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# Synthesis and characterisation of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ - a cationic iodo analogue of the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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## Abstract

Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with a number of transition metal iodo complexes leads to the formation of the cationic iodo analogue $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$, identified using electrospray ionisation mass spectrometry (ESI MS). Synthetic routes to this complex were developed, using the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with either $[PtI_2(PPh_3)_2]$ or elemental iodine. The complex was characterised by NMR spectroscopy, ESI MS and an X-ray structure determination, which reveals the presence of a planar, disordered $\{Pt_2SI\}^+$ core. Monitoring the iodine reaction by ESI MS allows the identification of various iodine species, including the short-lived intermediate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4I]^+$, which allows a mechanism for the reaction to be proposed.

*Keywords:* Platinum complexes; Sulfido complexes; Iodide complexes; Crystal structure; Electrospray mass spectrometry

## Introduction

The dinuclear sulfide-bridged complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** is well-known and has an extensive chemistry [1,2]. The sulfide ligands in this complex are highly nucleophilic and can be reacted with alkylating agents to give bridging thiolate complexes [1,3,4,5], and with a range of metal complexes (typically halide complexes) to give higher nuclearity sulfide bridged aggregates [1,2,6]. One of our recent emphases in this area of chemistry has been the application of electrospray ionisation mass spectrometry (ESI-MS) to the study of **1** [7,8,9] and the selenide $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ [10,11,12,13]. This approach has various advantages, including rapid screening of reaction mixtures and identification of unusual species, for subsequent study on the macroscopic scale. In some reactions with metal-iodo complexes we have identified, in mass spectra, a new species of the composition $[Pt_2SI(PPh_3)_4]^+$. In this paper we describe studies into the synthesis, characterisation and preliminary reactivity of this complex.

As far as we are aware, only one complex has been reported that contains platinum atoms bridged by both sulfide and iodide ligands, this being the platinum(IV) derivative $[CpCr(\mu\text{-}SCMe_3)]_2(\mu_4\text{-}S)[PtMe_3(\mu\text{-}I)]_2$.**[14]** A small number of compounds of other metals containing bridging thiolate and bridging iodide are also known.**[15,16,17]** $[Cp^*Ir(PMe_3)(\mu\text{-}S)(\mu\text{-}I)IrI(NO)(PPh_3)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) is a rare example of a late transition metal complex containing an isolated $\{M_2(\mu_2\text{-}S)(\mu_2\text{-}I)\}$ core.**[18]**

## Results and discussion

### Synthesis and spectroscopic characterisation of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ 2

The species $[Pt_2SI(PPh_3)_4]^+$, subsequently characterised as the μ-iodo complex $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ **2**, was initially identified as an ion at *m/z* 1597 in reactions between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and the iodo complexes $[Os_2(CO)_6(\mu\text{-}I)_2]$ and $[CpCo(CO)I_2]$. This was the sole ion observed for the cobalt complex, while in the osmium system it was the base peak in a complex spectrum which also showed a wide range of other mono- and di-osmium adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, including $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Os(CO)_n]^+$ (n = 2, *m/z* 1750; n = 3, *m/z* = 1778; n = 4, *m/z* = 1806), and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Os_2(CO)_nI]^+$ (n = 5, *m/z* 2151; n = 6, *m/z* 2179; n = 7, *m/z* 2207). We therefore set about to develop a macroscopic synthesis of **2** and to investigate its structural and reactivity characteristics.

We speculated whether free iodide ions in solution could generate **2**. However, attempted reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with an excess of potassium iodide in refluxing methanol for 1 hour does not lead to the formation of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$, presumably because the dianionic sulfide centres of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ are poor leaving groups, and cannot easily be displaced by iodide. However, reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with *cis*-$[PtI_2(PPh_3)_2]$ in refluxing methanol gave an orange solution, which contains $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ as shown by positive-ion ESI MS. In this system, one of the sulfide centres is presumably activated towards displacement by prior coordination to another platinum centre. In order to determine the optimum reaction stoichiometry and detect reaction intermediates, reaction mixtures with a $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ / $[PtI_2(PPh_3)_2]$ stoichiometry of 1:1 and 1:2 were monitored by ESI MS. The reaction proceeded slowly, with the 1:1 reaction stoichiometry appearing to give the slightly cleaner conversion. Various intermediate species were observed in the reaction, and include trinuclear species $[Pt_3(\mu\text{-}S)_2(PPh_3)_6Pt]^{2+}$ (*m/z* 1111, formed by addition of $Pt(PPh_3)_2{}^{2+}$) and $[Pt_3(\mu\text{-}S)_2(PPh_3)_5I]^+$ (*m/z* 2090, formed by addition of $Pt(PPh_3)I^+$). The formation of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ then presumably proceeds by nucleophilic attack of iodide on these species.

On a synthetic scale, reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with 2 equivalents of *cis*-$[PtI_2(PPh_3)_2]$, followed by addition of excess $NH_4PF_6$ to the filtered reaction solution, gave an orange precipitate of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+PF_6^-$ (**2**·$PF_6$) in 44% yield (assuming all sulfide is incorporated in the product, giving a molar ratio of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ of 1:2); recrystallisation from dichloromethane-petroleum spirits gave material that was pure by ESI MS. However, the reaction was generally slow and poorly reproducible on a larger scale, probably due to the poor solubility of both reactants, and is thus not a preferred route for the synthesis of this complex. The attempted synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ by reaction of $[PtI_2(PPh_3)_2]$ with 0.5 mole equivalents of $Na_2S.9H_2O$ in refluxing methanol gave a wide range of species as shown by positive-ion ESI MS, including some of the desired $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$, but no further studies were carried out to optimise this route.

Because of the poor yield and reproducibility of the synthesis from $PtI_2(PPh_3)_2$, an alternative, room temperature and higher yield process was sought. Reaction with elemental iodine was considered to be a prospect, because oxidation of a sulfide with iodine should labilise it towards displacement by the iodide anion generated in the reaction mixture. The feasibility of this approach was indicated by the ESI mass spectrum of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with a small quantity of added iodine, which rapidly generated an orange solution which contained the desired $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ cation at *m/z* 1597.

In order to obtain information about intermediates in the reaction between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and iodine, 1 mole equivalent of iodine was added in aliquots to a stirred methanol suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and the reaction monitored by positive ion ESI MS. This resulted in gradual dissolution of the sparingly soluble Pt complex giving an orange solution, with a smooth increase in intensity of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ at *m/z* 1597. A short-lived monocation at *m/z* 1630 was observed immediately after addition of an aliquot of iodine, and is assigned as $[Pt_2(\mu\text{-}S)_2(PPh_3)_4I]^+$. Occasionally, an ion at *m/z* 1603 was observed at intermediate stages of the reaction, and is assigned as $[Pt_3SI_2(PPh_3)_5]^{2+}$. At the end of the reaction, the dominant ion observed is due to $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$, as well as some unidentified minor ions at *m/z* 2148 and 2117. The product was isolated in 58% yield by precipitation with $PF_6^-$.

The structures of the intermediate species in the iodine oxidation reaction are not unequivocally identifiable from MS data alone. However, one possibility for $[Pt_3SI_2(PPh_3)_5]^{2+}$ is that it contains $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ acting as a metalloligand towards a $PtI(PPh_3)^+$ unit. If both the iodine and sulfur coordinate, a possible structure for this species is **3**; this is a close analogue of the wide range of $\{Pt_2M(\mu_3\text{-}S)_2\}$ aggregates that have been synthesised,[1,2] including those of Pt(II) and Pd(II).[8] The preliminary observation, described later, that isolated $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ is able to coordinate to metal centres - as can the isoelectronic monoalkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ (R = e.g. n-butyl)[19] - is consistent with this proposal.

The identity of the intermediate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4I]^+$ is of somewhat greater interest. We propose that this complex contains a direct S-I bond, *i.e.* it is a sulfenyl iodide complex. Complexes containing the coordinated SI group have been synthesised previously by reaction of μ-sulfido ligands with elemental iodine, for example $[Mo_2(C_5Me_5)_2(\mu\text{-}S)(\mu\text{-}SMe)_2(CO)_2]$ with $I_2$ gives $[Mo_2(C_5Me_5)_2(\mu\text{-}SI)(\mu\text{-}SMe)_2(CO)_2]$.[20] Iridium[21] and tungsten[22] complexes with μ-SI ligands have also been reported, but we are unaware of any isolated complexes with Pt-S-I linkages. In fact there only appears to be one other species that is likely to contain a direct S-I bond in the $\{Pt_2S_2\}$ system, this being the iodine(III) species $[Pt_2(\mu\text{-}S)_2(PPh_3)_4IPh_2]^+$, formed as a transient intermediate in the reaction of diphenyliodonium chloride ($Ph_2ICl$) with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$.[7] It is not surprising that metal sulfido complexes are able to act as 'metalloligands' towards the $I^+$ fragment because there are many examples of $I^+$ cations stabilised by coordination of neutral sulfur-donor ligands of various types.[23,24]

In crystallographically characterised examples of bis(ligand) species $[L_2I]^+$ (L = neutral sulfur donor ligand) there is a *linear* S-I-S geometry,[25] such an arrangement being obviously precluded by the chelating nature of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. In structurally characterised sulfenyl iodide complexes such as $[Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}SI)(\mu\text{-}SMe)_2(CO)_2]$ the iodine is bonded to a single sulfur[20] and we therefore consider structure **4** as a likely possibility for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4I]^+$.

We cannot rule out the ESI MS generation and observation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4I]^+$ by gas-phase dissociation of a neutral, *molecular* charge-transfer adduct of the type $[Pt_2(\mu\text{-}S)(\mu\text{-}S^{\cdots}I\text{-}I)(PPh_3)_4]$; analogous adducts are well-known to form in reactions of Lewis acidic $I_2$ with neutral sulfur donors such as dialkyl sulfides[26,27] and phosphine sulfides,[28,29] as well as μ-sulfido complexes; reaction of $[Mo(\eta^5\text{-}C_5H_5)(\mu\text{-}S)(\mu\text{-}N^tBu)]_2$ with $I_2$ gave the adduct $[Mo(\eta^5\text{-}C_5H_5)(\mu\text{-}S^{\cdots}I_2)(\mu\text{-}N^tBu)]_2$, which was structurally characterised.[30] Loss of $I^-$ from a species containing a $Pt_2(\mu\text{-}S^{\cdots}I_2)$ moiety would be expected to be very facile. A possible mechanism which accounts for the major observed species is given in Scheme 1. There are similarities with the proposed pathway for phenylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with PhSSPh, which proceeds *via* a species of composition $[Pt_2(\mu\text{-}S)_2(PPh_3)_4SPh]^+$;[31] this species is analogous to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4I]^+$, and the reagents PhS-SPh and I-I can be equated as mild oxidants that furnish a chemically soft, monoanionic reduction product ($PhS^-$ or $I^-$) that can act as a bridging ligand.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ shows two triplet $PPh_3$ resonances at δ 25.1 and 22.4, showing coupling to $^{195}Pt$ of 2619 and 4265 Hz respectively, assigned to phosphines *trans* to sulfide and lower *trans*-influence iodide ligands. The value of $^1J(PtP)$

for the phosphine *trans* to sulfide compares favourably with a $^1J(PtP)$ value of 2705 Hz for the $PPh_3$ *trans* to sulfide in $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_2]^+$[32] and a range of mono-alkylated derivatives e.g. $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CN)(PPh_3)_4]^+$ (2579 Hz).[3] Simulation assuming $^2J(PP)$ 18 Hz, $^4J(PP)_{trans}$ 18 Hz and $^4J(PP)_{cis}$ 0 Hz gave a good match with the observed spectrum.

The ESI MS behaviour of isolated $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ has been studied at a range of cone voltages, and is shown in Figure 1. At a low cone voltage (20V, Figure 1a) the parent monocation is exclusively observed, as would be expected for this type of cationic species. Upon increasing the cone voltage, the parent ion remains the base peak up to moderate cone voltages, e.g. 50V (Figure 1b), where fragment ions begin to be observed. At a cone voltage of 70V, Figure 1c, the full range of fragment ions can be clearly seen. These include $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_3]^+$ (*m/z* 1335), and a species at *m/z* 1041 assigned as $[Pt_2I(PPh_3)_2]^+$ on the basis of its *m/z* value and isotope pattern; the solvated analogue $[Pt_2I(PPh_3)_2(MeOH)]^+$ was also seen as a weak ion at *m/z* 1073. These non-sulfide species probably contain an iodide-bridged Pt(I)-Pt(I) dinuclear unit, of the type **5**; this is analogous to the thiophenolate ion $[Pt_2(\mu\text{-}SPh)(PPh_3)_2]^+$ observed in the MS fragmentation of the complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$,[31] further strengthening the formally isoelectronic relationship between $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$. The reduction of platinum(II) to platinum(I) is not unexpected since many metal centres undergo such reduction processes under high energy CID conditions,[33,34] and Pt(I)-Pt(I) dimers are well known. Species **5** is formally analogous to the known species $[Pt_2(\mu\text{-}S)(PPh_3)_4]$[35] and related CO-substituted analogues $[Pt_2(\mu\text{-}S)(PPh_3)_{4-x}(CO)_x]$,[36] by replacement of a dianionic $S^{2-}$ by monoanionic $I^-$ (and loss of phosphines).

Finally, at high cone voltages the cyclometallated mono-platinum complex $[Pt(Ph_2PC_6H_4)(PPh_3)]^+$ (*m/z* 718) is seen; this is typical of Pt-$PPh_3$ complexes subjected to high cone voltages.[37]

## X-ray crystal structure of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ ($2{\cdot}PF_6$)

In order to fully characterise this new system, an X-ray diffraction study was carried out. The structure of the cation together with the atom numbering scheme is shown in Figure 2, and selected bond lengths and angles are given in Table 1. The cation lies on a centre of symmetry, and by definition is therefore strictly planar. The S and I atoms are disordered but it was possible to resolve the individual components of the disorder, which refined with 50% occupancy factors. The crystal packing of **2** provides a clear example of "sextuple phenyl embrace" interactions between adjacent cations with a P···P distance of 7.09 Å.[38]

The Pt-S bond distances of **2** are 2.261(7) and 2.277(7) Å. The reported structure of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$[39] has very short Pt-S distances [2.068 and 2.110 Å] which led to querying[40] and recent rejection of this structure as $[Pt_2(\mu\text{-}OH)_2(PPh_3)_4]^{2+}$.[41] However, in the ethanol solvate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$.2EtOH the Pt-S distances are somewhat longer than in **2**, averaging 2.3318(8) and 2.3491(9) Å for the non hydrogen-bonded and hydrogen bonded sulfides respectively.[42] Indeed, related complexes containing the underivatised $\{Pt_2S_2\}$ core with alternative phosphine ligands show similar Pt-S bond distances, as in complexes with $Ph_2P(CH_2)_3PPh_2$ [2.3318(14)–2.3505(13) Å],[43] $Ph_2P(CH_2)_2PPh_2$ [2.3412(12)–2.3581(13) Å][44] and $Ph_2Ppy$ [2.333(1) Å].[45] Pt-S(sulfide) bond lengths in monoalkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ are also around 2.32-2.34 Å.[3,4] This indicates that the presence of the large bridging iodide ion in $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ has the effect of *shortening* the Pt-S bonds.

## Preliminary investigation of the reactivity of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$

The parent complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ is well-known to contain highly nucleophilic sulfide centres that can undergo facile alkylation and arylation reactions, as well as being able to act as ligands towards a wide range of metal centres.[1-13] It was therefore of interest to carry out a preliminary comparison of the reactivity of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$, expected to be much less reactive as a result of the deactivating effect of the positive charge. In support of this, $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ appears to be fully stable in chlorinated solvents, like the monoalkylated species $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$, but in contrast to the disulfide systems $[Pt_2(\mu\text{-}S)_2(L)_4]$, which react rapidly with solvents such as $CHCl_3$ and $CH_2Cl_2$ *via* alkylation reactions which have been thoroughly studied.[46,47,48]

In light of the interesting reactivity that $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ displays towards an alkylating agent such as MeI,[1,5] the corresponding reactivity with $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ was monitored, using ESI MS. Rapid monomethylation occurred, presumably at the sulfide centre, giving $[Pt_2(\mu\text{-}SMe)(\mu\text{-}I)(PPh_3)_4]^{2+}$, observed as the dominant base peak at *m/z* 806. This ion showed the characteristic 0.5 *m/z* separation of adjacent peaks in the isotope distribution pattern. The $[Pt_2(\mu\text{-}SMe)(\mu\text{-}I)(PPh_3)_4]^{2+}$ species was fairly stable in this reaction mixture on standing overnight, in contrast to the complex $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$ (formed by dimethylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$) which undergoes facile nucleophilic attack of iodide with concomitant phosphine displacement, giving [Pt$_2$($\mu$-

SMe)$_2$(PPh$_3$)$_3$I]$^+$ at *m/z* 1397.**5** The corresponding ion [Pt$_2$(μ-SMe)(μ-I)(PPh$_3$)$_3$I]$^+$ is formed as only a minor ion on standing overnight, by nucleophilic attack of iodide on [Pt$_2$(μ-SMe)(μ-I)(PPh$_3$)$_4$]$^{2+}$.

A preliminary study of the reactivity of [Pt$_2$(μ-S)(μ-I)(PPh$_3$)$_4$]$^+$ towards metal-halide complexes has also been carried out. Addition of an excess of [IrCl(COD)]$_2$ (COD = cyclo-octa-1,5-diene) to a solution of [Pt$_2$(μ-S)(μ-I)(PPh$_3$)$_4$]PF$_6$ in methanol-dichloromethane gave a clear solution which showed [Pt$_2$(μ-S)(μ-I)(PPh$_3$)$_4$Ir(COD)]$^{2+}$ as the base peak at the expected *m/z* value of 949, with an 0.5 *m/z* separation of adjacent peaks in the isotope pattern being indicative of the formation of a dication.

## Conclusions

The cationic species [Pt$_2$(μ-S)(μ-I)(PPh$_3$)$_4$]$^+$ has been found to be a ubiquitous product in systems involving combinations of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with oxidising and non-oxidising iodine sources. Because of its cationic nature, ESI mass spectrometry is a valuable technique for detecting its presence in reaction solutions, and in optimising the synthesis of this complex. Reaction of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with 1 mole equiv of elemental iodine provides a practical route to this complex, isolable as its hexafluorophosphate salt. Preliminary studies indicate that this species is still able to coordinate to metal centres despite its cationic nature. The chemistry defined in this paper suggests that this methodology should be useful in the synthesis of related heteroatom-bridged systems.

## Experimental

### Materials

Dichloromethane and methanol were AR grade and used as supplied. Petroleum spirits refers to the fraction of boiling range 40 – 60 ºC. The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was prepared by the literature procedure from *cis*-$[PtCl_2(PPh_3)_2]$ and sodium sulfide nonahydrate.[49] The complex *cis*-$[PtI_2(PPh_3)_2]$ was prepared from *cis*-$[PtCl_2(PPh_3)_2]$ by metathetical reaction with sodium iodide in methanol-acetone, by a minor modification of the literature procedure.[50] The following compounds were prepared by the literature procedures: $[Os_2(CO)_6(\mu\text{-}I)_2]$,[51] $[IrCl(COD)]_2$[52] and $[CpCo(CO)I_2]$.[53]

### Instrumentation

Electrospray mass spectra were recorded in positive-ion mode using a VG Platform II instrument, typically using a range of cone voltages from 20 - 80V. Mass spectrometry reaction samples containing $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ were suspended in methanol, centrifuged, and the solution introduced *via* a microlitre syringe and a Rheodyne injector. Isolated $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ was dissolved in a small quantity of $CH_2Cl_2$ and then diluted with methanol prior to MS analysis. Spectra were typically an average of 6 - 10 scans. Isotope patterns of some ions were confirmed using a Finnigan LCQ instrument, and species assignment achieved by comparison with calculated isotope distribution patterns for the ion, obtained using the *Isotope* program.[54]

### Synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ ($2^{\cdot}PF_6$) from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and *cis*-$[PtI_2(PPh_3)_2]$

A mixture of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (50 mg, 0.0333 mmol) and *cis*-$[PtI_2(PPh_3)_2]$ (66 mg, 0.0678 mmol) in methanol (20 mL) was refluxed for 1 hour whereupon an orange solution and precipitate were slowly produced. The mixture was filtered, and to the filtrate was added excess $NH_4PF_6$, giving an orange precipitate which was filtered, washed with water, and dried to give $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ (51.5 mg, 44%, based on $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and assuming all sulfide is incorporated into product).

### Synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ ($2^{\cdot}PF_6$) from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and $I_2$

To a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (200 mg, 0.133 mmol) in methanol (30 mL) was added a solution of iodine (34 mg, 0.134 mmol) in methanol (40 mL) in 8 portions, with monitoring of the reaction progress by positive-ion ESI MS. At the end of the addition, the resulting orange solution was filtered to remove a small amount of solid, and $NH_4PF_6$ (200 mg, 1.23 mmol) added to the filtrate. Water (30 mL) was added to assist precipitation, and the resulting orange solid was isolated by filtration, washed with water (10 mL) and diethyl ether (10 mL) and dried *in vacuo* to give $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ 135 mg (58%). Found: C, 48.6; H, 3.7. $C_{72}H_{60}F_6I_1P_5Pt_2S_1$ requires C, 49.6; H, 3.5%. ESI MS (positive ion, 20 V), $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ (*m/z* 1597, 100%). $^{31}P\text{-}\{^1H\}$ NMR, $\delta$ 25.1 [t, $^1J(PtP)$ 2619, $^2J(PP)$ 18 Hz, $^4J(PP)_{trans}$ 18 Hz] and 22.4 [t, $^1J(PtP)$ 4265, $^2J(PP)$ 18 Hz, $^4J(PP)_{trans}$ 18].

## X-ray structure determination of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ ($2^{\cdot}PF_6$)

Orange crystals were obtained by slow evaporation of a dichloromethane-petroleum spirits solution at room temperature. Unit cell dimensions and reflection data were collected at the University of Canterbury on a Bruker Nonius Apex II CCD diffractometer at 93 K. Absorption corrections to the data were made by SADABS.[55] Crystal and refinement data for the complex are presented in Table 2.

The structure was solved by direct methods using SHELXS-97[56] and refined using SHELXL-97[57], with all non-H atoms anisotropic and H atoms included in calculated positions. The cation lies on a crystallographic inversion centre, requiring strict planarity of the $\{Pt_2SI\}$ core and a 50:50 disorder of the I/S ligands. Because of the difference in bond lengths, the separate components could be resolved and included in the refinement. The anion is disordered over two equal symmetry-related lattice sites, with 50% occupancies. A final difference map shows some significant features adjacent to the Pt atom which presumably is unresolved variation in position brought about by the disorder

## Supplementary information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 743333. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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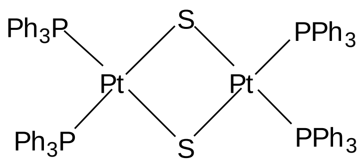
**Table 1** Selected bond distances (Å) and angles (º) for $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ (**2**$\cdot PF_6$)

| | | | |
|---|---|---|---|
| Pt(1)-S(1) | 2.261(7) | Pt(1)-S(1’) | 2.277(7) |
| Pt(1)-P(1) | 2.286(3) | Pt(1)-P(2) | 2.301(3) |
| Pt(1)-I(1) | 2.689(2) | Pt(1)-I(1’) | 2.702(2) |
| | | | |
| S(1)-Pt(1)-S(1’) | 68.5(3) | S(1)-Pt(1)-P(1) | 99.3(2) |
| S(1’)-Pt(1)-P(2) | 94.6(2) | P(1)-Pt(1)-P(2) | 97.87(10) |
| P(1)-Pt(1)-I(1) | 87.49(8) | P(2)-Pt(1)-I(1’) | 82.84(8) |
| I(1)-Pt(1)-I(1’) | 91.81(6) | Pt(1)-I(1)-Pt(1’) | 88.19(6) |
| Pt(1)-S(1)-Pt(1’) | 111.5(3) | | |

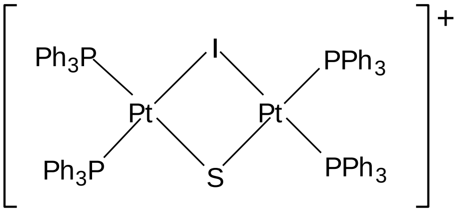
Symmetry transformations used to generate equivalent atoms: #1 –*x*+1, -*y*+1, -*z*

**Table 2** Crystal, collection and refinement data for $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ (**2**·$PF_6$)

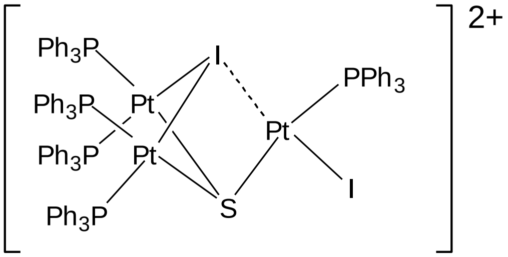
| | | |
|---|---|---|
| *Crystal data* | | |
| Empirical formula | | $C_{72}H_{60}F_6IP_5Pt_2S$ |
| Formula weight | | 1743.19 |
| Crystal system | | Triclinic |
| Space group | | $P\bar{1}$ |
| $a$ (Å) | | 9.8727(11) |
| $b$ (Å) | | 13.0937(15) |
| $c$ (Å) | | 14.0346(15) |
| $\alpha$ (°) | | 92.057(2) |
| $\beta$ (°) | | 103.564(2) |
| $\gamma$ (°) | | 104.600(2) |
| V (Å$^3$) | | 1698.0(3) |
| $Z$ | | 1 |
| $D_c$ (g cm$^{-3}$) | | 1.705 |
| *Data collection* | | |
| Crystal size (mm) | | 0.24 x 0.19 x 0.11 |
| Radiation, wavelength (Å) | | Mo-$K_\alpha$, $\lambda = 0.71073$ |
| Temperature (K) | | 111(2) K |
| $\theta$ range for data collection (°) | | 2.09 to 26.41 |
| Reflections collected | | 13970 |
| Independent reflections | | 6577 [$R_{int} = 0.0391$] |
| Absorption coefficient (mm$^{-1}$) | | 4.775 |
| F(000) | | 846 |
| *Structure analysis and refinement* | | |
| Solution by | | Direct methods |
| Refinement method | | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | | 6577 / 0 / 443 |
| Goodness-of-fit on $F^2$ | | 1.021 |
| Final R indices [$I > 2\sigma(I)$] | $R_1$ | 0.0579 |
| | $wR_2$ | 0.1419 |
| R indices (all data) | $R_1$ | 0.0921 |
| | $wR_2$ | 0.1703 |
| Largest difference peak (e Å$^{-3}$) | | 3.042 |
| Largest difference hole (e Å$^{-3}$) | | -3.946 |


Ph3P
S
PPh3
Pt
Pt
Ph3P
S
PPh3

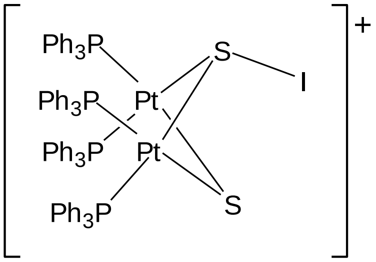
**1**


+
Ph3P
I
PPh3
Pt
Pt
Ph3P
S
PPh3

**2**


2+
Ph3P
I
PPh3
Ph3P
Pt
Pt
Ph3P
Pt
I
Ph3P
S

**3**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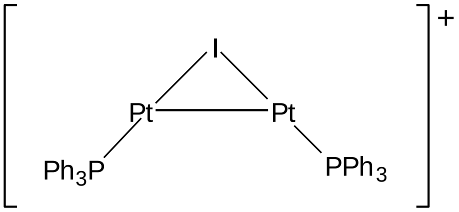
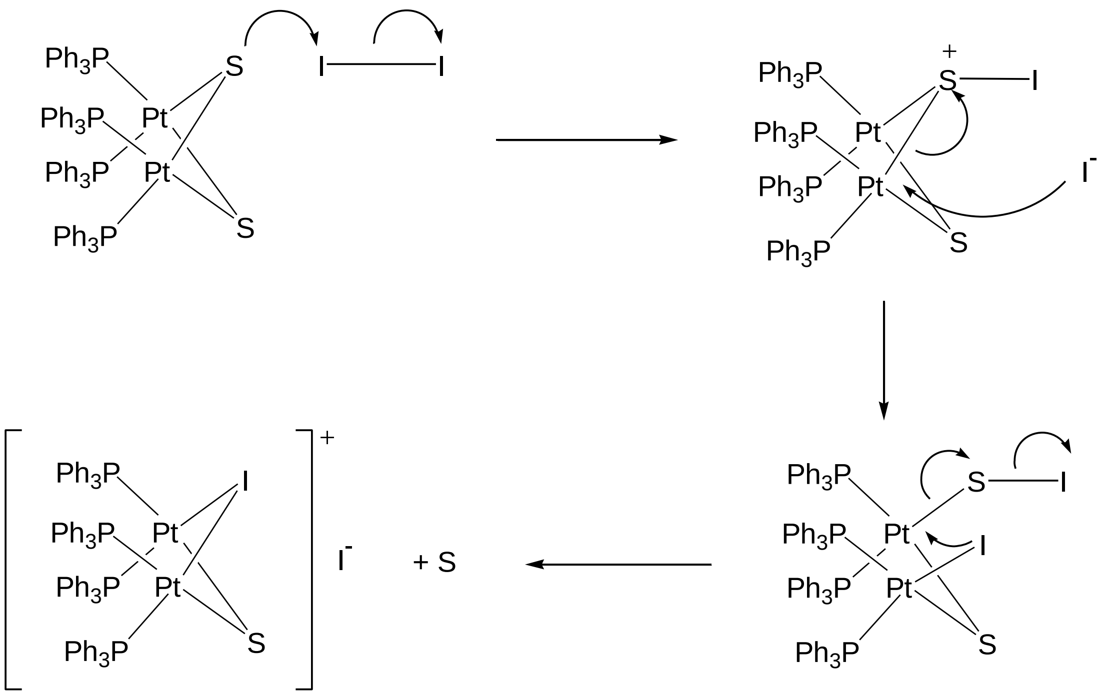
S
I
Ph3P
Pt
Ph3P
Pt
Ph3P
S

**4**


+
I
Pt
Pt
Ph3P
PPh3

**5**



**Scheme 1** A possible mechanism for the conversion of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ with $I_2$.

## Captions for Figures

**Figure 1** Positive-ion ESI mass spectra of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ at a range of cone voltages, showing the fragmentation behaviour; (a) 20V, (b) 50V, (c) 70V. The inset to spectrum (a) shows a comparison of the observed and calculated isotope patterns for $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$.

**Figure 2** The centrosymmetric core of the cation of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ showing the I/S bridging ligands disordered about the inversion centre. The symmetry-related atoms are generated by 1-x, 1-y, -z. Only the *ipso* carbons of the triphenylphosphine ligands are shown for clarity.

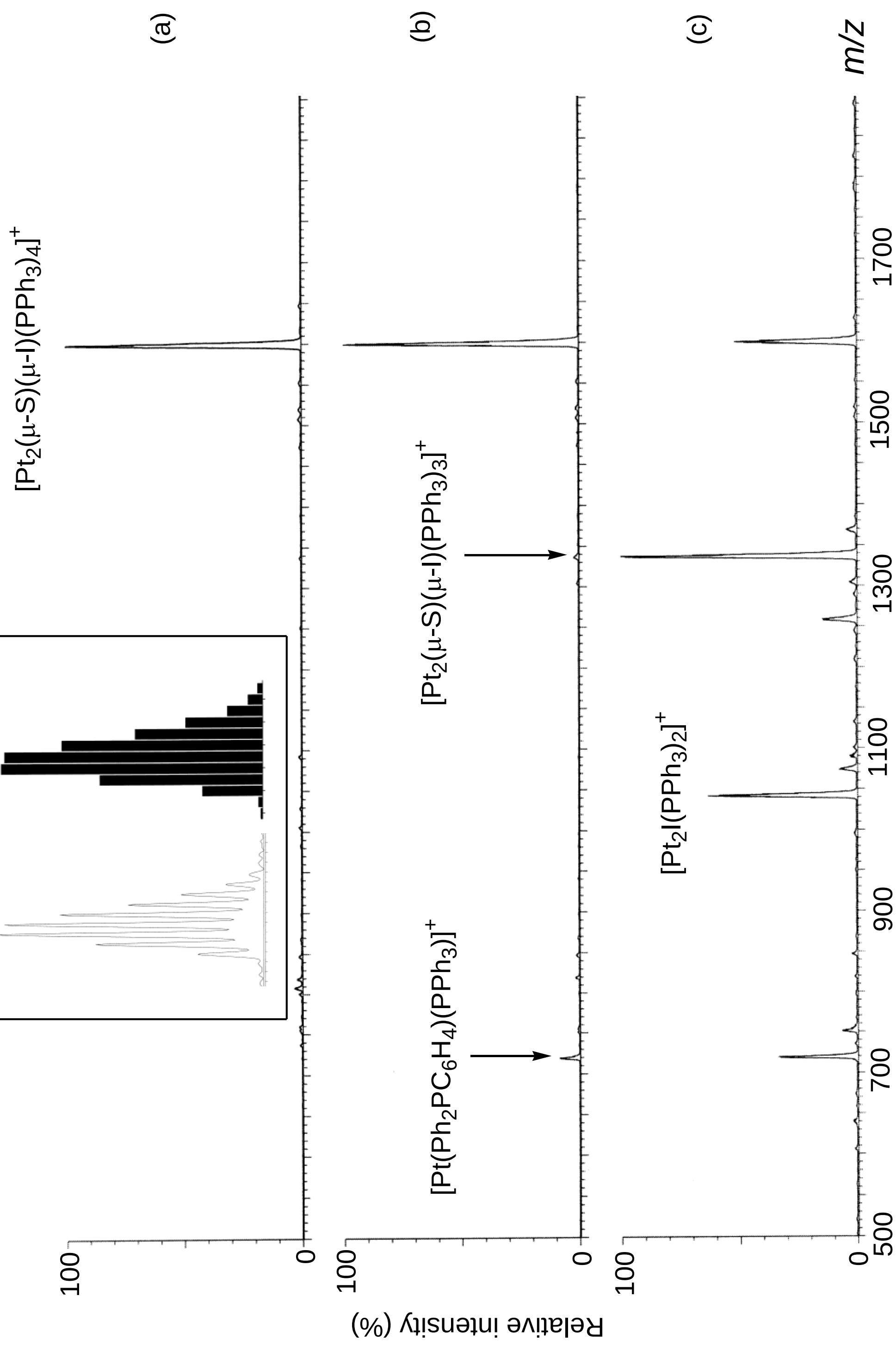

(a)
(b)
(c)
[Pt2(μ-S)(μ-I)(PPh3)4]+
[Pt2(μ-S)(μ-I)(PPh3)3]+
[Pt(Ph2PC6H4)(PPh3)]+
[Pt2I(PPh3)2]+
100
0
Relative intensity (%)
500
700
900
1100
1300
1500
1700
m/z

**Figure 1**

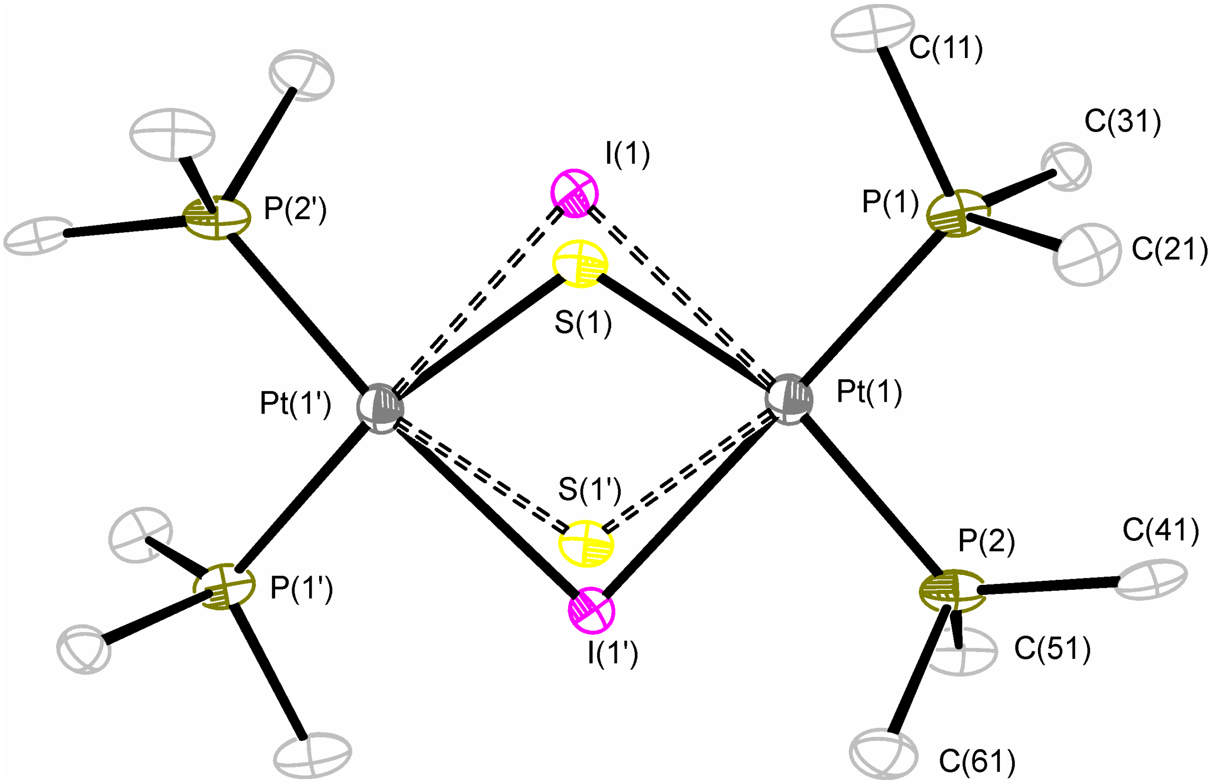


**Figure 2**

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