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An investigation of the mixed-bridge dinuclear complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$

William Henderson [a],*, Allen G. Oliver [b]

[a] Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand
[b] Molecular Structure Facility, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

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ABSTRACT

The product formed by reaction of *cis*-$[PtCl_2(PPh_3)_2]$, NH_3 and Na_2S in ethanol, previously reported as $[Pt_2(\mu\text{-}S)(PPh_3)_4]$, has been reinvestigated by electrospray ionisation mass spectrometry (ESI MS) and found to consist of the ethanol solvate of the well-known metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ together with the novel mixed-ligand complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$. Upon prolonged ageing in air, a mixture of this complex with $[Pt_2(\mu\text{-}S)(\mu\text{-}O)(PPh_3)_4 + H]^+$ is observed by ESI MS. $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ can be prepared from *cis*-$[PtCl_2(PPh_3)_2]$ and aqueous NH_3 using a stoichiometric quantity of sodium sulfide, or by reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with 2-chloro-1-methylpyridinium tetraphenylborate and ammonia; the complex was structurally characterised as its tetraphenylborate salt. This novel desulfurisation reaction was serendipitously discovered during investigations on the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards 2-chloro-1-methylpyridinium iodide giving the known iodo complex $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$, isolated as either the PF_6^- or I^- salts.

1. Introduction

The platinum(II) sulfide complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** has been known for many years [1], and has a rich and constantly evolving chemistry both as a nucleophile (towards organic electrophiles) [2–6] and as a metalloligand [7–9]; its chemistry has been previously reviewed [10,11]. The chemistry of this complex can be conveniently probed using electrospray ionisation mass spectrometry (ESI MS) [12], a technique which allows analysis of either reaction solutions or isolated products, using miniscule quantities of sample, and which generally provides an accurate picture of speciation. We have been using ESI MS to identify interesting reaction products of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ which can then be characterised by more traditional macroscopic techniques. As an illustration of this approach, we have previously identified the mixed sulfido–iodo complex $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ **2** in reaction mixtures of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with various iodine sources (metal iodide complexes, elemental I_2), which led to the successful synthesis and characterisation of this complex [13]. In this paper we report studies into the novel, hybrid sulfido–amido complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ **3**, which was also initially identified using ESI MS investigations.

2. Results and discussion

2.1. Initial identification of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ 3 from a mass spectrometric re-investigation of $[Pt_2(\mu\text{-}S)(PPh_3)_4]$

Our initial entry into the chemistry of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ **3** arose from a re-investigation of the platinum(I) sulfide complex $[Pt_2(\mu\text{-}S)(PPh_3)_4]$ **4** reported by Chatt and Mingos [14]. The ease of ESI MS detection of the platinum(II) complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** *via in situ* protonation of a sulfide ligand [15,16] and the known metalloligand properties of the sulfide ligand of related platinum(I) complexes with $\{Pt_2S\}$ cores (promoted by ancillary monodentate $Ph_2PCH_2PPh_2$ ligands) [17] suggested that $[Pt_2(\mu\text{-}S)(PPh_3)_4]$ **4** might also show significant basicity and be observable by ESI MS, leading to exploration of a parallel chemistry of this platinum(I) sulfide complex.

The literature synthesis of **4** involves reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with Na_2S in ethanol in the presence of added ammonia, giving a yellow solid product. With the benefit of ESI MS (a technique not available to Chatt and Mingos), investigations on this material (below) suggest that it is better formulated as an impure sample of the ethanol solvate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]{\cdot}2EtOH$ [18]. Firstly, the ESI mass spectrum of a freshly prepared sample of Chatt and Mingos' product, hereafter **5**, in methanol showed predominantly $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, as its protonated ion

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* Corresponding author. Tel.: +64 7 838 4656.
E-mail address: w.henderson@waikato.ac.nz (W. Henderson).

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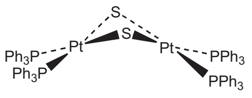
$[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$ [15,16], though other species were also observed in varying amounts depending on the conditions (*vide infra*). Secondly, heating the yellow solid product **5** briefly to 100 °C caused it to turn orange; when this orange solid was re-suspended in methanol, it rapidly turned yellow (consistent with the behaviour of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and its alcohol solvates) [18], and the ESI mass spectrum was unchanged by this procedure. Thirdly, Chatt and Mingos reported [14] that the yellow product can be recrystallised from benzene-light petroleum to give an orange solid, and we concur with these findings. However, we also observe that an authentic sample of yellow $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 2MeOH$ [18] gives an orange suspension and solution upon stirring in benzene, with the orange solution fairly quickly depositing an orange solid which was visibly indistinguishable from a sample of unsolvated $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ suspended in benzene.

In the ESI mass spectrum of the isolated putative complex $[Pt_2(\mu\text{-}S)(PPh_3)_4]$, hereafter numbered **5**, a number of other species were observed, the most significant being a monocationic species at *m*/*z* 1486. Examination of the high resolution isotope pattern of this ion suggested it to be $[Pt_2SNH_2(PPh_3)_4]^+$ [observed *m*/*z* 1486.280, calculated for $C_{72}H_{62}NP_4Pt_2S$ 1486.284, with excellent agreement between observed and calculated isotope patterns]. This complex was subsequently shown to be the μ-amido complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ (*vide infra*). The source of the nitrogen is clearly the ammonia used in the synthesis, but no nitrogen analytical data were reported by Chatt and Mingos [14]. Elemental microanalysis of the sample of $[Pt_2(\mu\text{-}S)(PPh_3)_4]$ (**5**) showed a low nitrogen content (<0.2%), so the amount of the nitrogen-containing complex in the isolated solid product must be relatively small since $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]Cl$ would have 0.92% N. When the yellow solid of **5** is thoroughly washed with methanol, and the solid residue analysed by ESI MS, the amido derivative is eliminated, and only $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$ was observed. These observations are consistent with sample **5** (as prepared by the method of Chatt and Mingos) being predominantly the sparingly soluble di-ethanol solvate of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** containing some of the (more soluble) cation $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ **3**, presumably as its chloride salt.

The reaction between *cis*-$[PtCl_2(PPh_3)_2]$, NH_3 and excess Na_2S in ethanol was subsequently investigated by ESI MS. Analysis of a small aliquot of the homogenous mixture showed $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ as essentially the only species, but some yellow solid (insoluble $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ as its alcohol solvate) was present. Acidification of the aliquot for MS analysis with formic acid resulted in protonation of the platinum species, providing a more representative indication of the relative amounts of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$ (*ca.* 50% of each). Consistent with these observations, isolation, washing and ESI MS analysis of the yellow solid from the reaction mixture showed almost exclusively $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$.

Supporting evidence for the incorporation of an amido group in **3** came from an analogous reaction mixture involving *cis*-$[PtCl_2(PPh_3)_2]$ with $EtNH_2$ (in place of ammonia) and Na_2S in ethanol; this also gave a yellow suspension which showed $[Pt_2(\mu\text{-}S)(\mu\text{-}NHEt)(PPh_3)_4]^+$ (*m*/*z* 1514.37) as the base peak in the ESI mass spectrum. When formic acid was added to the sample used for MS analysis, the yellow solid dissolved and MS analysis showed a mixture of $[Pt_2(\mu\text{-}S)(\mu\text{-}NHEt)(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$ in approximately equal amounts.



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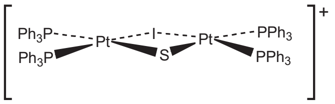

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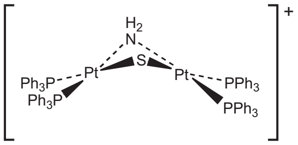

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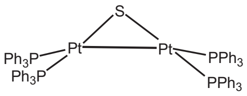

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Re-examination of a sample of **5** which had been allowed to stand in air for *ca.* 4 years revealed interesting observations. ESI MS analysis showed a peak in the expected region, however the isotope pattern did not match that of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$, and peaks were shifted slightly to higher *m*/*z* values. The isotope pattern could however be interpreted if a contribution from the (1 Da heavier) species $[Pt_2(\mu\text{-}S)(\mu\text{-}O)(PPh_3)_4 + H]^+$ is included; this mixed oxo-sulfido species has not been reported previously, and so the site of protonation is therefore not known. However, it is quite probable that the more basic O atom is protonated, resulting in a hydroxo ligand, i.e. $[Pt_2(\mu\text{-}S)(\mu\text{-}OH)(PPh_3)_4]^+$. Fig. 1 shows a comparison of the experimental isotope pattern of the *m*/*z* 1487 ion with the modelled isotope pattern generated with contributions from 42% $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ and 58% $[Pt_2(\mu\text{-}S)(\mu\text{-}O)(PPh_3)_4 + H]^+$,

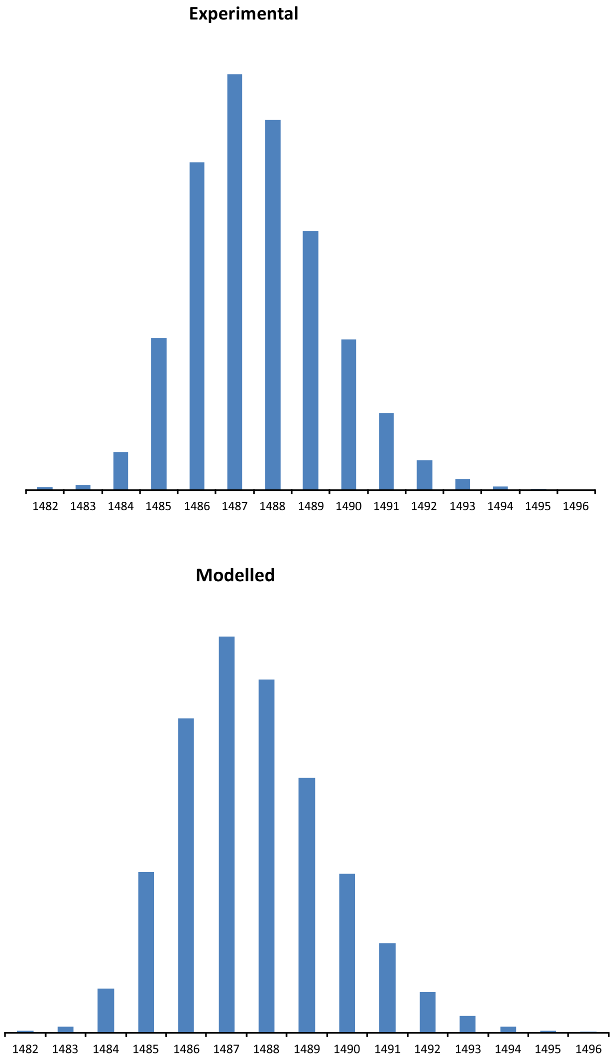


Fig. 1. A comparison of the (upper) experimental isotope pattern for the *m*/*z* 1487 ion observed for an aged sample of putative $[Pt_2(\mu\text{-}S)(PPh_3)_4]$ **5** compared to (lower) the modelled isotope pattern generated with contributions from 42% $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ (calculated *m*/*z* 1486.28) and 58% $[Pt_2(\mu\text{-}S)(\mu\text{-}O)(PPh_3)_4 + H]^+$ (calculated *m*/*z* 1487.27).

which gave the best agreement with the observed pattern. An independently prepared sample, analysed after a different amount of time, showed a *m*/*z* 1487 ion with a different isotope pattern, supportive of the presence of two species in differing amounts.

2.2. Synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]BPh_4$ from cis-$[PtCl_2(PPh_3)_2]$

Unlike the multitude of complexes containing the $\{Pt_2(\mu\text{-}S)_2\}$ core, to date there are no reported examples of complexes containing $\{Pt_2(\mu\text{-}S)(\mu\text{-}N)\}$ cores. We therefore set out to develop rational syntheses of the complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$, in order to fully characterise it. Synthetic methods are summarised in Scheme 1.

$[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ can be obtained from the reaction between *cis*-$[PtCl_2(PPh_3)_2]$, NH_3 and Na_2S in ethanol (Scheme 1) – effectively the method used by Chatt and Mingos [14] in their synthesis of putative $[Pt_2(\mu\text{-}S)(PPh_3)_4]$ (*vide supra*). However, this is not the preferred method due to the low yield resulting from the formation of considerable amounts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (as its ethanol solvate), even when one mole equivalent of Na_2S is used, and added slowly to the solution of *cis*-$[PtCl_2(PPh_3)_2]$ in ammonia–ethanol. After filtration to remove sparingly soluble $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, addition of excess $NaBPh_4$ to the filtrate gave the product $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]BPh_4$ (**3**·**BPh₄**) as a cream-coloured solid in 22% yield based on *cis*-$[PtCl_2(PPh_3)_2]$.

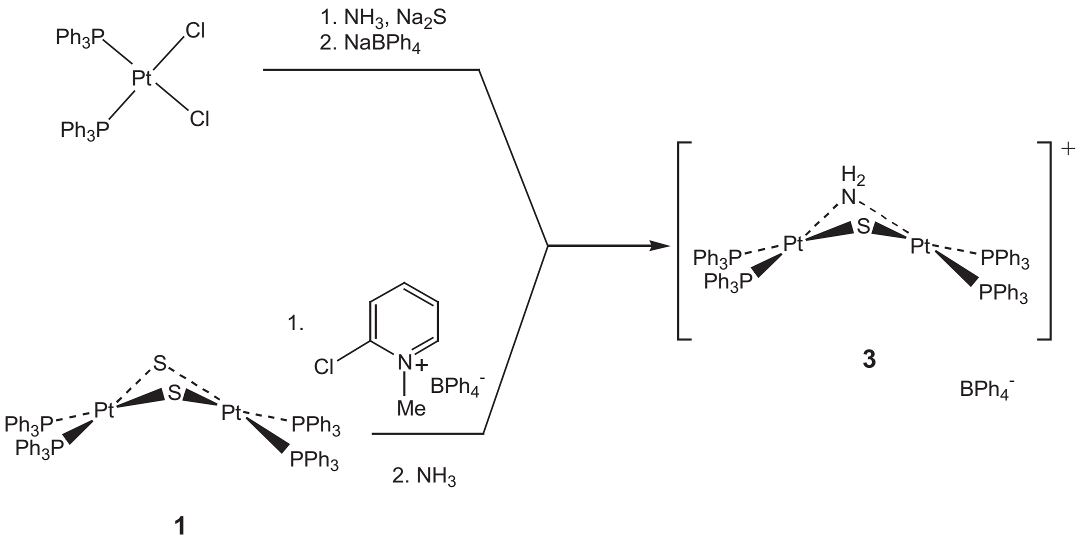
Despite the low yield, the product obtained by this method is, however, very pure by elemental microanalysis and by positive-ion ESI MS; Fig. 2 shows the ESI mass spectrum of the isolated product, with a dominant base peak due to the parent cation, and excellent agreement between observed (upper inset) and calculated (lower inset) isotope patterns for the ion. A minor dication at *ca.* *m*/*z* 751 was assigned as doubly protonated $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, presumably arising from traces of this compound present in the filtrate from which **3**·**BPh₄** was isolated. A deuterium exchange experiment, involving addition of a small quantity of NaOD in D_2O to a solution of **3**·**BPh₄** in 2:1 MeCN-D_2O, showed a 2 Da mass increase of the *m*/*z* 1486 ion, with no change in the isotope pattern, consistent with the presence of two exchangeable protons in the ion $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$. At elevated capillary exit voltages (>190 V), fragmentation occurs, initially by loss of a single PPh_3 ligand giving $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_3]^+$ at *m*/*z* 1223.8, together with a second fragment ion, which becomes more significant at capillary exit voltages >230 V, formed by loss of NH_3 (17 Da) from $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_3]^+$.

Complex **3**·**BPh₄** is very soluble in dichloromethane, in which it is stable, in contrast to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and other complexes with $\{Pt_2(\mu\text{-}S)_2\}$ cores, which are alkylated by CH_2Cl_2 [19-21]. The difference is undoubtedly related to the cationic charge on $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$, which reduces the nucleophilicity of the complex. Mono-alkylated and -arylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ [2–6,10] and $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ [13] are likewise stable in CH_2Cl_2.

2.3. Synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]BPh_4$ (**3**·**BPh₄**) from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ by non-reductive desulfurisation

During our ongoing investigations into the alkylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** the reaction with commercially available 2-chloro-1-methylpyridinium iodide was investigated, as a potential synthetic route to dicationic monoalkylated derivatives. However, this chemistry leads to the serendipitous discovery of a novel desulfurisation reaction of the complex, which has been exploited to provide a facile synthesis of the complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ (*vide infra*). While desulfurisation reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ have been described previously, they inevitably involve a reductive process, involving metal–metal bond formation [22–24].

Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with 2-chloro-1-methylpyridinium iodide in methanol gave an orange solution which on addition of excess NH_4PF_6 gave an orange precipitate, identified as the sulfido–iodo complex $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]PF_6$ **2**·**PF₆**. This salt has been previously prepared by reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with iodine (followed by precipitation with NH_4PF_6) [13], a reaction which, while successful, is not particularly convenient due to the requirement for small, stoichiometric quantities of iodine. The positive ion ESI mass spectrum of the complex showed the $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ cation as the base peak at *m*/*z* 1597.17, with the isotope pattern in complete agreement with that expected. In addition, two minor ions were observed: $[Pt_2(\mu\text{-}SH)(\mu\text{-}I)(PPh_3)_4]^{2+}$ at *m*/*z* 798.15 (5%), due to protonation of the complex $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$, and $[Pt_2(\mu\text{-}S)(\mu\text{-}Cl)(PPh_3)_4]^+$ at *m*/*z* 1506.24 (3%). The latter complex is the chloride analogue of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$, and may represent an intermediate and/or by-product in the reaction. When $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was reacted with excess 2-chloro-1-methylpyridinium iodide, followed by addition of excess KI (in place of NH_4PF_6), an orange solid was



Scheme 1. Synthetic routes to the sulfido–amido complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]BPh_4$ **3**·**BPh₄**.

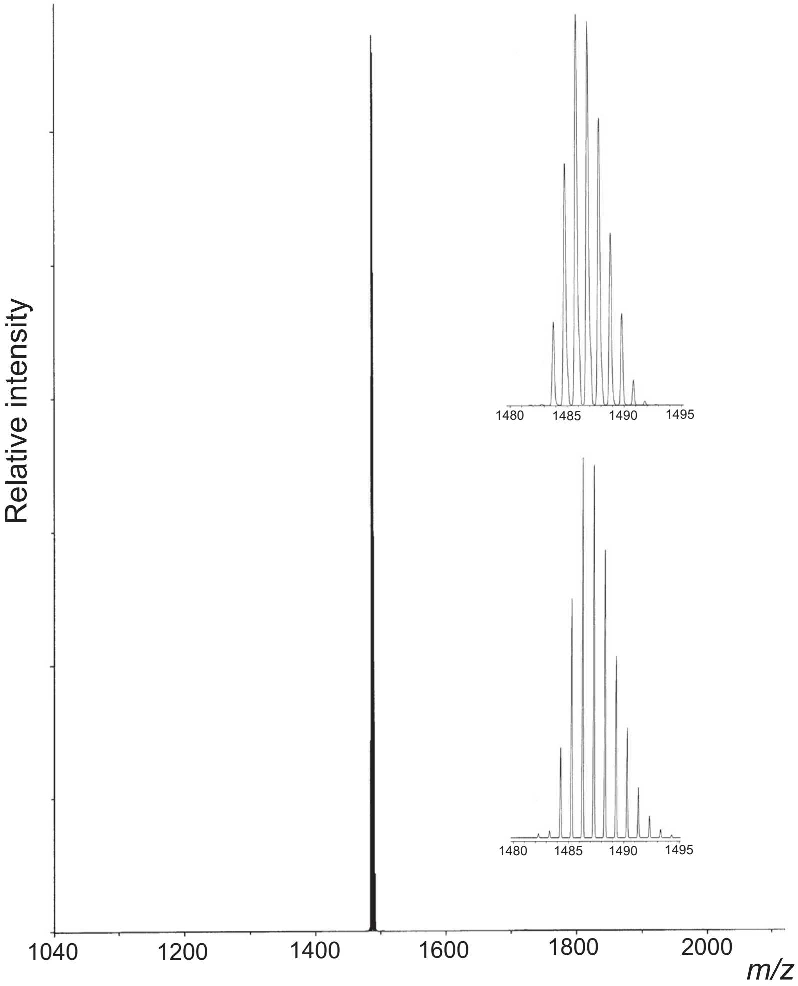


Fig. 2. Positive-ion ESI mass spectrum (CH_2Cl_2-MeOH solvent, capillary exit voltage 150 V) of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]BPh_4$ **3·BPh₄**, prepared from *cis*-$[PtCl_2(PPh_3)_2]$, NH_3 and $Na_2S{\cdot}9H_2O$; the insets show (upper) experimental and (lower) calculated isotope patterns for the ion $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$.

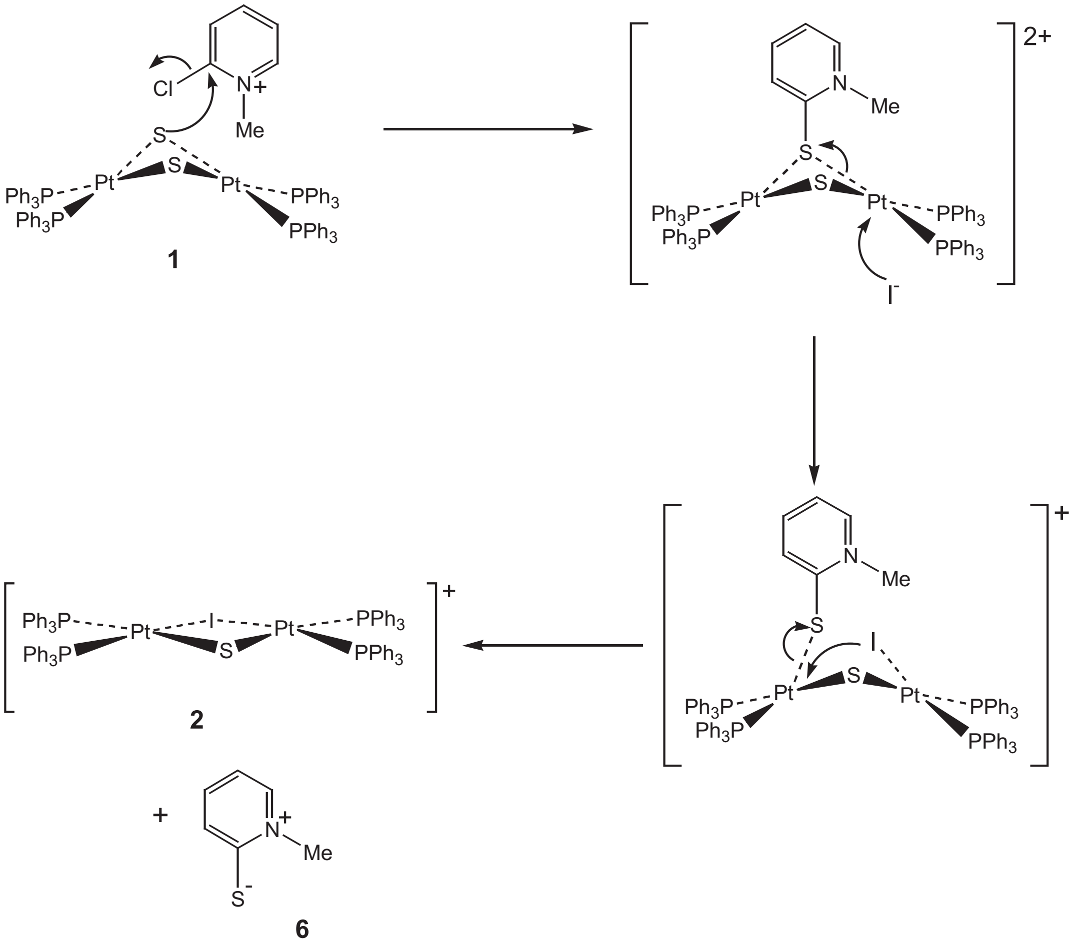
obtained in good yield, which was shown by ESI MS and NMR spectroscopy to be a highly pure sample of the $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ cation as its iodide salt, *viz* $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]I$ (**2·I**), with no detectable impurity ions. The formation of a pure product is clearly promoted by the excess iodide ions, which displace any weakly-binding chloride. The iodide salt gave $^{31}P\{^1H\}$ NMR data that were virtually indistinguishable from the PF_6^- salt.

A possible reaction sequence for the conversion of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ is shown in Scheme 2. The first step involves arylation of a μ-sulfido ligand with the 2-chloropyridinium arylating agent to form a dicationic monoarylated derivative. 2-Halopyridines are known to have reactive C–Cl bonds that are susceptible to nucleophilic substitution reactions, and more specifically the C–Cl bond of 2-chloro-1-methylpyridinium has been reported to undergo reaction with sulfur-based nucleophiles [25,26]. The dicationic nature of the resulting complex imparts unique reactivity; nucleophilic attack of the iodide counterion at platinum (promoted by its dipositive charge), with concomitant loss of 1-methylpyridinium-2-thiolate **6** (Scheme 2) results in conversion to the product cation. The pyridinium thiolate leaving group is uncharged, and we believe that it is this feature which makes it a good leaving group.

The observation of the μ-chloro analogue $[Pt_2(\mu\text{-}S)(\mu\text{-}Cl)(PPh_3)_4]^+$ in the mass spectrum of the complex $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ suggested that the former might be a useful precursor to a wide range of new complexes with $\{Pt_2(\mu\text{-}S)(\mu\text{-}X)\}$ cores, including $\{Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)\}$. However, in order to eliminate the nucleophilic iodide ion, 2-chloro-1-methylpyridinium iodide was metathesised to the tetraphenylborate salt. This salt has been previously reported in the patent literature [27,28]. A convenient synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ **3** then results from addition of excess NH_3 to the crude reaction suspension generated from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and 2-chloro-1-methylpyridinium tetraphenylborate, Scheme 1. ESI MS analysis of the product isolated by simple filtration and washing showed it to contain the $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ cation (*m*/*z* 1486.98) with good purity, while the negative ion ESI mass spectrum showed an intense ion at *m*/*z* 319 confirming the BPh_4^- ion. Comparison of the experimental isotope pattern of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ with the calculated pattern also showed good agreement.

2.4. Characterisation of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]BPh_4$ (**3·BPh₄**)

The $^{31}P\{^1H\}$ NMR spectrum of **3·BPh₄** showed two resonances as multiplets at δ 21.2 and 17.8 showing $^1J(PtP)$ coupling constants of 2610 and 3313 Hz, respectively. The overall spectral appearance is very similar to that of $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ [13]. The smaller coupling constant is assigned to the phosphines *trans* to the higher *trans* influence sulfide ligand, and not surprisingly the value in $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ (2610 Hz) is very similar to $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ (2619 Hz) [13]. The coupling constant for the phosphines *trans* to NH_2 (3313 Hz) is reasonably comparable to the value of 3053 Hz in the amido bridged complex $[Pt_2(\mu\text{-}NH_2)_2(PMePh_2)_4](BF_4)_2$ [29], and is considerably smaller than the



Scheme 2. Proposed reaction scheme for the conversion of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] to [Pt$_2$(μ-S)(μ-I)(PPh$_3$)$_4$]$^+$ using 2-chloro-1-methylpyridinium iodide. The corresponding chloro species [Pt$_2$(μ-S)(μ-Cl)(PPh$_3$)$_4$]$^+$ can be formed as a trace impurity species from the (leaving group) Cl$^-$.

coupling constant for phosphines *trans* to iodide in [Pt$_2$(μ-S)(μ-I)(PPh$_3$)$_4$]$^+$ (4265 Hz). The ^{1}H NMR spectrum shows, in addition to the complex set of PPh$_3$ resonances, a singlet at δ −0.41 that is tentatively assigned to the NH$_2$ protons. This resonance is assigned on the basis of broadening of the base of the resonance (due to ^{195}Pt coupling), and comparison with the ^{1}H NMR chemical shifts of μ-NH$_2$ groups in a series of platinum(II) μ-amido complexes such as [Pt$_2$(μ-NH$_2$)$_2$H$_2$(PPh$_3$)$_2$], which has μ-NH$_2$ resonances at δ 0.06 and −1.10 for the *anti* and *syn* isomers, respectively [30,31]. The IR spectrum of **3**·**BPh$_4$** showed the expected features due to an aryl-rich complex (e.g. bands at 1435 and 1480 cm^{-1}) together with two weak bands at 3352 and 3277 cm^{-1}, which compare well with values of 3358 and 3263 cm^{-1} reported for the NH$_2$ stretches in the complex [Pt$_2$(μ-NH$_2$)$_2$(PMePh$_2$)$_4$](BF$_4$)$_2$ [29].

In order to unambiguously characterise the complex, a single-crystal X-ray diffraction study was carried out; suitable crystals of **3**·**BPh$_4$** were obtained from dichloromethane–diethyl ether. There are four molecules of the Pt complex, associated BPh$_4$ anions and diethyl ether of crystallisation in the unit cell of the primitive, centrosymmetric, monoclinic space group $P2_1/n$. The molecular structure of the core of the cation together with the atom numbering scheme is shown in Fig. 3, and selected bond lengths and angles are summarised in Table 1. The complex contains a four-membered {Pt$_2$(μ-S)(μ-NH$_2$)} core with platinum centres coordinated in a square-planar fashion by two triphenylphosphines and bridged to the other Pt by μ$_2$-sulfido and μ$_2$-amido (NH$_2$) ligands. Support for the presence of an NH$_2$ group (as opposed to μ-SH and μ-NH groups) is the location of the amide hydrogens at reasonable positions from a difference Fourier map. Chemically, this is also the most sensible arrangement, with protonation occurring at the more basic N atom.

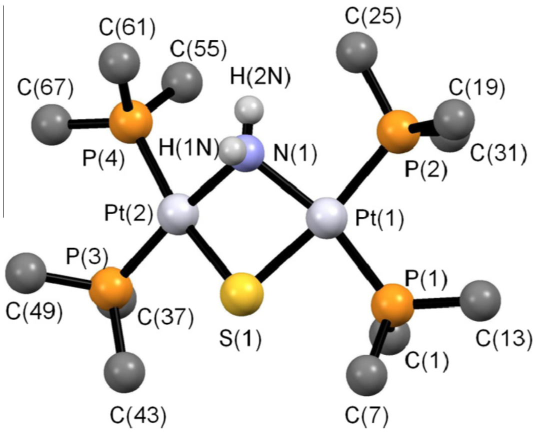


Fig. 3. X-ray structure of the core of the cation of [Pt$_2$(μ-S)(μ-NH$_2$)(PPh$_3$)$_4$]BPh$_4$ **3**·**BPh$_4$** showing the atom numbering scheme; only *ipso* carbon atoms of the PPh$_3$ ligands are shown for clarity.

The bond distances and angles within the molecules are as expected. The Pt–S–Pt angle is acute at 85.45(2)°, while the Pt–N–Pt angle shows less strain at 95.14(7)°. The complexes [Pt$_2$(μ-NH$_2$)$_2$

Table 1
Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]BPh_4$ **3·BPh₄**.

Pt(1)–N(1)	2.1358(17)	Pt(2)–N(1)	2.1525(17)
Pt(1)–S(1)	2.3427(6)	Pt(2)–S(1)	2.3225(7)
Pt(1)–P(1)	2.2696(6)	Pt(1)–P(2)	2.3010(6)
Pt(2)–P(3)	2.2482(6)	Pt(2)–P(4)	2.2835(6)
N(1)–H(1N)	0.8827	N(1)–H(2N)	0.8900
Pt(2)–S(1)–Pt(1)	85.45(2)	Pt(1)–N(1)–Pt(2)	95.14(7)
N(1)–Pt(1)–P(1)	165.33(5)	N(1)–Pt(1)–P(2)	91.44(5)
P(1)–Pt(1)–P(2)	102.62(2)	N(1)–Pt(1)–S(1)	80.12(5)
P(1)–Pt(1)–S(1)	85.78(2)	P(2)–Pt(1)–S(1)	171.56(2)
N(1)–Pt(2)–P(3)	171.30(5)	N(1)–Pt(2)–P(4)	89.13(5)
P(3)–Pt(2)–P(4)	98.77(2)	N(1)–Pt(2)–S(1)	80.24(5)
P(3)–Pt(2)–S(1)	91.98(2)	Pt(1)–N(1)–H(1N)	111.7
Pt(2)–N(1)–H(1N)	108.2	Pt(1)–N(1)–H(2N)	122.4
Pt(2)–N(1)–H(2N)	123.6	H(1N)–N(1)–H(2N)	95.8

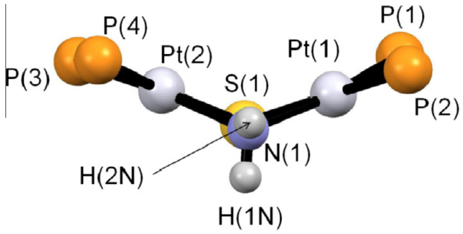


Fig. 4. Side view of the core of the complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ **3·BPh₄** (view along the S···N vector) showing the puckering of the four-membered $\{Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)\}$ core.

$(PMePh_2)_4]^{2+}$ [29] and *anti*-$[PtMe(PPh_3)(\mu\text{-}NH_2)_2PtMe(PPh_3)]$ [30,31] provide good examples of previous structural determinations of platinum(II) dimers containing $\mu\text{-}NH_2$ groups and phosphine ligands. The Pt–N–Pt angles are in the range of 95.2(4)° and 95.1(3)° in two independent molecules of *anti*-$[PtMe(PPh_3)(\mu\text{-}NH_2)_2PtMe(PPh_3)]$. The corresponding angle in $[Pt_2(\mu\text{-}NH_2)_2(PMePh_2)_4]^{2+}$ is 97.4(2)°.

The higher *trans*-influence [32] of sulfido compared to amido ligands is manifest in the Pt(1)–P(2) and Pt(2)–P(4) bond distances *trans* to sulfido [2.3010(6) and 2.2835(6) Å, respectively] being noticeably longer than Pt(1)–P(1) and Pt(2)–P(3) *trans* to amido [2.2696(6) and 2.2482(6) Å, respectively]. The four-membered $\{Pt_2SNH_2\}$ metallacycle is puckered (Fig. 4) with a dihedral angle of the intersecting coordination spheres across the S N vector of 135.04(2)°. This compares very well to the fold angle of *ca.* 135° in *anti*-$[PtMe(PPh_3)(\mu\text{-}NH_2)_2PtMe(PPh_3)]$ but is more puckered than $[Pt_2(\mu\text{-}NH_2)_2(PMePh_2)_4]^{2+}$ which has a fold angle of 148°.

3. Conclusions

From mass spectrometric investigations into the putative platinum(I) sulfide complex $[Pt_2(\mu\text{-}S)(PPh_3)_4]$ the novel amido complex $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ has been identified, leading to the development of two methods for its synthesis. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with NH_3 and one equivalent of Na_2S in ethanol results in the formation of the complex but significant $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ by-product is also formed. A preferable alternative utilises the arylation of a sulfide ligand of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with 2-chloro-1-methylpyridinium tetraphenylborate followed by reaction with ammonia to give $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]BPh_4$. This study has demonstrated the continued utility of ESI MS to explore this chemistry, and suggests that this methodology could provide an entry into a wide range of other new dinuclear platinum complexes with $\{Pt_2(\mu\text{-}S)(\mu\text{-}X)\}$ cores.

4. Experimental

4.1. Materials and instrumentation

Syntheses were carried out in LR grade solvents without regard for the exclusion of light, air or water. *cis*-$[PtCl_2(PPh_3)_2]$ was prepared by ligand substitution of the cyclo-octa-1,5-diene (cod) ligand of $[PtCl_2(cod)]$ [33] with 2 mol equivalents of PPh_3 in dichloromethane, followed by precipitation of the product with petroleum spirits. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was prepared by the literature procedure from *cis*-$[PtCl_2(PPh_3)_2]$ and $Na_2S{\cdot}9H_2O$ (Aldrich) in benzene suspension following the literature procedure [18]. The following chemicals were used as supplied from commercial sources: sodium tetraphenylborate (Aldrich), potassium iodide (BDH), concentrated aqueous ammonia (Ajax Chemicals), ammonium hexafluorophosphate (Aldrich), aqueous ethylamine solution (BDH), sodium deuteroxide in deuterium oxide (40 wt%, Aldrich), 2-chloro-1-methylpyridinium iodide (Aldrich).

Electrospray mass spectra were recorded on a Bruker MicrOTOF instrument, typically using a capillary exit voltage of 150 V for routine spectra. Solid compounds (*ca.* 0.5 mg) were dissolved in methanol (1.5 mL), or a few drops of dichloromethane followed by methanol in an Eppendorf tube, and centrifuged prior to MS analysis. Identification of ions utilised a comparison of *m*/*z* values and isotope patterns of observed and calculated ions, the latter obtained using either an internet-based program [34] (for low resolution matching), or proprietary instrument-based software. Reported *m*/*z* values are for the most intense peak in the isotopic envelope of the ion. Modelling of the isotope pattern produced by differing contributions of $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}S)(\mu\text{-}O)(PPh_3)_4 + H]^+$ was carried out using Microsoft Excel.

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solution on Bruker Avance spectrometers at 300 or 400 MHz (^1H); coupling constants are in Hz. Melting points were recorded on a Reichert Thermopan melting point instrument. Elemental analyses were obtained from the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

4.2. Synthesis of "$[Pt_2(\mu\text{-}S)(PPh_3)_4]$" **5**

This material was prepared following the procedure of Chatt and Mingos [14] from *cis*-$[PtCl_2(PPh_3)_2]$ (333 mg, 0.422 mmol) and $Na_2S{\cdot}9H_2O$ (330 mg, 1.37 mmol) in ethanol-aqueous ammonia. The yellow solid product was isolated by filtration and washed with a few mL of cold ethanol to remove soluble salts (N.B. washing was not reported in the literature procedure). The product was air-dried to give a yellow solid (247 mg), which was characterised by ESI MS.

4.3. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$, Na_2S and NH_3 in ethanol with ESI MS monitoring

cis-$[PtCl_2(PPh_3)_2]$ (100 mg) was suspended in ethanol (20 mL), concentrated aqueous NH_3 solution (0.5 mL) added and the mixture stirred for 5 min to give an almost clear, colourless solution. Solid $Na_2S{\cdot}9H_2O$ (110 mg) was added in one portion, giving the immediate formation of an orange solution which rapidly deposited a yellow solid. The reaction mixture was stirred for 24 h, and analysed by ESI MS. Methanol was used to dilute samples. A drop of the homogenised reaction suspension was analysed (showing predominantly $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$), and a portion of the yellow solid was isolated for MS analysis (showing predominantly $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$) by centrifugation and washing with ethanol.

4.4. Reaction of cis-[$PtCl_2(PPh_3)_2$], Na_2S and $EtNH_2$ in ethanol with ESI MS monitoring

This reaction was carried out as per the preceding reaction but replacing ammonia with ethylamine solution (0.5 mL), giving a yellow suspension. ESI MS *m*/*z* 1514.37 (calculated 1514.32), $[Pt_2(\mu\text{-}S)(\mu\text{-}NHEt)(PPh_3)_4]^+$ (100%). Addition of 2 drops 0.2% formic acid solution to the aliquot for MS analysis resulted in dissolution of the yellow solid giving a clear solution; ESI MS analysis showed $[Pt_2(\mu\text{-}S)(\mu\text{-}NHEt)(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$ in approximately equal amounts.

4.5. Synthesis of [$Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4$]$BPh_4$ from cis-[$PtCl_2(PPh_3)_2$], NH_3 and Na_2S

cis-$[PtCl_2(PPh_3)_2]$ (361 mg, 0.457 mmol) was suspended in ethanol (40 mL), concentrated aqueous ammonia (4 mL) added, and the mixture stirred for 5 min. to give an almost clear, colourless solution. To this was added dropwise a freshly prepared solution of Na_2S $9H_2O$ (110 mg, 0.458 mmol) in water (5 mL), resulting in an immediate yellow colouration to the solution followed by the gradual formation of a yellow precipitate. The mixture was stirred for 72 h, with no further change. The mixture was filtered to give a bright yellow solid (105 mg, which was shown to be $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ from ESI MS analysis of an acidified sample), and a pale yellow filtrate. Addition of $NaBPh_4$ (300 mg, 0.878 mmol) to the filtrate resulted in immediate formation of a cream precipitate which was filtered, washed with methanol–water (1:3, 10 mL) and dried under vacuum to give **3**·**BPh₄** (90 mg, 22% based on *cis*-$[PtCl_2(PPh_3)_2]$). Found: C, 63.62; H, 4.69; N, 0.80. $C_{96}H_{82}BNP_4Pt_2S$ requires C, 63.80; H, 4.58; N, 0.78%. ESI MS showed $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ as the dominant base peak, with a very minor dication at *ca.* *m*/*z* 751 assigned as $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + 2H]^{2+}$. $^{31}P\{^1H\}$ NMR (162 MHz), δ 21.2 [m, ^1J(PtP) 2610 and 17.8 [m, ^1J(PtP) 3313]. ^1H NMR, δ 7.49–6.89 (m, Ph) and −0.41 (s, br, NH_2).

4.6. Synthesis of [$Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4$]$PF_6$ (**2**·**PF₆**)

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (281 mg, 0.187 mmol) and 2-chloro-1-methylpyridinium iodide (56 mg, 0.219 mmol) in methanol (40 mL) was stirred, whereupon the platinum complex quickly dissolved giving an orange solution. After 15 min. the solution was filtered to remove a trace of insoluble matter, and NH_4PF_6 (300 mg, excess) was added to the filtrate to give an orange precipitate. Water (5 mL) was added to assist precipitation, the product filtered, washed with water (2 × 10 mL) and dried under vacuum to give 210 mg (64%) of **2**·**PF₆**. ESI MS *m*/*z* 1597.17, $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ (100%), *m*/*z* 1506.24, $[Pt_2(\mu\text{-}S)(\mu\text{-}Cl)(PPh_3)_4]^+$ (3%), *m*/*z* 798.15, $[Pt_2(\mu\text{-}SH)(\mu\text{-}I)(PPh_3)_4]^{2+}$ (5%). The compound was further characterised by $^{31}P\{^1H\}$ NMR spectroscopy, giving parameters as previously reported [13].

4.7. Synthesis of [$Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4$]I (**2**·**I**)

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (295 mg, 0.196 mmol) and 2-chloro-1-methylpyridinium iodide (90 mg, 0.352 mmol, excess) in methanol (30 mL) was stirred, whereupon the Pt complex appeared to react and dissolve, and a new orange suspension quickly formed. After stirring for 5 min., solid KI (300 mg, 1.81 mmol) was added with no further visible change. After stirring for 20 min. the resulting yellow-orange suspension was filtered, washed with methanol (5 mL) and then water (5 mL) and dried under vacuum to give **2**·**I** as an orange solid (265 mg, 78%). Found: C, 49.20; H, 3.67; N, 0.00. $C_{72}H_{60}I_2P_4Pt_2S$ requires C, 50.11; H, 3.51; N, 0.00%. ESI MS *m*/*z* 1597.17, $[Pt_2(\mu\text{-}S)(\mu\text{-}I)(PPh_3)_4]^+$ (100%). The complex gave $^{31}P\{^1H\}$ NMR data that were virtually indistinguishable from the PF_6^- salt **2**·**PF₆** [13].

4.8. Synthesis of 2-chloro-1-methylpyridinium tetraphenylborate

A solution of 2-chloro-1-methylpyridinium iodide (1.00 g, 3.60 mmol) in water (30 mL) was filtered to remove a small amount of dark impurity. To this solution was added a solution of $NaBPh_4$ (1.50 g, 4.39 mmol) in water (20 mL), immediately forming a milky white precipitate. The precipitate was filtered, washed with water (2 × 20 mL) and dried to give the product (1.42 g, 88%). The compound can be purified by recrystallisation from hot acetone.

4.9. Synthesis of [$Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4$]$BPh_4$ (**3**·**BPh₄**) from [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] using 2-chloro-1-methylpyridinium tetraphenylborate

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (300 mg, 0.200 mmol) and 2-chloro-1-methylpyridinium tetraphenylborate (92 mg, 0.206 mmol) in methanol (25 mL) was stirred for 24 h, giving a pinkish-orange suspension. Concentrated aqueous ammonia (4 mL, excess) was added, with no immediate change, and the mixture was stirred for 48 h giving a cream suspension. The solid product was filtered, washed with methanol (5 mL) and dried under vacuum to give **3**·**BPh₄** (255 mg, 71%). ESI MS *m*/*z* 1486.98, $[Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4]^+$ (100%).

4.10. X-ray structure determination on [$Pt_2(\mu\text{-}S)(\mu\text{-}NH_2)(PPh_3)_4$]$BPh_4$ (**3**·**BPh₄**)

Yellow-orange block crystals were obtained by vapour diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature. An arbitrary sphere of data was collected on a yellow block-like crystal, having dimensions of 0.192 × 0.123 × 0.105 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5° [35]. Data were corrected for absorption and polarisation effects and analysed for space group determination [36]. The structure was solved by Patterson methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded ($1.2 \times U_{eq}$(C,N)).

The nitrogen was restrained to approximate isotropic behaviour. Its proximity to two heavy Pt centres results in a non-positive definite thermal parameter. Further support for the presence of a NH_2 group is the location of the amide hydrogens at reasonable positions from a difference Fourier map. NH_2 hydrogen atoms were fixed at their observed locations.

Crystal data for $C_{100}H_{92}BNOP_4Pt_2S$; M_r = 1880.67; monoclinic; space group $P2_1/n$; a = 13.834(2) Å; b = 19.729(3) Å; c = 30.971(5) Å; α = 90°; β = 96.186(2)°; γ = 90°; V = 8404(2) Å^3; Z = 4; T = 120(2) K; λ(Mo Kα) = 0.71073 Å; μ(Mo Kα) = 3.476 mm^{-1}; d_{calc} = 1.486 g cm^{-3}; 201654 reflections collected; 21050 unique (R_{int} = 0.0379); giving R_1 = 0.0219, wR_2 = 0.0466 for 18374 data with [$I > 2\sigma(I)$] and R_1 = 0.0299, wR_2 = 0.0492 for all 21050 data. Residual electron density (e$^-$ Å^{-3}) maximum/minimum: 1.892/−0.715.

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Appendix A. Supplementary material

CCDC 974383 contains the supplementary crystallographic data for **3·BPh$_4$**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.03.005.

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