled water, and dried under vacuum to give **2** as an orange solid (220 mg, 21%). The complex could not be obtained analytically pure: Found: C, 45.9; H, 3.45%;  $\text{C}_{72}\text{H}_{60}\text{As}_4\text{Pt}_2\text{S}_2$  requires: C, 51.5; H, 3.6%.

#### 4.3. Synthesis of $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ incorporating free $\text{AsPh}_3$

The method above was repeated, except that triphenylarsine (0.50 g, 1.63 mmol) was added to the reaction

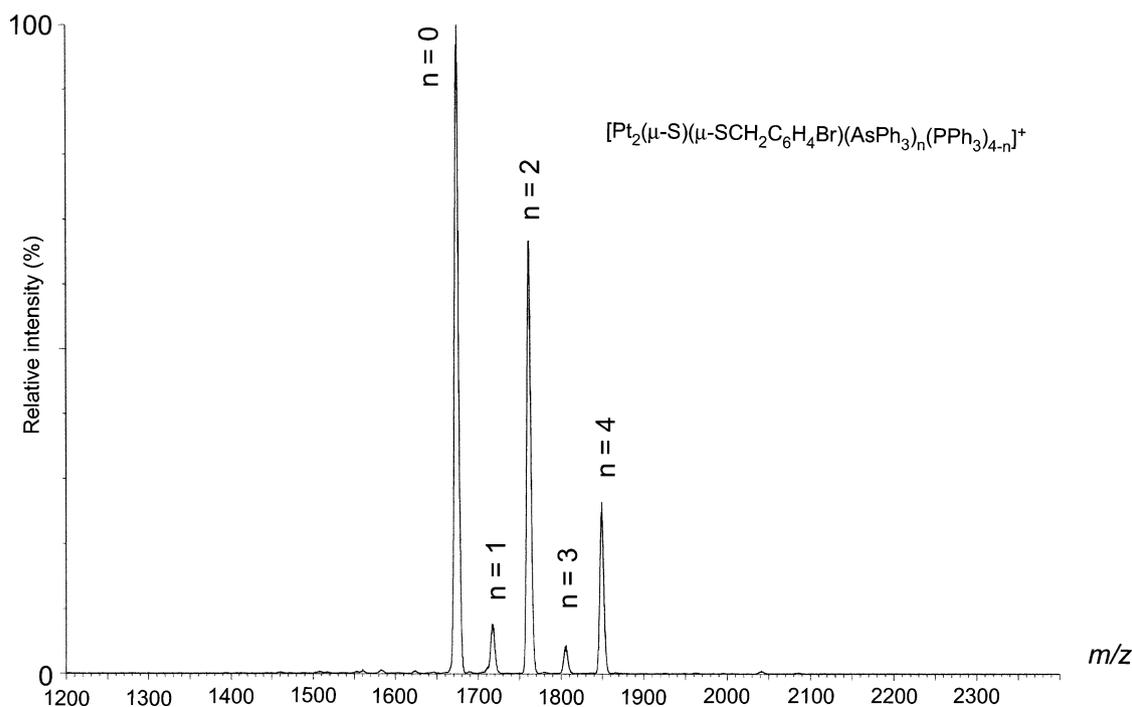


Fig. 6. Positive-ion ESI mass spectrum of the reaction mixture *cis*- $[\text{PtCl}_2(\text{AsPh}_3)_2]$  + *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  +  $\text{Na}_2\text{S}$ , after isolation and derivatisation with 4-bromobenzyl bromide, showing a series of mixed phosphine–arsine derivatives  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{Br})(\text{PPh}_3)_n(\text{AsPh}_3)_{4-n}]^+$ .

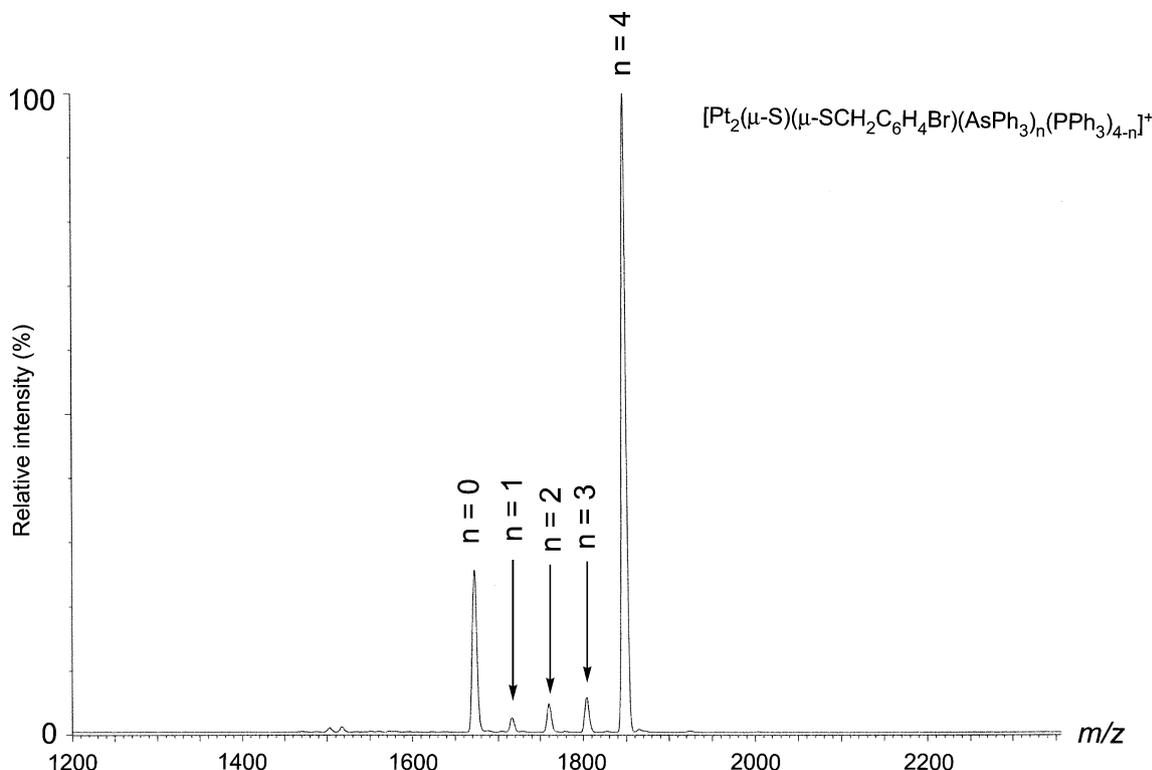


Fig. 7. The formation of ligand-exchanged species  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_n(\text{PPh}_3)_{4-n}]^+$  from the reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  and excess  $\text{PPh}_3$  in methanol (after derivatisation with 4-bromobenzyl bromide) is shown by the ESI mass spectrum of the reaction mixture at a cone voltage of 20 V.

mixture.  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  was isolated as a deep orange solid (588 mg, 62%). Found: C, 42.2; H, 3.6%.

#### 4.4. Protonation study of $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ and $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$

An equimolar mixture of the complexes  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  (10 mg) and  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  (9 mg) in methanol (30 mL) was stirred for 10 min, giving a light yellow solution and some undissolved solid. An aliquot of this mixture was taken, centrifuged, and analysed by positive-ion ESI MS, revealing a major peak due to  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4+\text{H}]^+$  ( $m/z$  1503).

#### 4.5. Alkylation study of $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ and of $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]/[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ mixtures

$[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  (10 mg) or an equimolar mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  in methanol (30 mL) was treated with an excess of the appropriate alkylating agent (*n*-butyl chloride or 4-bromobenzyl bromide) with stirring. Aliquots of the reaction mixture were taken and analysed by ESI MS.

#### 4.6. Synthesis of $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{Br})(\text{AsPh}_3)_4]\text{PF}_6$ (**3a**)

4-Bromobenzyl bromide (150 mg, 0.600 mmol) was added to a stirred suspension of  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  (150 mg, 0.089 mmol) in methanol (30 mL), resulting in

rapid dissolution of the starting materials and formation of a cloudy orange solution containing some dark, insoluble matter. After 15 min the solution was filtered, and the filter washed with an additional 10 mL of methanol, giving a clear lemon-yellow solution. Solid  $\text{NH}_4\text{PF}_6$  (300 mg, excess) was added with stirring. After 10 min, water was added dropwise until the solution turned cloudy, and the mixture was stirred for 20 min. The yellow solid product was filtered, washed successively with water (10 mL) and petroleum spirits (10 mL) and dried under vacuum to give **3a** as a yellow solid (95 mg, 53%). Found: C, 47.2; H, 3.4%.  $\text{C}_{79}\text{H}_{66}\text{As}_4\text{BrF}_6\text{-PPt}_2\text{S}_2$  requires: C, 47.6; H, 3.3%. M.p. 174–178 °C. ESI MS ( $\text{CH}_2\text{Cl}_2\text{-MeOH}$ ), 20 V,  $m/z$  1849,  $[\text{M}]^+$  (100%).

#### 4.7. Synthesis of $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C}_6\text{H}_5)(\text{AsPh}_3)_4]\text{PF}_6$ (**3b**)

Following an analogous method for complex **3a**, from  $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$  (100 mg, 0.060 mmol) gave complex **3b** as a yellow solid (89 mg, 78%). Found: C, 48.9; H, 3.5%.  $\text{C}_{79}\text{H}_{67}\text{As}_4\text{F}_6\text{PPt}_2\text{S}_2$  requires: C, 49.5; H, 3.5%. M.p. decomp. >250 °C. ESI MS ( $\text{CH}_2\text{Cl}_2\text{-MeOH}$ ), 20 V,  $m/z$  1770,  $[\text{M}]^+$  (100%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  7.37–6.85 (m, Ph), 3.99 [s,  $\text{CH}_2$ ,  $^3J(\text{PtH})$  not resolved].

#### 4.8. Complex formation with $[\text{Pt}_2(\mu\text{-S})_2(\text{AsPh}_3)_4]$ , monitored by ESI MS

The complex (ca. 0.1 mg) and the metal halide substrate (ca. 0.1 mg) were suspended in methanol (2 mL) and shaken to effect reaction and formation of a clear solution.

After centrifugation, the ESI MS spectrum was recorded using a cone voltage of 20 V.

#### 4.9. Synthesis of $[Pt_2(\mu-S)_2(AsPh_3)_4Pt(cod)](PF_6)_2$ (**4**)

$[Pt_2(\mu-S)_2(AsPh_3)_2]$  (237 mg, 0.141 mmol) and  $[PtCl_2(cod)]$  (53 mg, 0.142 mmol) were suspended in methanol (30 mL) and stirred for 30 min, giving a cloudy yellow solution, which was filtered. To the filtrate was added, with stirring,  $NH_4PF_6$  (300 mg, excess), producing a yellow precipitate. After 20 min, water (20 mL) was added to assist precipitation of the product, which was filtered, washed successively with water (20 mL) and petroleum spirits (20 mL), and dried under vacuum to give **4** as a yellow solid (110 mg, 34%). Found: C, 41.7; H, 3.2%.  $C_{80}H_{72}As_4F_{12}P_2Pt_3S_2$  requires: C, 42.25; H, 3.2%. M.p. 260–262 °C. The complex was recrystallised by vapour diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature. ESI MS ( $CH_2Cl_2$ –MeOH), 20 V,  $m/z$  991,  $[M]^{2+}$  (100%),  $m/z$  2127,  $[M+PF_6]^+$  (5%).  $^1H$  NMR,  $\delta$  7.35–7.19 (m, Ph), 4.70 [s, Pt–CH,  $J(PtH)$  ca. 52] and 2.64 (s, br,  $CH_2$ ).

#### 4.10. Synthesis of $[Pt_2(\mu-S)_2(AsPh_3)_4Pd(bipy)](PF_6)_2$ (**5**)

$[Pt_2(\mu-S)_2(AsPh_3)_4]$  (200 mg, 0.119 mmol) and  $[PdCl_2(bipy)]$  (60 mg, 0.180 mmol) were suspended in methanol (30 mL) and stirred for 40 min, giving a cloudy orange solution, which was filtered. To the stirred filtrate was added  $NH_4PF_6$  (300 mg, excess), producing an orange-brown precipitate. After 20 min, water (15 mL) was added to assist precipitation of the product, which was filtered, washed successively with water (10 mL) and petroleum spirits (10 mL), and dried under vacuum to give **5** as an orange-brown solid (120 mg, 45%). Found: C, 43.3; H, 3.3; N, 1.35%;  $C_{82}H_{68}N_2As_4F_{12}P_2PdPt_2S_2$  requires: C, 44.1; H, 3.1; N, 1.3%. M.p. >250 °C. ESI MS ( $CH_2Cl_2$ –MeOH), 20 V,  $m/z$  970.5,  $[M]^{2+}$  (100%),  $m/z$  2086,  $[M+PF_6]^+$  (8%).

#### 4.11. Synthesis of mixed $[Pt_2(\mu-S)_2(PPh_3)_n(AsPh_3)_{4-n}]$ from $cis-[PtCl_2(EPh_3)_2]$

A suspension of  $cis-[PtCl_2(PPh_3)_2]$  (250 mg, 0.316 mmol),  $cis-[PtCl_2(AsPh_3)_2]$  (280 mg, 0.319 mmol) and powdered  $Na_2S \cdot 9H_2O$  (0.8 g, 3.33 mmol) in benzene (25 mL) was stirred vigorously for 24 h, giving an orange suspension. Isolation of the product as for  $[Pt_2(\mu-S)_2(AsPh_3)_4]$  gave an orange solid (90 mg) that was analysed by ESI MS after derivatisation of an aliquot in methanol with excess 4-bromobenzyl bromide or *n*-butyl chloride.

#### 4.12. Synthesis of mixed $[Pt_2(\mu-S)_2(PPh_3)_n(AsPh_3)_{4-n}]$ from $[Pt_2(\mu-S)_2(AsPh_3)_4]$ and $PPh_3$

$[Pt_2(\mu-S)_2(AsPh_3)_4]$  (63 mg, 0.038 mmol) was suspended in methanol (30 mL) and triphenylphosphine (83 mg,

0.317 mmol) added. The mixture was stirred and after several days the ESI mass spectrum of an aliquot, derivatised with excess 4-bromobenzyl bromide, showed all possible  $[Pt_2(\mu-S)_2(PPh_3)_n(AsPh_3)_{4-n}CH_2C_6H_4Br]^+$  ions.

#### 4.13. Investigation of exchange between $[Pt_2(\mu-S)_2(PPh_3)_4]$ and $[Pt_2(\mu-S)_2(AsPh_3)_4]$

$[Pt_2(\mu-S)_2(AsPh_3)_4]$  (22 mg, 0.013 mmol) and  $[Pt_2(\mu-S)_2(PPh_3)_4]$  (19 mg, 0.013 mmol) were dissolved in methanol (40 mL) and the mixture refluxed for 6 h. An aliquot of the reaction mixture was treated with excess 4-bromobenzyl bromide, and analysed by positive-ion ESI MS.

#### 4.14. X-ray structure determination of $[Pt_2(\mu-S)_2(AsPh_3)_4Pt(cod)](PF_6)_2 \cdot CH_2Cl_2$ (**4** · $CH_2Cl_2$ )

A yellow crystal of moderate quality was obtained from  $CH_2Cl_2$ /ether. Data were collected on a Siemens SMART CCD diffractometer using standard procedures and software [34]. Icing problems near the end of collection meant only 85% of the theoretical data were collected, but the set gave a reasonable refinement. Empirical absorption corrections were applied (SADABS [35]). The structure was solved by direct methods and developed and refined on  $F^2$  using the SHELX programmes [36].

*Crystal data:*  $C_{81}H_{74}P_2F_{12}As_4S_2Cl_2Pt_3$ ,  $M_r$  2357.31, monoclinic, space group  $C2/c$ ,  $Z = 4$ ,  $a = 16.118(16)$  Å,  $b = 22.87(2)$  Å,  $c = 23.15(2)$  Å,  $\beta = 91.682(17)^\circ$ ,  $V = 8531(14)$  Å<sup>3</sup>,  $D_{calc} = 1.835$  g cm<sup>-3</sup>,  $\mu(Mo-K\alpha) = 6.66$  mm<sup>-1</sup>, size  $0.90 \times 0.38 \times 0.36$  mm<sup>3</sup>,  $T_{max,min} = 1.000, 0.392$ ,  $F(000) = 4520$ ,  $T = 93$  K. Total data 12832, unique data 6803 ( $R_{int} = 0.0446$ ),  $3^\circ < 2\theta < 51^\circ$ ,  $R_1$  ( $I > 2\sigma(I)$ ) = 0.0550,  $wR_2$  (all data) = 0.1557, goodness-of-fit = 1.119, residual  $\Delta e$  +3.8/–3.6 e Å<sup>-3</sup>.

The atoms of the cations, anions and  $CH_2Cl_2$  were refined anisotropically with H atoms included in calculated positions. The cation and one of the anions lie on twofold axes, the other anion on an inversion centre, and the solvent molecule is disordered about an inversion centre and was poorly behaved during refinement.

## 5. Supplementary information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 272628 (**4**). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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