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**Thallium(III) complexes of the metalloligands [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] and [Pt<sub>2</sub>(μ-Se)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>]**

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## Abstract

Reactions of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with the diarylthallium(III) bromides  $\text{Ar}_2\text{TlBr}$  [ $\text{Ar} = \text{Ph}$  and  $p\text{-ClC}_6\text{H}_4$ ] in methanol gave good yields of the thallium(III) adducts  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlAr}_2]^+$ , isolated as their  $\text{BPh}_4^-$  salts. The corresponding selenide complex  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4\text{TlPh}_2]\text{BPh}_4$  was similarly synthesised from  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ ,  $\text{Ph}_2\text{TlBr}$  and  $\text{NaBPh}_4$ . The reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with  $\text{PhTlBr}_2$  gave  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBrPh}]^+$ , while reaction with  $\text{TlBr}_3$  gave the dibromothallium(III) adduct  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2]^+[\text{TlBr}_4]^-$ . The latter complex is a rare example of a thallium(III) dihalide complex stabilised solely by sulfur donor ligands. X-ray crystal structure determinations on the complexes  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlPh}_2]\text{BPh}_4$ ,  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBrPh}]\text{BPh}_4$  and  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2][\text{TlBr}_4]$  reveal a greater interaction between the thallium(III) centre and the two sulfide ligands on stepwise replacement of  $\text{Ph}$  by  $\text{Br}$ , as indicated by shorter  $\text{Tl-S}$  and  $\text{Pt}\cdots\text{Tl}$  distances, and an increasing  $\text{S-Tl-S}$  bond angle. Investigations of the ESI MS fragmentation behaviour of the thallium(III) complexes are reported.

*Keywords:* Platinum complexes; Thallium complexes; Sulfide ligands; Crystal structures; Electrospray mass spectrometry

## Introduction

Although the platinum(II) sulfido complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** has been known for over 30 years [1], investigations on the chemistry of complexes containing the

enigmatic  $\{\text{Pt}_2\text{S}_2\}$  core are continuing [2,3], particularly in areas of sulfide oxidation [4], hydrogen-bonding [5] and protonation, [6] alkylation and arylation reactions [7,8,9,10,11,12,13,14] and coordination chemistry.[15,16,17] With the exception of the very hardest metals, **1** acts as a very general metalloligand towards a diverse range of metal centres.[18] While a number of complexes of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with main group metal centres are known [19], such as lead [20], indium and gallium [21] and bismuth [22,23,24], organometallic derivatives are limited to organo-tin [25] and organo-lead [26] compounds. In this paper we report our studies on thallium(III) derivatives, including organometallics. Only a single thallium adduct of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  has been reported to date, being the complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{Tl}]^+$  **2**, containing two sulfide donors coordinated to the ‘bare’  $\text{Tl}^+$  cation, giving a ‘Mexican-hat’ like structure [27]; the related  $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2$  (dppf) complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{dppf})_2\text{Tl}]^+$  has also been reported.[28]

## Results and discussion

Organothallium(III) halide precursors are readily obtained by the reaction of thallium(III) bromide [generated *in situ* from  $\text{TlBr}$  and a slight excess of  $\text{Br}_2$ ] with an arylboronic acid in refluxing water, from which the desired product is isolated by simple filtration and washing. Using this method (reported for the synthesis of  $\text{Ph}_2\text{TlBr}$  **3a** [29]) we have also prepared bis(4-chlorophenyl)thallium(III) bromide **3b** as a white solid. Compound **3b** has been reported only as an uncharacterised by-product from the coupling of  $4\text{-ClC}_6\text{H}_4\text{MgBr}$  and  $\text{TlBr}$  to give the biaryl  $(4\text{-ClC}_6\text{H}_4)_2$ . [30]

The diarylthallium(III) compounds have poor solubility for NMR spectroscopic characterisation, but can be conveniently analysed by positive-ion ESI MS in methanol-

pyridine solution. ESI MS has been used in the analysis of methyl-thallium(III) complexes [31,32], but aryl derivatives do not appear to have been previously studied. Thus, at a cone voltage of 20V Ph<sub>2</sub>TlBr **3a** gave [Ph<sub>2</sub>Tl(C<sub>5</sub>H<sub>5</sub>N)]<sup>+</sup> (*m/z* 438) as the base peak in the spectrum, together with [Ph<sub>2</sub>Tl]<sup>+</sup> (*m/z* 359, 60%), [Ph<sub>2</sub>Tl(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>]<sup>+</sup> (*m/z* 517), and [(Ph<sub>2</sub>Tl)<sub>2</sub>Br]<sup>+</sup> (*m/z* 797). At a cone voltage of 5V, [Ph<sub>2</sub>Tl(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>]<sup>+</sup> was the base peak, while at 50V [Ph<sub>2</sub>Tl]<sup>+</sup> dominated, indicating that the pyridine ligand is relatively weakly coordinated. However, at these higher cone voltages, fragmentation to the Tl<sup>+</sup> ion (*m/z* 203/205) occurred with significant intensity (60% relative intensity at 50V). The negative-ion ESI spectrum of Ph<sub>2</sub>TlBr shows the ion [Ph<sub>2</sub>TlBr<sub>2</sub>]<sup>-</sup> (*m/z* 519) as the base peak, together with a weak ion at *m/z* 473 that is identified as [Ph<sub>2</sub>TlBrCl]<sup>-</sup>, presumably formed from adventitious chloride in the system. The positive ion ESI mass spectrum of **3b** showed analogous ions to those of Ph<sub>2</sub>TlBr. The identification of these various ions is readily achieved by inspection of their isotopic fingerprints that arise as a result of the bi-isotopic nature of Tl, Br and Cl.

Reaction of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] with Ph<sub>2</sub>TlBr **3a** proceeds rapidly in methanol with dissolution of the sparingly soluble platinum complex and formation of a clear yellow solution containing the cation [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]<sup>+</sup>, identified by positive-ion ESI MS (*m/z* 1861, 100%). The product is readily isolated in good yields by addition of an excess of either NH<sub>4</sub>PF<sub>6</sub> or NaBPh<sub>4</sub> to the reaction mixture, giving salts [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]BPh<sub>4</sub> **4a** and [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]PF<sub>6</sub> **4b** respectively. The corresponding selenide complex [Pt<sub>2</sub>(μ-Se)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]BPh<sub>4</sub> **5** can be prepared by the same method as a dark orange-brown solid in 77% yield. In an analogous fashion, reaction of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] with **3b** yielded [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>Tl(C<sub>6</sub>H<sub>4</sub>Cl-*p*)<sub>2</sub>]BPh<sub>4</sub> **4c**.

The complexes are soluble and stable in chlorinated hydrocarbon solvents such as dichloromethane and chloroform, but sparingly soluble in alcohols.

Reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** with a slight excess of the mono-phenyl compound  $\text{PhTlBr}_2$  produced a cloudy yellow solution, which after filtration and addition of excess  $\text{NaBPh}_4$  yielded a pale orange solid. This was identified as the complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBrPh}]\text{BPh}_4$  **6** on the basis of positive-ion ESI MS. The cation  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBrPh}]^+$  (with the base peak in the isotope distribution pattern at  $m/z$  1865) has a similar, but distinctly different pattern to that of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlPh}_2]^+$  ( $m/z$  1861), due to changes as a result of the two isotopes of bromine ( $^{79}\text{Br}$ ,  $^{81}\text{Br}$ ).

Following the successful synthesis of the arylthallium complexes above, we decided to explore the reactivity with thallium(III) bromide. Inorganic thallium(III) is well-known to have oxidising properties [33], such that complexes of inorganic thallium(III) with sulfur donor ligands, especially neutral and monodentate ligands, are relatively rare [33,34]. The reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with 2 equivalents of  $\text{TlBr}_3$  (prepared in aqueous solution from  $\text{TlBr}$  and a slight excess of  $\text{Br}_2$ ) resulted in the rapid formation of an orange suspension of the complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2]^+[\text{TlBr}_4]^-$  **7**. This is reminiscent of the reactivity of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  towards  $\text{GaCl}_3$ , which gave the corresponding  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{GaCl}_2]^+[\text{GaCl}_4]^-$  [21]. Complex **7** was assigned on the basis of microelemental analysis together with positive- and negative-ion ESI MS, which yielded the ions  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2]^+$  ( $m/z$  1867) and  $[\text{TlBr}_4]^-$  ( $m/z$  525) respectively. Minor ions were formed by chloride exchange, presumably from traces of chloride in the  $\text{CH}_2\text{Cl}_2$  used in preparation of the sample for MS analysis. Thus, a very minor ion  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2\text{Cl}]^+$  ( $m/z$  1866) was observed.

$\text{S})_2(\text{PPh}_3)_4\text{TlBrCl}]^+$  ( $m/z$  1823) was observed in some positive-ion spectra, and a weak negative ion  $[\text{TlBr}_3\text{Cl}]^-$  ( $m/z$  479) was also seen in negative-ion spectra.

Attempted conversion of the known thallium(I) complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{Tl}]\text{PF}_6$  [27] to  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2]^+$ , by reaction with one equivalent of pyridinium tribromide (as a conveniently handled source of  $\text{Br}_2$ ) in dichloromethane was not successful, only generating the desired  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2]^+$  cation in low yield (by ESI MS), with considerable decomposition occurring.

### Spectroscopic characterisation

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the arylthallium derivatives **4a**, **4c** and **5** show a single slightly broad resonance, with coupling to  $^{195}\text{Pt}$  [**4a** 3022; **4c** 3036; **5** 3061 Hz], consistent with symmetrical coordination of the thallium(III) centre. This can be compared to a  $^1\text{J}(\text{PtP})$  value of 2983 Hz in the thallium(I) adduct  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{Tl}]\text{PF}_6$  [27]. The dibromothallium complex **7** shows a rather different spectrum, with slightly broadened doublets together with the associated symmetric platinum satellites. To account for this type of spectrum through asymmetry, this would need to arise from two inequivalent  $\text{Pt}(\text{PPh}_3)_2$  groups on the  $\{\text{Pt}_2\text{S}_2\}$  core [as opposed to inequivalent phosphines on a single platinum  $\text{Pt}(\text{P}^a\text{Ph}_3)(\text{P}^b\text{Ph}_3)$ , which would lead to  $^2\text{J}(\text{PP})$  coupling, which is not observed]; given the high symmetry of complex **7** observed in the X-ray structure (*vide infra*), this is highly unlikely. In **7** it is therefore proposed that  $^3\text{J}(\text{TlP})$  coupling (257 Hz) to  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$  (both  $I = 1/2$ ) occurs. For the mixed bromo/phenyl complex **6**, two singlet resonances were observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, at  $\delta$  17.9 [ $^1\text{J}(\text{PtP})$  3100] and 17.2 [ $^1\text{J}(\text{PtP})$  3090]; in this case, asymmetry of the complex would render the two

Pt(PPh<sub>3</sub>)<sub>2</sub> units inequivalent. The presence of slightly different coupling constants also supports the assignment, with no Tl coupling observed in this case. We are unaware of any <sup>3</sup>J(TlP) coupling constant data in the literature, but values of <sup>2</sup>J(TlP) in the range 481-1781 Hz have been reported in solid-state inorganic Tl compounds [35], together with <sup>1</sup>J(TlP) coupling constants of 3203 and 3144 Hz for Ph<sub>2</sub>P(Me<sub>2</sub>Tl)<sub>2</sub>PPh<sub>2</sub> in solution [36].

Samples of complex **7** recrystallised from dichloromethane-ether typically yielded a small amount of off-white powdery material, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **7** invariably show the presence (in variable quantities) of a sharp singlet at δ 14.9, showing <sup>195</sup>Pt coupling of 3617 Hz, assigned as *cis*-[PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. This presumably forms through decomposition of the adduct, which is not entirely surprising given that non-organo thallium(III) compounds are typically rather oxidising [33]. Oxidation and loss of the sulfides would lead to the formation of the stable dibromoplatinum complex.

The availability of the series of TlPh<sub>2</sub><sup>+</sup>, TlPhBr<sup>+</sup> and TlBr<sub>2</sub><sup>+</sup> adducts of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>], together with [Pt<sub>2</sub>(μ-Se)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]<sup>+</sup>, afforded the opportunity to investigate trends in mass spectrometric behaviour, specifically fragmentation at elevated cone voltages. For the diphenylthallium complexes [Pt<sub>2</sub>(μ-E)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]<sup>+</sup>, (**4a**, E = S; **5**, E = Se) the parent ions at *m/z* 1861 (S) and 1956 (Se) were essentially the only significant ions observed up to moderately high cone voltages, e.g. 70V, indicating appreciable stability. At 80V and above, fragmentation occurred, giving dominant fragment ions at *m/z* 1317 (S) and 1413 (Se), identified as the phenyl species [Pt<sub>2</sub>E<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>Ph]<sup>+</sup>. Complex **4c** likewise gives the parent ion as the base peak at *m/z* 1930, which fragments to [Pt<sub>2</sub>S<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>Cl-*p*)]<sup>+</sup> at *m/z* 1352.

At 80V,  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBrPh}]^+$  (**6**) and  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2]^+$  (**7**) gave the same major fragment ion at  $m/z$  1321, assigned as  $[\text{Pt}_2\text{S}_2(\text{PPh}_3)_3\text{Br}]^+$  on the basis of its  $m/z$  value and isotope pattern. The isotope patterns of the ions generated from both species are almost identical, except for the presence of two low  $m/z$  shoulders on the ion generated from  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBrPh}]^+$ , which could be due to a contribution from  $[\text{Pt}_2\text{S}_2(\text{PPh}_3)_3\text{Ph}]^+$ . The formation of  $[\text{Pt}_2\text{S}_2(\text{PPh}_3)_3\text{Br}]^+$  begins to occur at a cone voltage of 50V from  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2]^+$  while  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBrPh}]^+$  showed no fragmentation at 50V. While the structure of these fragment ions is not clear, they presumably form by transfer of a thallium-bound ligand (Ph, or preferentially Br) to either the S and/or Pt centre, with concomitant reduction and loss of the Tl as TlPh or TlBr. In this regard we note that main group element aryl compounds are able to act as aryl transfer agents [37], and the ‘parent’ species containing a phenylated sulfur such as  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SPh})(\text{PPh}_3)_4]^+$  have been obtained by phenylation of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with PhBr or Ph<sub>2</sub>ICl [38,39].

### **X-ray crystal structure determinations of 4a, 6 and 7**

X-ray structure determinations were carried out on the series of complexes containing TlPh<sub>2</sub><sup>+</sup> (**4a**), TlPhBr<sup>+</sup> (**6**) and TlBr<sub>2</sub><sup>+</sup> (**7**) moieties, in order to characterise the bonding of the thallium centres to the  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  metalloligand, and identify structural trends effected by replacement of Ph by Br. It is worth noting that to date there have been no structural determinations on complexes containing  $\text{STl}^{\text{III}}(\text{halogen})_2$  or  $\text{S}_2\text{Tl}^{\text{III}}(\text{halogen})_2$  coordination environments, and only one determination of a complex



with two sulfur donors and a coordinated halide, in  $[\text{Tl}(\text{mnt})_2\text{Br}]^{2-}$  [ $\text{mnt} = \text{SC}(\text{CN})=\text{C}(\text{CN})\text{S}$ ] [40].

Selected bond lengths and angles for the three structures are given in Table 1, and the structures of the cores of the cations are given in Figures 1-3. The three complexes contain the familiar  $\{\text{Pt}_2\text{S}_2\}$  butterfly core, coordinated to the respective thallium(III) fragment, which has the expected approximately tetrahedral geometry.

In the case of the  $\text{TlBr}_2^+$  adduct, residual electron density indicated a small fraction ( $< 10\%$ ) of the polynuclear cationic complex  $[\{\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\}_2\text{Tl}_2\text{Br}_5]^+$  which had co-crystallised with the main  $\text{TlBr}_2^+$  species (see Experimental). The heavy element core of this component is shown in Figure 4, and consists of two approximately tetrahedral  $\text{TlBr}_2$  centres, linked by a bridging bromide, with each thallium coordinated by one sulfur of a monodentate  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  metalloligand. The relationship between the major  $[\{\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\}\text{TlBr}_2]^+$  and minor  $[\{\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\}_2\text{Tl}_2\text{Br}_5]^+$  components of the crystal are shown in Figure 5, and is described in the Experimental section. The presence of this polynuclear component (expected  $m/z$  3815) could not have been ascertained by ESI MS using our instrumentation, which had a maximum  $m/z$  of 3000.

The major trend on stepwise changing the thallium substituents from Ph to Br is to increase the thallium-sulfur interaction, as measured by a decrease in S-Tl and Pt...Tl distances, and an increase in the S-Tl-S bond angle. This is understandable given the higher Lewis acidity of a  $\text{TlBr}_2^+$  group compared with  $\text{TlPh}_2^+$ , which itself can be related to  $^{205}\text{Tl}$  NMR chemical shifts [41]. Thus, in the series with substituents Ph/Ph (**4a**) – Ph/Br (**6**) – Br/Br (**7**) the average Tl-S bond distances decrease from 2.6985(10) Å (**4a**) to

2.5878(12) Å in **6**, to 2.537(3) Å in **7**, and the S-Tl-S bond angle correspondingly increases from 69.91(3)° (**4a**) to 73.54(3)° (**6**) to 75.84(8)° in (**7**). These parameters can be compared with a Tl-S bond distance of 2.764(3) Å and a S-Tl-S bond angle of 68.9(1)° in the previously characterised thallium(I) adduct [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>Tl]PF<sub>6</sub> (**2**) [27]. As expected, bond distances are shorter in the thallium(III) systems. A number of structures of diphenylthallium(III) complexes with monoanionic sulfur donor ligands have been structurally characterised with longer Tl-S bond distances than **4a**, for example [Ph<sub>2</sub>Tl(S<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] [2.809(2) and 2.846(2) Å] [42], [Ph<sub>2</sub>Tl(S<sub>2</sub>PEt<sub>2</sub>)] [2.854(5) and 2.933(4) Å] [43], [Ph<sub>2</sub>Tl(S<sub>2</sub>COMe)] [2.845(3) and 3.001(2) Å] [44] and [Ph<sub>2</sub>Tl(SPPPh<sub>2</sub>NPPPh<sub>2</sub>S)] [range 2.736(3) to 2.788(2) for 2 independent molecules] [45]. As a consequence of the tighter S-Tl binding in **7**, the average Pt-S bond distance in this complex [2.391(2) Å] is longer than in the other two complexes **6** [2.3765(11) Å] and **4a** [2.3740(10) Å].

The Tl-Br bond distances in **7** [Tl(1)-Br(2) 2.5492(12) and Tl(1)-Br(1) 2.5540(12) Å] are significantly shorter than the Tl(1)-Br(1) bond distance in **6** [2.6346(6) Å]. Likewise, the Tl(1)-C(1) bond distance in **6** [2.174(5) Å] is shorter than in the diphenyl compound **4a** [Tl(1)-C(11) 2.209(4), Tl(1)-C(21) 2.184(4) Å]. Presumably due to the steric effects involving the phenyl rings, there is a decrease in the bond angle to the Br or C ligands, from C(11)-Tl(1)-C(21) 129.07(16)° in **4a**, to C(1)-Tl(1)-Br(1) 107.44(14)° in **6**, to Br(1)-Tl(1)-Br(2) 102.32(4)° in **7**.

The range of S-Tl-X bond angles (X = C or Br) is smallest for **7** [114.78(6) to 122.90(6)°], compared to **4a** [100.44(12) to 124.43(11)°] and **6** [109.13(3) to 133.70(14)°]. Examination of specific bond angles suggests that the thallium centres are slightly distorted from tetrahedral geometry in order to accommodate the steric bulk of

the phenyl rings. For example in **6**, the bond angles C(1)-Tl(1)-S(1) and C(1)-Tl(1)-S(2) are 116.04(14) and 133.70(14)° respectively, while the difference in the Br(1)-Tl(1)-S(1) [112.87(3)°] and Br(1)-Tl(1)-S(2) [109.13(3)°] angles is considerably less. Similar differences in the C-Tl-S bond angles occur in **4a**, for example C(21)-Tl(1)-S(1) is 101.61(13)°, but C(21)-Tl(1)-S(2) is 124.43(11)°.

The non-bonded Pt...Tl distances, though not the same within each complex, decrease on going from **4a** [average 3.3885(2) Å] to **6** [average 3.2838(3) Å] to **7** [average 3.2419(6) Å], paralleling the increasing S-Tl interaction in the series. The corresponding Pt...Tl separation in [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>Tl]PF<sub>6</sub> **2** is 3.379(1) Å [27], indicating that weak heterometallic interactions, as proposed for [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>Tl]<sup>+</sup>, could also occur in these thallium(III) systems.

The [TlBr<sub>4</sub>]<sup>-</sup> counterion of **7** is slightly distorted from a regular tetrahedral geometry, with Br-Tl-Br bond angles in the range 104.14(4) to 114.56(4)°, a range similar to those in other [TlBr<sub>4</sub>]<sup>-</sup> salts [46,47,48].

In conclusion, we have prepared a series of new thallium(III) adducts of the [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] metalloligand, and have shown that the binding of the Tl centre to the sulfur ligands is dependent on the Lewis acidity conferred by the Tl-bound groups, in this study Ph or Br. We have previously found similar effects to occur in organo-lead adducts [26].

## Experimental

### General experimental procedures

*Warning: thallium and its compounds are highly toxic and should be handled with appropriate precautions [49].*

$^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AC300P instrument in  $\text{CDCl}_3$  solution at 121.51 MHz, with chemical shifts relative to external 85%  $\text{H}_3\text{PO}_4$ . Elemental analyses were obtained by the Campbell Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand. Electrospray (ESI) mass spectra were recorded on a VG Platform II instrument, in methanol solvent using a cone voltage of 20V unless otherwise stated. Reaction solution aliquots were diluted with methanol and centrifuged prior to analysis, while isolated salts were dissolved in several drops of  $\text{CH}_2\text{Cl}_2$  before diluting with MeOH, in each case to give a total solid concentration of *ca.*  $0.1 \text{ mg mL}^{-1}$ . Isotope patterns were calculated using the *Isotope* program [50]. Accurate mass measurements were carried out using a Bruker Daltonics MicrOTOF instrument, calibrated using a sodium formate solution.

Reactions were carried out in LR grade methanol as the solvent, without prior purification; no precautions were taken to exclude air, light or moisture.  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** [51] and  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  [52] were prepared by the literature procedures. The compounds thallium(I) bromide (BDH), bromine (BDH), pyridinium tribromide (Aldrich), sodium tetraphenylborate (BDH), ammonium hexafluorophosphate (Aldrich) and 4-chlorophenylboronic acid (Aldrich) were used as supplied.

Diphenylthallium(III) bromide **3a** was prepared by the literature procedure [22] by reaction of phenylboronic acid with  $\text{TlBr}_3$  (generated *in situ* from  $\text{TlBr}$  and a slight excess of  $\text{Br}_2$ ) in boiling water. ESI MS (MeOH-pyridine), positive ion, cone voltage

20V,  $[\text{Ph}_2\text{Tl}]^+$  ( $m/z$  359, 60%),  $[\text{Ph}_2\text{Tl}(\text{C}_5\text{H}_5\text{N})]^+$  ( $m/z$  438, 100%),  $[\text{Ph}_2\text{Tl}(\text{C}_5\text{H}_5\text{N})_2]^+$  ( $m/z$  517, 5%),  $[(\text{Ph}_2\text{Tl})_2\text{Br}]^+$  ( $m/z$  797, 8%); cone voltage 50V,  $[\text{Ph}_2\text{Tl}]^+$  ( $m/z$  359, 100%),  $[\text{Tl}]^+$  ( $m/z$  203/205, 60%); negative ion, cone voltage 20V,  $[\text{Ph}_2\text{TlBrCl}]^-$  ( $m/z$  473, 12%),  $[\text{Ph}_2\text{TlBr}_2]^-$  ( $m/z$  519, 100%). Phenylthallium(III) dibromide was similarly prepared by the literature procedure from  $\text{PhB}(\text{OH})_2$  and  $\text{TlBr}_3$  [53].

### Synthesis of bis(4-chlorophenyl)thallium(III) bromide **3b**

Following the general procedure for **3a**, an aqueous solution of  $\text{TlBr}_3$  was generated *in situ* from  $\text{TlBr}$  (0.81 g, 2.85 mmol) and a slight excess of bromine, until a permanent orange colour was formed. 4-Chlorophenylboronic acid (0.936 g, 5.99 mmol) was added, and the mixture refluxed for 6 h. The reaction mixture was an off-white suspension throughout. After cooling to room temperature, the product was isolated by filtration, washed with distilled water (2 x 5 mL) and dried *in vacuo* to give **3b** as an off-white solid (0.957 g, 66 %). ESI MS (MeOH-pyridine, cone voltage 20V,  $[(\text{ClC}_6\text{H}_4)_2\text{Tl}(\text{C}_5\text{H}_5\text{N})]^+$  ( $m/z$  506, 100%),  $[(\text{ClC}_6\text{H}_4)_2\text{Tl}(\text{C}_5\text{H}_5\text{N})_2]^+$  ( $m/z$  585, 20%); cone voltage 50V,  $[(\text{ClC}_6\text{H}_4)_2\text{Tl}]^+$  ( $m/z$  427, 100%).

### Synthesis of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlPh}_2]\text{BPh}_4$ **4a**

A mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** (300 mg, 0.200 mmol) and  $\text{Ph}_2\text{TlBr}$  **3a** (96 mg, 0.219 mmol) in methanol (30 mL) was stirred, rapidly giving a clear, pale yellow solution. After stirring overnight, the solution was filtered to remove a trace of insoluble matter, and to the filtrate was added  $\text{NaBPh}_4$  (200 mg, 0.585 mmol), immediately giving a cream precipitate. The solid was isolated by filtration, washed with methanol (5 mL), water (5

mL) and petroleum spirits (5 mL) and dried *in vacuo* to give **4a** (369 mg, 85%). Found: C, 59.35; H, 4.23. C<sub>108</sub>H<sub>90</sub>BP<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>Tl requires C, 59.47; H, 4.16%. ESI MS, [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]<sup>+</sup> *m/z* 1861 (100%). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 18.9 [s, <sup>1</sup>J(PtP) 3022].

#### Synthesis of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]PF<sub>6</sub> **4b**

Following the procedure for **4a** [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] **1** (300 mg, 0.200 mmol) and Ph<sub>2</sub>TlBr (97 mg, 0.221 mmol) gave a pale yellow precipitate of **4b** (300 mg, 75 %) upon addition of NH<sub>4</sub>PF<sub>6</sub> (200 mg, 1.23 mmol) to the filtered reaction solution. ESI MS, [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]<sup>+</sup>, *m/z* 1861 (100%).

#### Synthesis of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>Tl(C<sub>6</sub>H<sub>4</sub>Cl-*p*)<sub>2</sub>]BPh<sub>4</sub> **4c**

Following the procedure for **4a**, [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] **1** (200 mg, 0.133 mmol) and BrTl(C<sub>6</sub>H<sub>4</sub>Cl-*p*)<sub>2</sub> **3b** (74 mg, 0.146 mmol) in methanol (25 mL), with NaBPh<sub>4</sub> (200 mg, 0.585 mmol) gave **4c** as a cream powder (215 mg, 72%). Found: C, 57.67; H, 4.09. C<sub>108</sub>H<sub>88</sub>BCl<sub>2</sub>P<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>Tl requires C, 57.65; H, 3.94%. ESI MS, [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>Tl(C<sub>6</sub>H<sub>4</sub>Cl-*p*)<sub>2</sub>]<sup>+</sup>, *m/z* 1930 (100%). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 18.7 [s, <sup>1</sup>J(PtP) 3036].

#### Synthesis of [Pt<sub>2</sub>(μ-Se)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]BPh<sub>4</sub> **5**

A mixture of [Pt<sub>2</sub>(μ-Se)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (304 mg, 0.190 mmol) and Ph<sub>2</sub>TlBr **3a** (98 mg, 0.224 mmol) in methanol (30 mL) was stirred for 16 h to give a slightly cloudy dark brown solution. After filtration, NaBPh<sub>4</sub> (200 mg, 0.585 mmol) was added to the filtrate giving a brown precipitate, which was isolated by filtration, washed with water (10 mL), methanol

(10 mL) and petroleum spirits (10 mL), and dried *in vacuo* to give **5** as a tan powder (333 mg, 77%). Crystallisation by vapour diffusion of diethyl ether into a dichloromethane solution gave dark orange-brown blocks that lost solvent and crumbled upon removal from the supernatant. Found: C, 57.01; H, 3.94. C<sub>108</sub>H<sub>90</sub>BP<sub>4</sub>Pt<sub>2</sub>Se<sub>2</sub>Tl requires C, 57.02; H, 3.99%. ESI MS, [Pt<sub>2</sub>(μ-Se)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]<sup>+</sup>, *m/z*. 1956 (100%). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 18.3 [s, <sup>1</sup>J(PtP) 3061].

#### **Synthesis of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlBrPh]BPh<sub>4</sub> **6****

A mixture of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] **1** (200 mg, 0.133 mmol) and PhTlBr<sub>2</sub> (70 mg, 0.159 mmol) in methanol (20 mL) was stirred for 16 h, giving a cloudy yellow solution. After filtration, NaBPh<sub>4</sub> (200 mg, 0.585 mmol) was added to the clear yellow filtrate, giving a pale orange precipitate. The product was isolated by filtration, washed with methanol (5 mL), water (5 mL) and petroleum spirits (5 mL), and dried *in vacuo* to give **6** (159 mg, 55%). Found: C, 56.21; H, 4.08. C<sub>102</sub>H<sub>85</sub>BBrP<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>Tl requires C, 56.09; H, 3.92%. ESI MS, [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlBrPh]<sup>+</sup>, *m/z*. 1865 (100%). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 17.9 [s, <sup>1</sup>J(PtP) 3100], 17.2 [s, <sup>1</sup>J(PtP) 3090].

#### **Synthesis of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlBr<sub>2</sub>][TlBr<sub>4</sub>] **7****

An aqueous solution of TlBr<sub>3</sub> (*ca.* 0.0493 mmol Tl mL<sup>-1</sup>) was prepared by adding a slight excess of bromine to a suspension of TlBr (350 mg) in water (25 mL) until a permanent orange colour was formed, followed by briefly removing the excess bromine under reduced pressure.

To a suspension of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** (410 mg, 0.273 mmol) in methanol (30 mL) was added aqueous  $\text{TlBr}_3$  (11 mL, 0.546 mmol), resulting in rapid formation of an orange suspension. The mixture was stirred for 5h, the product filtered, washed with cold methanol (2 x 5 mL) and dried to give **7** (543 mg, 83%). Recrystallisation by vapour diffusion from dichloromethane-ether gave orange blocks, together with some white powdery material (*cis*- $\text{PtBr}_2(\text{PPh}_3)_2$ ). Found: C, 36.39; H, 2.55.  $\text{C}_{72}\text{H}_{60}\text{Br}_6\text{P}_4\text{Pt}_2\text{S}_2\text{Tl}_2$  requires C, 36.16; H, 2.53%. ESI MS, positive-ion  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2]^+$ ,  $m/z$  1867 (100%); negative-ion  $[\text{TlBr}_4]^-$ ,  $m/z$  525 (100%).  $^{31}\text{P}\{^1\text{H}\}$  NMR,  $\delta$  16.0 [d,  $^1\text{J}(\text{PtP})$  3155,  $^2\text{J}(\text{TlP})$  257].

### Crystal structure determinations

Crystal data and refinement details for the structures are given in Table 2. X-ray intensity data were collected on a Bruker SMART CCD diffractometer using standard procedures and software. Empirical absorption corrections were applied (SADABS) [54]. Structures were solved by direct methods and developed and refined on  $F_o^2$  using the SHELX programmes [55] operating under WinGX [56]. Hydrogen atoms were included in calculated positions.

### $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlPh}_2]\text{BPh}_4$ **4a**

Yellow crystals were obtained by vapour diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_2\text{Cl}_2$  solution of the complex at room temperature; the crystals readily lost solvent when removed from the supernatant.



Refinement of the cation and anion gave  $R_1$  0.075, with 10 residual peaks of 4-10  $e \text{ \AA}^{-3}$ , which were associated with a region of solvent about 1/2, 1/2, 1/2. These appeared to be very disordered  $\text{CH}_2\text{Cl}_2$  and/or  $\text{Et}_2\text{O}$ , which could not be modelled sensibly. This residual electron density was removed using the SQUEEZE routine of PLATON [57], which suggested there were approximately 3 solvent molecules on this site. Subsequent refinement against the corrected data led to the final residuals given.

*[Pt<sub>2</sub>( $\mu$ -S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlBrPh]BPh<sub>4</sub> 6*

Yellow-orange crystals were obtained by vapour diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_2\text{Cl}_2$  solution of the complex at room temperature; in contrast to **4a** the crystals were stable when removed from the supernatant. The presence of the heavy elements Pt, Tl, P, S and Br was confirmed by EDAX analysis on a crystal. Some residual electron density (3-4  $e \text{ \AA}^{-3}$ ) remained in the final difference map, which was clearly very poorly-ordered solvent, but this could not be sensibly modelled.

*[Pt<sub>2</sub>( $\mu$ -S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlBr<sub>2</sub>][TlBr<sub>4</sub>] 7*

Orange block crystals were obtained by vapour diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_2\text{Cl}_2$  solution of the complex at room temperature. The structure was solved by direct methods and developed normally. However when the main, expected, structure had been refined, there remained a large peak of electron density (12  $e \text{ \AA}^{-3}$ ) near the Tl(1) atom, and a smaller one on a nearby inversion centre. These were interpreted as coming from a small fraction (< 10%) which had co-crystallised with the main  $\text{TlBr}_2$  species, containing a  $\text{Tl}_2\text{Br}_5$  moiety bridging two  $\text{Pt}_2\text{S}_2$  clusters. This refined sensibly. Hence the main species in the

unit cell contains a tetrahedral Tl(III) coordinated to two Br<sup>-</sup> and two S atoms from one Pt<sub>2</sub>S<sub>2</sub> unit (Figure 3). The minor component has a *pseudo*-tetrahedral Tl(III) coordinated to one of the S atoms and to three Br<sup>-</sup> anions, two of which coincide with the Br positions of the major component, while the third bridges to a centrosymmetrically related neighbour (Figures 4 and 5).

The extra Br<sup>-</sup> in the minor component is presumably compensated for by incomplete occupancy of the [TlBr<sub>4</sub>]<sup>-</sup> site, but this was not accommodated in the refinement so this small effect would have been hidden in the temperature factors of the anion.

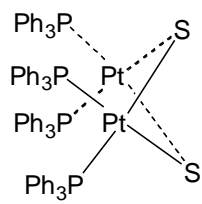
### **Supplementary information**

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 744027 (**4a**), 744028 (**6**) and 744029 (**7**). 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](mailto:deposit@ccdc.cam.ac.uk) or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

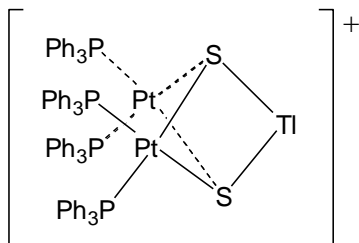
### **Acknowledgements**

We thank the University of Waikato and the National University of Singapore for financial support of this work, Dr. Tania Groutso (University of Auckland) and Dr. Jan Wikaira (University of Canterbury) for collection of the X-ray data sets. WH and TSAH

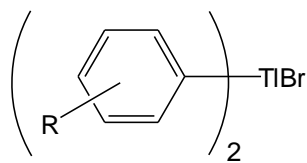
thank the Asia:NZ Foundation for a travel grant, facilitating exchange visits. WH thanks Pat Gread for technical support and Kelly Kilpin for recording the NMR spectra.



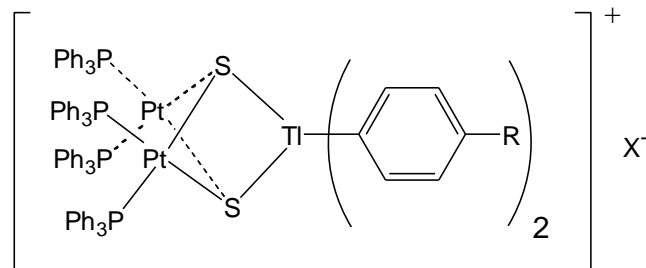
**1**



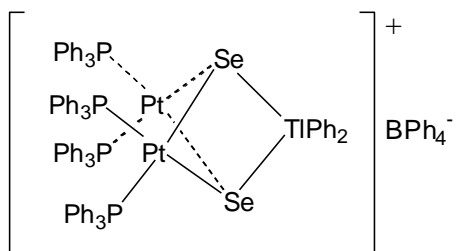
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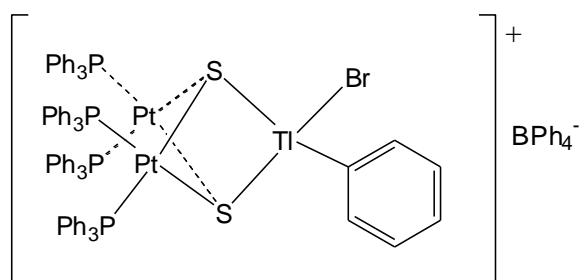
**3a**, R = H  
**3b**, R = *p*-Cl



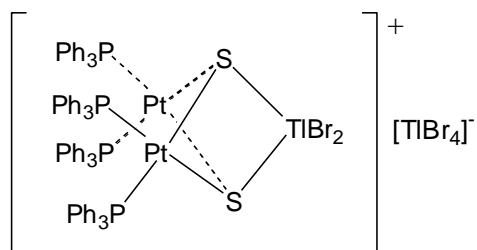
**4a**, R = H, X = BPh<sub>4</sub>  
**4b**, R = H, X = PF<sub>6</sub>  
**4c**, R = Cl, X = BPh<sub>4</sub>



**5**



**6**



**7**

**Table 1** Selected bond lengths (Å) and angles (°) for [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlPh<sub>2</sub>]BPh<sub>4</sub> **4a**, [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlBrPh]BPh<sub>4</sub> **6** and [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>TlBr<sub>2</sub>][TlBr<sub>4</sub>] **7**

	<b>4a</b>	<b>6</b>	<b>7</b>
Pt(1)-P(1)	2.2785(11)	2.2815(11)	2.277(3)
Pt(1)-P(2)	2.2944(11)	2.2907(11)	2.291(3)
Pt(2)-P(3)	2.2917(10)	2.2853(12)	2.296(3)
Pt(2)-P(4)	2.2867(10)	2.2936(11)	2.280(3)
Pt(1)-S(1)	2.3709(10)	2.3704(11)	2.379(2)
Pt(1)-S(2)	2.3752(10)	2.3934(11)	2.407(2)
Pt(2)-S(1)	2.3756(10)	2.3770(11)	2.379(2)
Pt(2)-S(2)	2.3742(10)	2.3653(10)	2.397(2)
Tl(1)-S(1)	2.7014(10)	2.6089(11)	2.543(3)
Tl(1)-S(2)	2.6957(10)	2.5667(12)	2.532(3)
Tl(1)-C(1)		2.174(5)	
Tl(1)-C(11)	2.209(4)		
Tl(1)-C(21)	2.184(4)		
Tl(1)-Br(1)		2.6346(6)	2.5540(12)
Tl(1)-Br(2)			2.5492(12)
Pt(1)···Tl(1)	3.3341(2)	3.1767(3)	3.1913(6)
Pt(2)···Tl(1)	3.4428(2)	3.3908(3)	3.2924(6)
P(1)-Pt(1)-P(2)	98.70(4)	101.28(4)	98.53(9)
P(3)-Pt(2)-P(4)	99.63(4)	98.27(4)	99.24(10)
S(1)-Pt(1)-S(2)	81.31(3)	81.14(4)	81.34(8)
S(1)-Pt(2)-S(2)	81.23(3)	81.59(4)	81.54(8)
Pt(1)-S(1)-Pt(2)	87.06(3)	86.08(4)	85.98(8)
Pt(1)-S(2)-Pt(2)	87.00(3)	85.83(4)	84.97(8)
Pt(1)-S(1)-Tl(1)	81.91(3)	79.12(3)	80.77(8)
Pt(1)-S(2)-Tl(1)	81.96(3)	79.57(3)	80.47(7)
Pt(2)-S(1)-Tl(1)	85.14(3)	85.57(3)	83.89(8)
Pt(2)-S(2)-Tl(1)	85.29(3)	86.77(4)	83.78(8)
S(1)-Tl(1)-S(2)	69.91(3)	73.54(3)	75.84(8)
C(11)-Tl(1)-C(21)	129.07(16)		
C(11)-Tl(1)-S(1)	116.81(11)		
C(11)-Tl(1)-S(2)	100.44(12)		
C(21)-Tl(1)-S(1)	101.61(13)		
C(21)-Tl(1)-S(2)	124.43(11)		
C(1)-Tl(1)-Br(1)		107.44(14)	
C(1)-Tl(1)-S(1)		116.04(14)	
C(1)-Tl(1)-S(2)		133.70(14)	
Br(1)-Tl(1)-S(1)		112.87(3)	120.85(6)
Br(1)-Tl(1)-S(2)		109.13(3)	122.90(6)
Br(2)-Tl(1)-S(1)			120.00(6)
Br(2)-Tl(1)-S(2)			114.78(6)
Br(2)-Tl(1)-Br(1)			102.32(4)

**Table 2** Crystal data and refinement details for **4a**, **6** and **7**

<b>Complex</b>	<b>4a</b>	<b>6</b>	<b>7</b>
Molecular formula*	C <sub>108</sub> H <sub>90</sub> BP <sub>4</sub> Pt <sub>2</sub> S <sub>2</sub> Tl	C <sub>102</sub> H <sub>85</sub> BBrP <sub>4</sub> Pt <sub>2</sub> S <sub>2</sub> Tl	C <sub>72</sub> H <sub>60</sub> Br <sub>6</sub> P <sub>4</sub> Pt <sub>2</sub> S <sub>2</sub> Tl <sub>2</sub>
Formula weight*	2181.16	2183.97	2391.58
Temperature (K)	89(2)	93(2)	89(2) K
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c	C2/c	P2 <sub>1</sub> /c
Unit cell dimensions			
<i>a</i> (Å)	13.2674(2)	45.2398(19)	14.3251(2)
<i>b</i> (Å)	28.5928(1)	16.4955(7)	17.1538(2)
<i>c</i> (Å)	26.8894(3)	29.4457(12)	29.6997(2)
β (°)	99.125(1)	122.714(2)	93.518(1)
<i>V</i> (Å <sup>3</sup> )	10071.46(19)	18488.4(13)	7284.35(14)
<i>Z</i>	4	8	4
<i>D</i> <sub>(calc)</sub> (g cm <sup>-3</sup> )*	1.438	1.569	2.181
μ(Mo-Kα) (mm <sup>-1</sup> )*	4.516	5.350	11.717
<i>F</i> (000)*	4288	8528	4448
Crystal size (mm)	0.38 x 0.32 x 0.24	0.80 x 0.45 x 0.02	0.32 x 0.26 x 0.22
θ range for data collection (°)	1.05 to 26.41	1.89 to 30.54	1.37 to 26.44
Reflections collected	59629	145009	42749
Independent reflections	20548	27812	14925
<i>R</i> <sub>(int)</sub>	0.0329	0.0563	0.0577
Max and min. transmission	0.4103 and 0.2787	1.000 and 0.424	0.1825 and 0.1173
Data/restraints/parameters	20548 / 0 / 1063	27812 / 0 / 1018	14925 / 0 / 804
GOF on <i>F</i> <sup>2</sup>	1.075	1.056	1.078
Final <i>R</i> indices			
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0313	0.0341	0.0520
<i>R</i> <sub>1</sub> (all data)	0.0395	0.0532	0.0830
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0639	0.1030	0.1042
<i>wR</i> <sub>2</sub> (all data)	0.0668	0.1143	0.1165
Largest peak and hole (e Å <sup>-3</sup> )	1.375 -1.526	4.432 -1.295	4.215 -2.438

\* These ignore the unidentified disordered solvent that was not included in the refinement for **4a** and **6**.

## Captions for Figures

**Fig. 1** Molecular structure of the cation of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlPh}_2]\text{BPh}_4$  **4a**, with phenyl rings of the triphenylphosphine ligands omitted for clarity.

**Fig. 2** Molecular structure of the cation of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBrPh}]\text{BPh}_4$  **6**, with phenyl rings of the triphenylphosphine ligands omitted for clarity.

**Fig. 3** Molecular structure of the cation of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{TlBr}_2][\text{TlBr}_4]$  **7**, with phenyl rings of the triphenylphosphine ligands omitted for clarity.

**Fig. 4** Molecular structure of the core of the minor co-crystallised species  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]\text{Tl}_2\text{Br}_5]^+$ , with phenyl rings omitted for clarity.

**Fig. 5** Structure of the composite core of the co-crystallised species in **7**, showing the major  $\text{TlBr}_2^+$  adduct (solid lines) and its relationship to the minor  $\text{Tl}_2\text{Br}_5^+$  component (dotted lines)

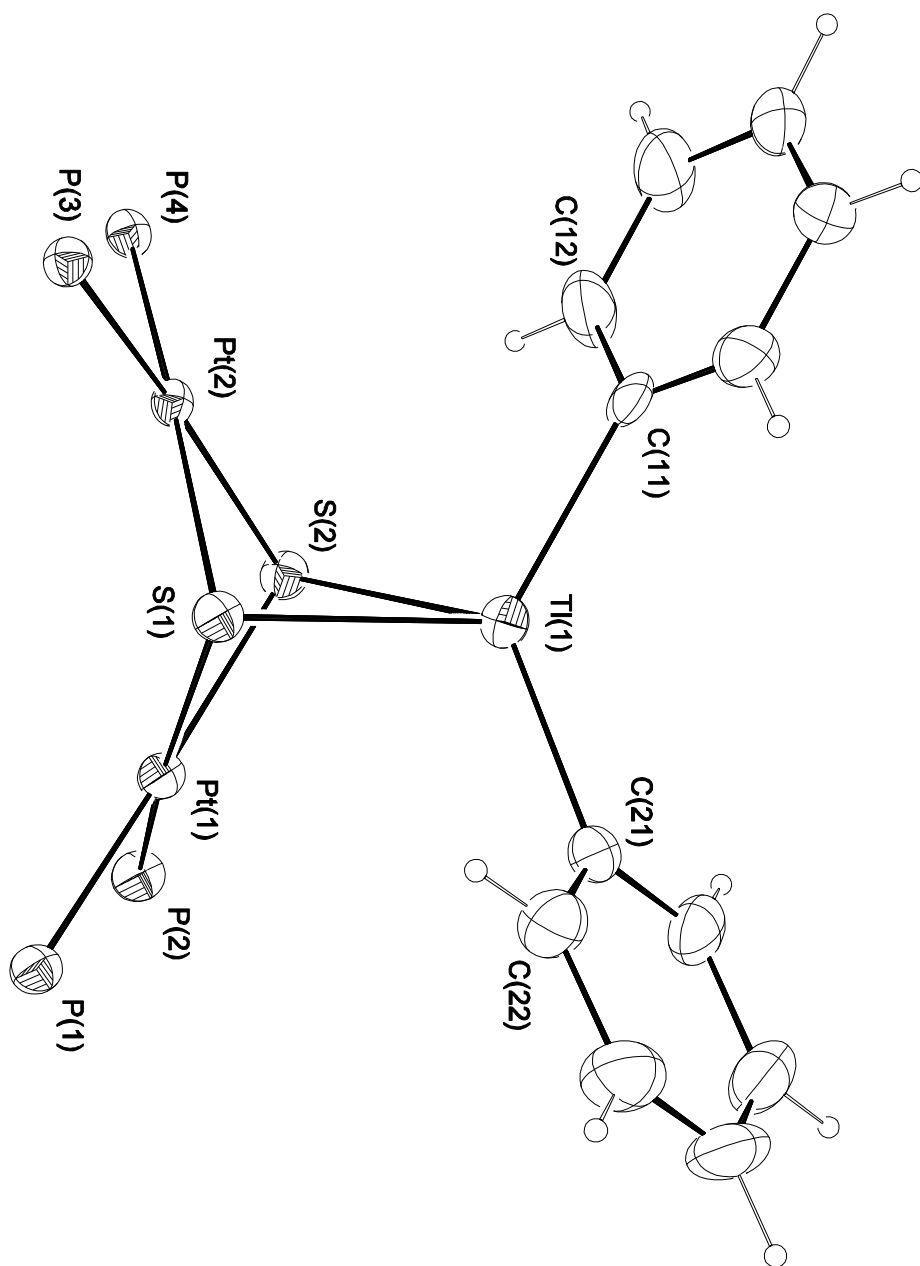


Figure 1



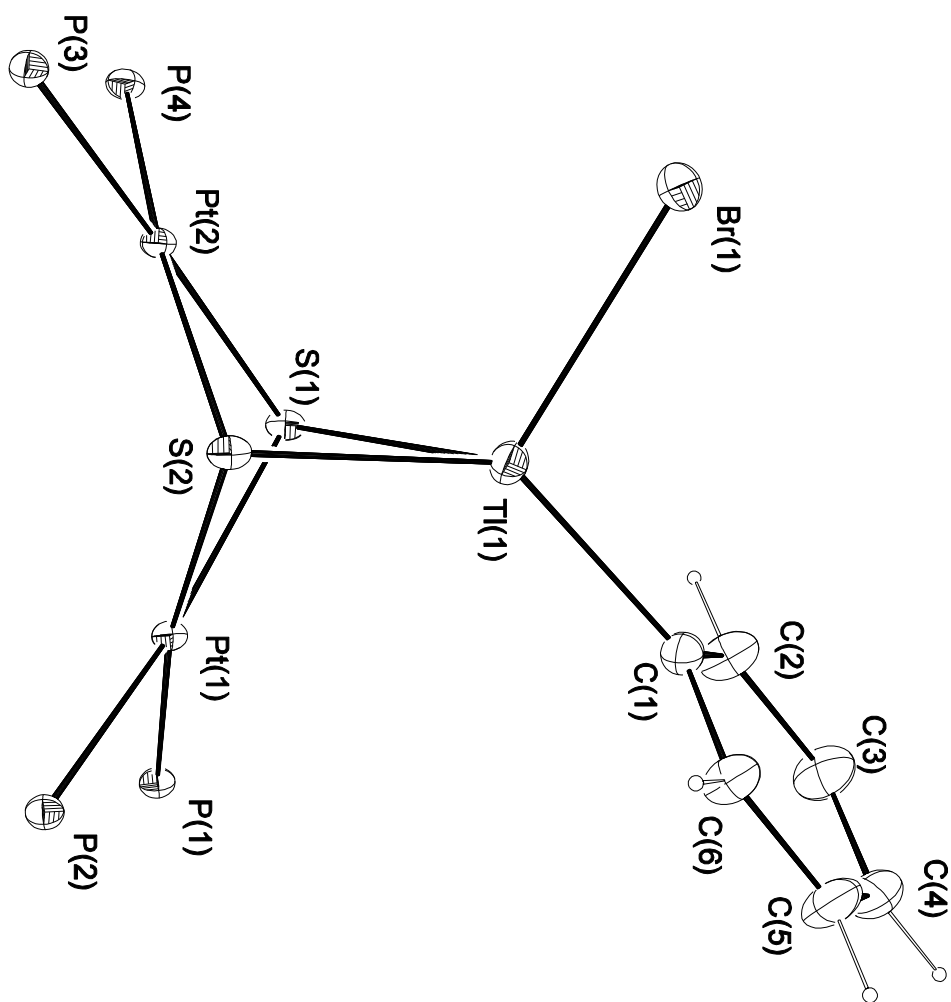
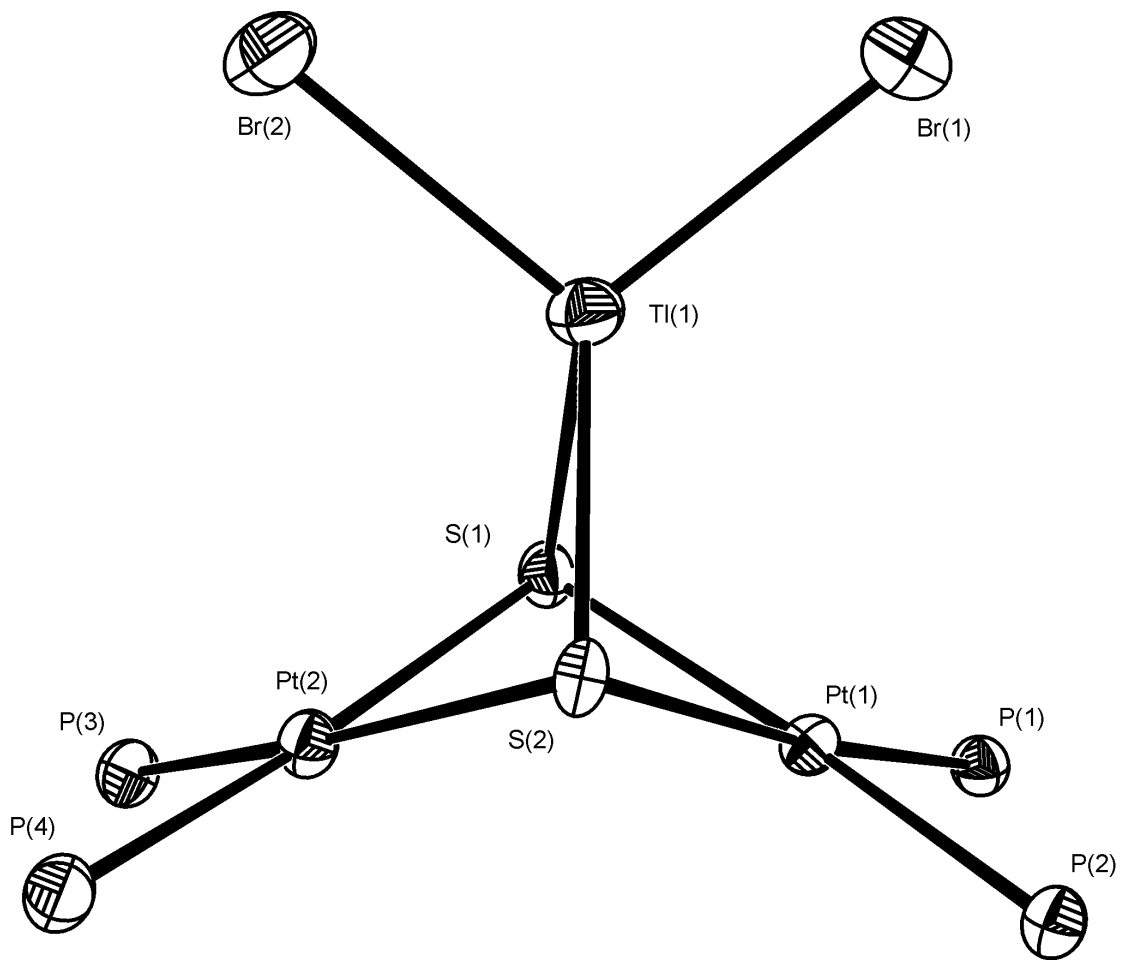
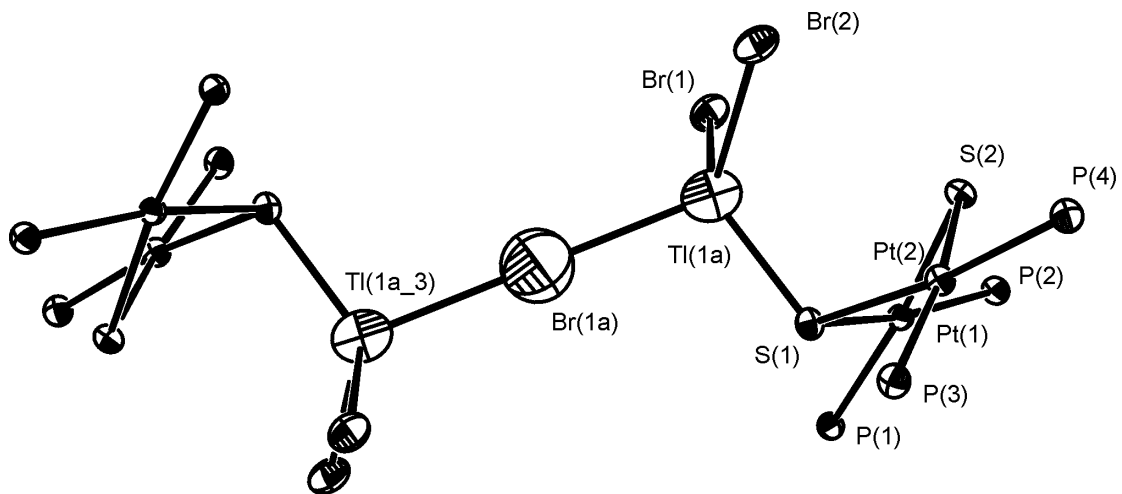


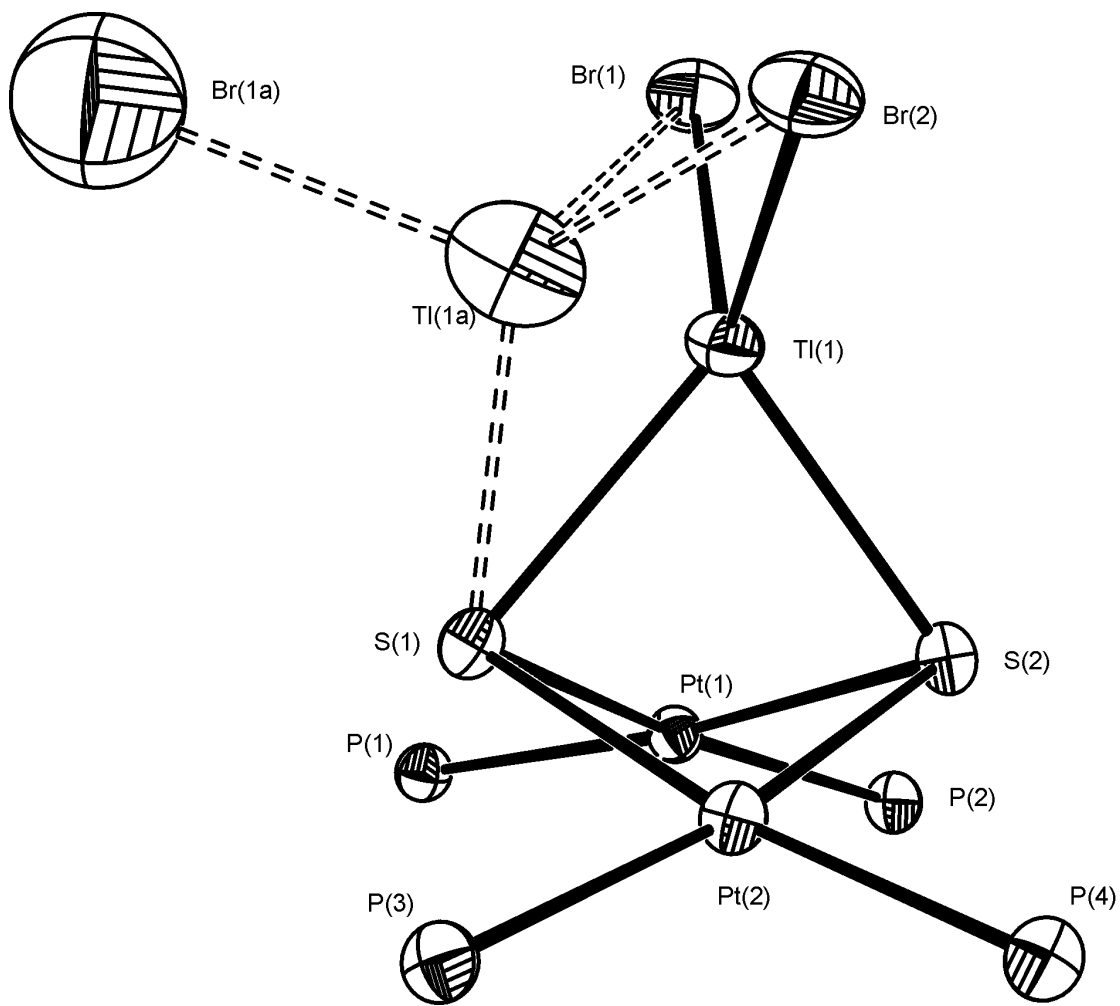
Figure 2



**Figure 3**



**Figure 4**



**Figure 5**

## References

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