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**The reactivity of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  towards difunctional chloroacetamide  
alkylating agents; formation of cyclised or bridged products**

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## Abstract

The reactions of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  towards some bis(chloroacetamide) alkylating agents have been investigated. Reaction with one mole equivalent of the hydrazine-derived compound  $\text{ClCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{Cl}$  led to the cyclised product  $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4]^{2+}$  which showed two different  $\text{PPh}_3$  environments in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, as a result of non-fluxional behaviour of the dithiolate ligand in solution. Reactions of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with the *ortho* and *para* isomers of the phenylenediamine-derived bis(chloroacetamides)  $\text{ClCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{Cl}$  gave tetrametallic complexes containing two  $\{\text{Pt}_2\text{S}_2\}$  moieties spanned by the  $\text{CH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2$  group. Both the *ortho* and *para* isomers were crystallographically characterised; in the *ortho* isomer there is intramolecular  $\text{C}=\text{O}\cdots\text{H}-\text{N}$  and  $\text{S}\cdots\text{H}-\text{N}$  hydrogen bonding involving the two amide groups.

*Keywords:* Platinum complexes; Thiolate ligands; Alkylation reactions; Crystal structures; Hydrogen-bonding

## Introduction

The platinum(II) sulfido complex  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** was shown from very early studies to have highly nucleophilic sulfide ligands that can act as metalloligands towards a wide variety of metal centres, or as nucleophiles in alkylation reactions.[1] Although reactions of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with simple alkyl halides such as methyl iodide and benzyl bromide were investigated in the very earliest studies on this complex,[2,3] until recently there were relatively few further investigations in this area. Using the technique of electrospray ionisation mass spectrometry (ESI MS) as a powerful technique to identify reaction products from micro-scale reactions,[4] the reactivity of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  towards a variety of alkylating and arylating [5] agents has been explored, including a mass spectrometric survey of the reaction landscape in this area.[6]

The product(s) formed upon alkylation of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  are dependent on the alkyl halide, with both mono-alkylated  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SR})(\text{PPh}_3)_4]^+$  and dialkylated  $[\text{Pt}_2(\mu\text{-SR})(\mu\text{-SR}')(\text{PPh}_3)_4]^{2+}$  products being accessible through appropriate choice of alkylating agent.[6,7] With dialkylating agents, reactions yield cyclised, dialkylated (“overhead-bridged”) products when the spacer chain length between the two alkylating carbons is relatively short (e.g.  $\text{Br}(\text{CH}_2)_4\text{Br}$  [8] or *cis*- $\text{ClCH}_2\text{CH}=\text{CHCH}_2\text{Cl}$  [9]), or when the presence of a suitable rigid aromatic backbone promotes cyclisation (e.g. 2,2'-bis(bromomethyl)-1,1'-biphenyl [10]). In contrast, longer-chain dialkylating agents (e.g.  $\text{Br}(\text{CH}_2)_{12}\text{Br}$ ),[8] or ones which inhibit cyclisation as a result of molecular geometry, e.g. a *para*-disubstituted aromatic ring [10] lead to the formation of derivatives where two  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  units are monoalkylated and bridged through a newly constructed dithiolate ligand. A similar spanning of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  moieties can be achieved using the 1,4-difunctional organomercury reagent  $\text{CH}_3\text{C}(\text{O})\text{OHgC}_6\text{Me}_4\text{HgOC}(\text{O})\text{CH}_3$ . [11]

Recently, we reported an investigation into the reactivity of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  towards a range of functionalised monoalkylating agents, which included  $\text{ClCH}_2\text{C}(\text{O})\text{NHPh}$ , readily prepared by the chloroacetylation of aniline using  $\text{ClCH}_2\text{C}(\text{O})\text{Cl}$ .<sup>[12]</sup> Amine-containing substrates, which are particularly abundant and widely commercially available, can be converted into alkylating agents by chloroacetylation (and other derivatisation methods), potentially allowing the incorporation of a wide range of functionality onto the  $\{\text{Pt}_2\text{S}_2\}$  framework. Given the ability of monoalkylated complexes to act as cationic metalloligands,<sup>[13,14]</sup> we wished to further explore the use of chloroacetamide alkylating agents towards  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  as a means of generating new dinuclear platinum(II) thiolate compounds. In this contribution we describe the reactivity of some short- and long-spacer bis(chloroacetamide) derivatives towards  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ , leading to cyclised and bridged products.

## Results and discussion

Reaction of chloroacetyl chloride with hydrazine gave the chloroacetamide-derived bis-alkylating agent  $\text{ClCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{Cl}$  following the literature procedure (refer Experimental section). Reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** with one mol. equivalent of  $\text{ClCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{Cl}$  in methanol involved a two-step reaction as shown in Scheme 1, with a fast initial monoalkylation of **1**, followed by a much slower dialkylation reaction to form  $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4]^{2+}$  **2**. After 24 hours, the ESI mass spectrum of the reaction mixture showed  $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4]^{2+}$  at  $m/z$  808 (100%) together with  $[\text{Pt}_2\{(\mu\text{-S})\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{Cl}\}\}(\text{PPh}_3)_4]^+$  ( $m/z$  1652, 38%). Complete formation of **2** was achieved after 120 hours without any trace of monoalkylated ion in the ESI mass spectrum, shown in Figure 1. The long time required for complete reaction can be attributed to the relatively long spacer length of six atoms, which slows down

the cyclisation reaction because of entropy considerations. Acetylhydrazine compounds have a preferred *trans* conformation [15,16,17] which may also play a part in determining the rate of the second alkylation step. The product **2** was isolated as its PF<sub>6</sub><sup>-</sup> salt following addition of excess NH<sub>4</sub>PF<sub>6</sub>. ESI MS, IR and NMR spectroscopic data confirmed the product to be the cyclised, dialkylated product [Pt<sub>2</sub>{SCH<sub>2</sub>C(O)NHNHC(O)CH<sub>2</sub>S}(PPh<sub>3</sub>)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> **2**·(PF<sub>6</sub>)<sub>2</sub>. This appears to be the first metal complex of this dithiolate ligand.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **2**·(PF<sub>6</sub>)<sub>2</sub> (Figure 2) showed two distinct resonances at δ 18.2 and 22.2 showing similar <sup>1</sup>J(PtP) couplings of 2978 and 3053 Hz respectively, corresponding to two different triphenylphosphine environments. Because of the length of the dithiolate ligand (with 6 spacer atoms between the two sulfurs), it must adopt a twisted conformation which places the phosphine ligands in two inequivalent sets. Scheme 2 shows a possible C<sub>2</sub>-symmetric conformation, that places the two hydrazide NH groups as close as possible to a preferred *trans* arrangement, which clearly results in inequivalent phosphorus atoms, P<sub>a</sub> and P<sub>b</sub>. At room temperature there is no fluxional process operating to average out the phosphine environments. When a (CD<sub>3</sub>)<sub>2</sub>SO solution of **2**·(PF<sub>6</sub>)<sub>2</sub> was heated to 360 K, there was effectively no change to the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, suggesting a high energy barrier to equilibration of the phosphine ligands. The same inequivalence of PPh<sub>3</sub> ligands was previously observed in the <sup>31</sup>P NMR spectrum of the biphenyl-bridged compound [Pt<sub>2</sub>{SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>S}(PPh<sub>3</sub>)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub>, which also has a potentially symmetric structure.[10] The <sup>1</sup>H NMR spectrum of the dithiolate ligand of **2** also showed two types of SCH<sub>2</sub> hydrogen environments as a result of the rigid nature of the ligand.

The dialkylating agents *p*-ClCH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>Cl **3** and *o*-ClCH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>Cl **4** [prepared by derivatisation of *para*- and *ortho*-phenylenediamines with chloroacetyl chloride] were also reacted with **1**. While cyclisation is not possible for the *para* isomer, both cyclisation and bridging are possible reaction outcomes

for the *ortho* isomer. Reactions proceeded in two stages; the first stage was the monoalkylation of **1** to give the monocation  $[\text{Pt}_2(\mu\text{-S})\{\mu\text{-SCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{Cl}\}(\text{PPh}_3)_4]^+$ , which then undergoes a second intermolecular nucleophilic attack by another molecule of **1** yielding the bridged Pt<sub>4</sub> aggregates **5** and **6** spanned by *p*- or *o*-SCH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>S respectively (Scheme 3). The *para*-dithiolate ligand has been considered in a theoretical study as a bridging ligand between gold nanoparticles,[18] but few complexes of either the *ortho* or *para* dithiolate ligands are known.[19]

The reaction of **3** and  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** in a 1:2 mole ratio indicated only the formation of  $[\text{Pt}_2\{(\mu\text{-S})\{\mu\text{-S-}p\text{-CH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{Cl}\}(\text{PPh}_3)_4\}^+$  after stirring for 1 hour in methanol. After 72 hours at room temperature there was a dominant peak *m/z* 1598 (100%), attributable to the Pt<sub>4</sub> aggregate **5**. The product was isolated as its BPh<sub>4</sub><sup>-</sup> salt by addition of excess NaBPh<sub>4</sub>, and purified by vapour diffusion of diethyl ether into a dichloromethane solution to give crystals which were analysed by ESI MS and showed to be pure **5**·(BPh<sub>4</sub>)<sub>2</sub>.

The reaction of a 1:2 molar ratio of *o*-ClCH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>Cl **4** with **1** was also complete after 24 hours, as confirmed from ESI MS, yielding the pure Pt<sub>4</sub> aggregate **also** isolated as its BPh<sub>4</sub><sup>-</sup> salt **6**·(BPh<sub>4</sub>)<sub>2</sub>. In order to investigate the possibility of a cyclisation reaction leading to the formation of the intramolecular dialkylated derivative  $[\text{Pt}_2\{\mu\text{-SCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4]^{2+}$  **7**, a low reaction temperature (0 °C) and larger reaction solvent volume was used to react equimolar quantities of **4** and **1**. ESI MS indicated two dicationic species; the major species at *m/z* 1598 corresponded to the intermolecular dialkylated Pt<sub>4</sub> aggregate **6**. The *m/z* value (849) and isotope pattern of the minor species (*ca.* 30% relative intensity) gave good agreement for **7**, but no further studies were carried out in an attempt to optimise the synthesis or isolation of **7**.

In order to confirm the nature of the products, X-ray structure determinations were carried out on the *para* and *ortho* isomers of the phenylenediamide derivatives **5**·(BPh<sub>4</sub>)<sub>2</sub> and **6**·(BPh<sub>4</sub>)<sub>2</sub> respectively. The molecular structures and atom numbering schemes are given in Figures 3 and 4 respectively, while selected bond lengths and angles are given in Tables 1 and 2.

The *para*-isomer **5**·(BPh<sub>4</sub>)<sub>2</sub> has an inversion centre and is thus centrosymmetric, with only half of the dication being unique. The structural features of the {Pt<sub>2</sub>S<sub>2</sub>} core are typical for monoalkylated derivatives of this type; [12] the {Pt<sub>2</sub>S<sub>2</sub>} core is puckered in the usual way with a dihedral angle (between the two PtS<sub>2</sub> planes) of 133.4°. The Pt-S distances to the sulfide ligand [Pt(1)-S(2) 2.313(3), Pt(2)-S(2) 2.323(3) Å] are shorter than to the thiolate ligand [Pt(1)-S(1) 2.374(3), Pt(2)-S(1) 2.361(2) Å]. Due to the higher *trans*-influence [20] of sulfide, the Pt(1)-P(3) [2.305(3) Å] and Pt(2)-P(2) [2.296(3) Å] bonds are longer than the Pt(1)-P(4) [2.259(3) Å] and Pt(2)-P(1) [2.279(3) Å] bonds that are *trans* to thiolate (SR<sup>-</sup>) ligands. The amide group is slightly twisted out of the plane of the bridging phenyl ring, with a C(5)-C(3)-N(1)-C(2) torsion angle of 14.3°. The packing of cations of **5** does not appear to result in any intermolecular hydrogen-bonding interactions with potentially hydrogen-bonding amide groups, which are kept separated by the considerable steric bulk of the eight PPh<sub>3</sub> ligands.

The X-ray structure of **6**·(BPh<sub>4</sub>)<sub>2</sub> also confirms the formation of a bridged Pt<sub>4</sub> aggregate comprised of two molecules of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] **1** spanned by the *ortho* isomer of -CH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>-. The C<sub>6</sub>H<sub>4</sub>(NH)<sub>2</sub> system is effectively planar but the carbonyl groups are significantly twisted out of the plane, adopting an arrangement *anti* to each other across the aromatic ring. Such an arrangement is also seen in the simple *ortho*-phenylene diamide derivative C<sub>6</sub>H<sub>4</sub>(NHC(O)CH<sub>3</sub>)<sub>2</sub>. [21] The carbonyl carbon atoms C(2) and C(3) lie respectively 0.750 and 0.777 Å from the least-squares plane of the C<sub>6</sub>H<sub>4</sub>N<sub>2</sub> group of

6. Although the amide hydrogens were not able to be located in the penultimate refinement (all hydrogens are in calculated positions), there appears to be an intramolecular hydrogen bond involving the two amide groups, from the hydrogen on nitrogen N(2) to the oxygen atom of the other carbonyl group O(1) [N(2)⋯O(1) 2.868 Å].

The other amide N-H group [N(1)-H(1)] is in relatively close proximity to the sulfide S(1) [N(1)⋯S(1) 3.297 Å], which on the basis of N⋯S distances in other systems known to show N-H⋯S hydrogen bonding may represent a modest interaction.[22] For example, in a ferredoxin model complex, containing an [Fe<sub>4</sub>S<sub>4</sub>(SBU<sup>t</sup>)<sub>4</sub>]<sup>2-</sup> core, N-H⋯S hydrogen bonding interactions involving N-H bonds of Me<sub>3</sub>NCH<sub>2</sub>C(O)NH<sub>2</sub><sup>+</sup> counterions have N⋯S bond distances of 3.356(3) Å to thiolate sulfur, and 3.625(3) Å to the triply-bridging sulfide.[23] The compound [Tm<sup>Ph</sup>]ZnSCH<sub>2</sub>C(O)NHPPh [Tm<sup>Ph</sup> = tris(2-mercapto-1-phenylimidazolyl)hydroborato ligand] and its ethanol adduct [Tm<sup>Ph</sup>]ZnSCH<sub>2</sub>C(O)NHPPh⋯O(H)Et have considerably shorter N⋯S separations of 3.06 and 2.99 Å respectively.[24] It is also worth noting that the di-ethanol adduct of [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>], containing an O-H⋯S hydrogen bond to a μ<sub>2</sub>-sulfide ligand, has an O⋯S distance of 3.42 Å.[25]

The two [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] groups and their attendant thiolate ligands in 6·(BPh<sub>4</sub>)<sub>2</sub> have slight structural differences; the dihedral angle between PtS<sub>2</sub> planes in one [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] moiety (148°) is slightly different to the other [Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (150°), which has an effect on the Pt⋯Pt separations [the Pt(3)⋯Pt(4) separation (3.412 Å) is longer than Pt(1)⋯Pt(2) (3.391 Å)]. One of {Pt<sub>2</sub>S<sub>2</sub>} rings [involving Pt(3), Pt(4), S(3) and S(4)] has the Pt-S(sulfide) bond distances [2.325(2), 2.321(3) Å] shorter than to the thiolate ligand [2.342(3), 2.355(3) Å], but in the other {Pt<sub>2</sub>S<sub>2</sub>} unit the trend was less clear. There are also small differences in the angles and bond distances on both sides of the aromatic ring of the



amide spanning the two  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  moieties. For instance the angle between N(1)-C(2)-C(1) is  $120.4^\circ$  while N(2)-C(3)-C(4) is  $116.3^\circ$ .

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complexes **5** and **6** are consistent with their symmetric nature, making each  $\{\text{Pt}_2\text{S}_2\}$  unit and its attached thiolate ligand equivalent and thus comparable to  $^{31}\text{P}$  NMR spectra of other monoalkylated derivatives  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SR})(\text{PPh}_3)_4]^+$ .<sup>[12]</sup> For example, the *ortho* derivative **6** showed a single central P resonance at  $\delta$  26.0 due to the two types of  $\text{PPh}_3$  ligand (*trans* to sulfide or thiolate) having coincidental chemical shifts, Figure 5. Two sets of satellites due to coupling to  $^{195}\text{Pt}$  are observed, showing  $^1\text{J}(\text{PtP})$  coupling constants of 3341 and 2579 Hz, for phosphines *trans* to thiolate and sulfide ligands respectively. The  $^1\text{H}$  NMR spectrum of **6**· $(\text{BPh}_4)_2$  shows, in addition to a multitude of signals due to the aromatic protons, a singlet for the NH protons at  $\delta$  9.3, and a single broad resonance at  $\delta$  2.1 for the equivalent  $\text{CH}_2$  protons. The NH proton of the *para* isomer **5** was not observed, and presumably is obscured by the phenyl resonances.

In conclusion, we have used the facile chloroacetylation reaction of diamines to generate new dialkylating agents for  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ . The products formed are dependent on the geometric nature of the alkylating agent backbone, as has been found in a previous study.<sup>[10]</sup> The *ortho* and *para* isomers of  $\text{ClCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{Cl}$  produce derivatives formed by bridging two molecules of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ , with the *ortho* isomer containing intramolecular  $\text{C}=\text{O}\cdots\text{H}-\text{N}$  and  $\text{S}\cdots\text{H}-\text{N}$  hydrogen bonding. When considered with our earlier observations that  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  forms hydrogen-bonded adducts with lower alcohols it suggests that  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  and its monoalkylated derivatives might participate more widely as a hydrogen-bond acceptor, which we plan to investigate.

## Experimental

The alkylating agents  $\text{ClCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{Cl}$  [26] *o*- $\text{ClCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{Cl}$  [27] and *p*- $\text{ClCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{Cl}$  [27] were synthesised according to the literature methods, from  $\text{ClCH}_2\text{C}(\text{O})\text{Cl}$ , and *o*- and *p*-phenylenediamine and hydrazine, all of which were supplied by BDH.  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** was synthesised by the metathesis reaction of *cis*- $\text{PtCl}_2(\text{PPh}_3)_2$  with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  in benzene.[3] Methanol, dichloromethane and diethyl ether were of laboratory reagent grade and used without further purification. Ammonium hexafluorophosphate (Aldrich) and sodium tetraphenylborate (BDH) were used as supplied.

NMR spectra were recorded in  $\text{CDCl}_3$  solution unless otherwise stated.  $^{31}\text{P}\{^1\text{H}\}$  spectra were recorded on Bruker DRX 300MHz spectrometer.  $^1\text{H}$  NMR spectra were recorded at 400 MHz on a Bruker DRX spectrometer. IR spectra were obtained as KBr disks with a Perkin Elmer Spectrum 100 FTIR spectrometer. Melting points of the compounds were determined with a Reichert hotstage apparatus and are uncorrected. ESI mass spectra of solid products were obtained by dissolving a small quantity of the material in 1-2 drops of dichloromethane or chloroform, followed by dilution to *ca.* 2 mL using methanol. Samples of reaction solutions were analysed by diluting one drop of the reaction mixture with methanol prior to analysis. Spectra were recorded, typically using a cone voltage of 20V, on a VG Platform II instrument, and comparison of observed and calculated (*Isotope* [28]) isotope patterns was used in ion assignment. Microelemental analyses were carried out at the Campbell Microanalytical Laboratory of the University of Otago.

### **Preparation of $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4](\text{PF}_6)_2 \cdot 2(\text{PF}_6)_2$**

$[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  (100 mg, 0.067 mmol) and  $\text{ClCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{Cl}$  (14.8 mg, 0.080 mmol) in methanol (25 mL) were stirred for 120 h at room temperature. Complete formation of the cyclised product was confirmed by ESI MS which showed  $[\text{Pt}_2\{$

SCH<sub>2</sub>C(O)NHNHC(O)CH<sub>2</sub>S}(PPh<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> at *m/z* 808. The solution was filtered and NH<sub>4</sub>PF<sub>6</sub> (43 mg, 0.264 mmol) added to the clear, colourless filtrate. The resulting precipitate was filtered, washed with water (40 mL) and diethyl ether (2 x 20 mL) and dried, giving **2**·(PF<sub>6</sub>)<sub>2</sub> (69 mg, 55%) as a white solid. Found; C 47.63; H 3.40; N 2.05. C<sub>76</sub>H<sub>66</sub>F<sub>12</sub>N<sub>2</sub>O<sub>2</sub>P<sub>6</sub>Pt<sub>2</sub>S<sub>2</sub> (M<sub>r</sub> 1906.44) requires C 47.85; H 3.49; N 1.47%. M.p. 184–186 °C. IR  $\nu_{\max}$  1097, 1436, 1481, 1683, 3437 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  18.2 [br s, <sup>1</sup>J(PtP) 2978] and 22.2 [br s, <sup>1</sup>J(PtP) 3053]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  0.42 [t, 2H, CH, <sup>4</sup>J(PH) 11.5, <sup>3</sup>J(PtH) *ca.* 60], 1.86 [m, 2H, CH, <sup>3</sup>J(PtH) *ca.* 48], 7.16-7.70 (m, Ph). ESI MS *m/z* 808, ([M]<sup>2+</sup> 100%).

**Preparation of [(Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>( $\mu$ -S){ $\mu$ -S-*p*-CH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>S}( $\mu$ -S)Pt<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>](BPh<sub>4</sub>)<sub>2</sub> **5**·(BPh<sub>4</sub>)<sub>2</sub>**

[Pt<sub>2</sub>( $\mu$ -S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (100 mg, 0.067 mmol) and *p*-ClCH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>Cl (8.7 mg, 0.033 mmol) in methanol (25 mL) was stirred for 24 h at room temperature. Complete formation of the product **5** was confirmed by ESI MS. The solution was filtered and NaBPh<sub>4</sub> (45 mg) added to the clear yellow-orange filtrate. The precipitate was filtered, washed with water (40 mL) and diethyl ether (2 x 20 mL) and dried, yielding (117 mg, 46%) of **5**·(BPh<sub>4</sub>)<sub>2</sub> as a yellow solid. Found; C 63.37; H 4.35; N 0.67. C<sub>202</sub>H<sub>170</sub>B<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P<sub>8</sub>Pt<sub>4</sub>S<sub>4</sub> (M<sub>r</sub> 3835.53) requires C 63.25; H 4.47; N 0.73%. M.p. 179-181 °C. IR  $\nu_{\max}$  1095, 1435, 1479, 1678, 3467 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR  $\delta$  24.8 [br s, <sup>1</sup>J(PtP) 3359 and 2613 Hz]. <sup>1</sup>H NMR  $\delta$  3.00 (4H, br, 2CH<sub>2</sub>), 6.84-7.5 (*m*, Ph). ESI MS *m/z* 1598, ([M]<sup>2+</sup> 100%).

**Preparation of [(Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>( $\mu$ -S){ $\mu$ -S-*o*-CH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>S}( $\mu$ -S)Pt<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>](BPh<sub>4</sub>)<sub>2</sub> **6**·(BPh<sub>4</sub>)<sub>2</sub>**

[Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (100 mg, 0.067 mmol) and *o*-ClCH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>Cl (8.7 mg, 0.033 mmol) in methanol (25 mL) was stirred for 24 h at room temperature. Complete formation of the product was confirmed by ESI MS. The solution was filtered and NaBPh<sub>4</sub> (45 mg) added to the clear yellow-orange filtrate. The precipitated product was filtered, washed with water (40 mL) and diethyl ether (2 x 20 mL) and dried, yielding (199 mg, 78%) of **6**·(BPh<sub>4</sub>)<sub>2</sub> as a yellow solid. Found; C 63.17; H 4.63; N 0.71. C<sub>202</sub>H<sub>170</sub>B<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P<sub>8</sub>Pt<sub>4</sub>S<sub>4</sub> (M<sub>r</sub> 3835.53) requires C 63.25; H 4.47; N 0.73%. M.p. 258-260 °C. IR ν<sub>max</sub> 1094, 1434, 1479, 1644, 3052 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR δ 26.0 [br s, <sup>1</sup>J(PtP) 3341 and 2579 Hz]. <sup>1</sup>H NMR δ 9.33 (2H, s, 2NH), 6.78-7.45 (m, Ph), 2.06 (4H, br, 2CH<sub>2</sub>); the NH proton was not observed. ESI MS *m/z* 1598, ([M]<sup>2+</sup> 100%).

### X-ray crystal structure determinations

Crystals of **5**·(BPh<sub>4</sub>)<sub>2</sub> and **6**·(BPh<sub>4</sub>)<sub>2</sub> suitable for X-ray structure analysis were obtained by vapour diffusion of diethyl ether into dichloromethane solutions of the complexes at room temperature. All crystallographic measurements were made on a Bruker APEX II diffractometer equipped with a CCD area detector using MoK<sub>α</sub> radiation (λ = 0.71073 Å). The software SMART [29] was used for the collection of data frames, for indexing reflections, and to determine lattice parameters; SAINT was used for the integration of the intensity of the reflections and for scaling; SADABS [30] was used for empirical absorption correction. The structures were solved and refined using the SHELX-97 suite of programs.[31] The structures were refined by full-matrix least-squares based on F<sub>o</sub><sup>2</sup> with anisotropic thermal parameters for non-hydrogen atoms. A summary of data collection and refinement parameters is given in Table 3.

The structure of **5**·(BPh<sub>4</sub>)<sub>2</sub> was solved by direct methods. The structure has a centre of symmetry so only half of the molecule makes up the asymmetric unit. All non hydrogen

atoms were refined as anisotropic. Refinement with the main cation and anion included converged with  $R_1 = 0.11$ . There were extra residual peaks that were associated with solvent but this could not be modelled sensibly. PLATON indicated a total  $1327.0 \text{ \AA}^3$  solvent accessible void. The SQUEEZE routine of PLATON was used to generate a modified data set which was used in the final refinement cycle. A higher residual peak than usual ( $5.34 \text{ e \AA}^{-3}$ ) was in the final difference map. This was adjacent to the Pt atom so it is a ripple peak from data that may have been caused by poor crystal quality.

The crystal structure of  $\mathbf{6} \cdot (\text{BPh}_4)_2$  was solved by Patterson methods. The refined structure contains partially disordered  $\text{CH}_2\text{Cl}_2$  solvent molecules. The residual peaks in the final difference map could not be refined and were treated as disordered solvent molecules, occupying a volume of  $748 \text{ \AA}^3$ , which explains the high values of  $R_1 = 0.0627$  and  $R_2 = 0.1529$ .

### **Supplementary material**

Crystallographic data for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 809467 and 809468. Copies of the data can be obtained free of charge on application to 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 for financial support of this work, including scholarship support to OTU. We also thank Pat Gread for technical assistance with the electrospray mass spectrometry, and Professor Alistair Wilkins for assistance with NMR spectroscopy.

**Table 1** Selected bond lengths and interatomic distances (Å) and bond angles (°) for  $[(\text{Ph}_3\text{P})_4\text{Pt}_2(\mu\text{-S})\{\mu\text{-}p\text{-SCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{S}\}(\mu\text{-S})\text{Pt}_2(\text{PPh}_3)_4](\text{BPh}_4)_2 \cdot 5 \cdot (\text{BPh}_4)_2$   
(Estimated standard deviations are in brackets).

Pt(1)-P(4)	2.259(3)	Pt(1)-S(1)	2.374(3)	S(1)-C(1)	1.825(11)
Pt(1)-P(3)	2.305(3)	Pt(1)-S(2)	2.313(3)	C(2)-N(1)	1.341(15)
Pt(2)-P(1)	2.279(3)	Pt(2)-S(1)	2.361(2)	N(1)-C(3)	1.394(14)
Pt(2)-P(2)	2.296(3)	Pt(2)-S(2)	2.323(3)	C(2)-O(1)	1.203(13)
S(1)⋯S(2)	3.055	Pt(1)⋯Pt(2)	3.262		
P(4)-Pt(1)-P(3)	100.66(12)	P(1)-Pt(2)-P(2)	101.84(10)		
P(4)-Pt(1)-S(2)	89.62(11)	P(1)-Pt(2)-S(2)	84.74(10)		
P(3)-Pt(1)-S(2)	169.63(10)	P(4)-Pt(1)-S(1)	170.62(11)		
P(3)-Pt(1)-S(1)	88.45(10)	P(2)-Pt(2)-S(1)	91.86(10)		
S(2)-Pt(1)-S(1)	81.34(10)	S(2)-Pt(2)-S(1)	81.42(9)		
Pt(1)-S(2)-Pt(2)	89.44(10)	Pt(2)-S(1)-Pt(1)	87.10(9)		
C(2)-C(1)-S(1)	111.8(7)	O(1)-C(2)-C(1)	120.6(11)		
C(2)-N(1)-C(3)	129.3(9)	N(1)-C(2)-C(1)	115.0(10)		
O(1)-C(2)-N(1)	124.4(12)				

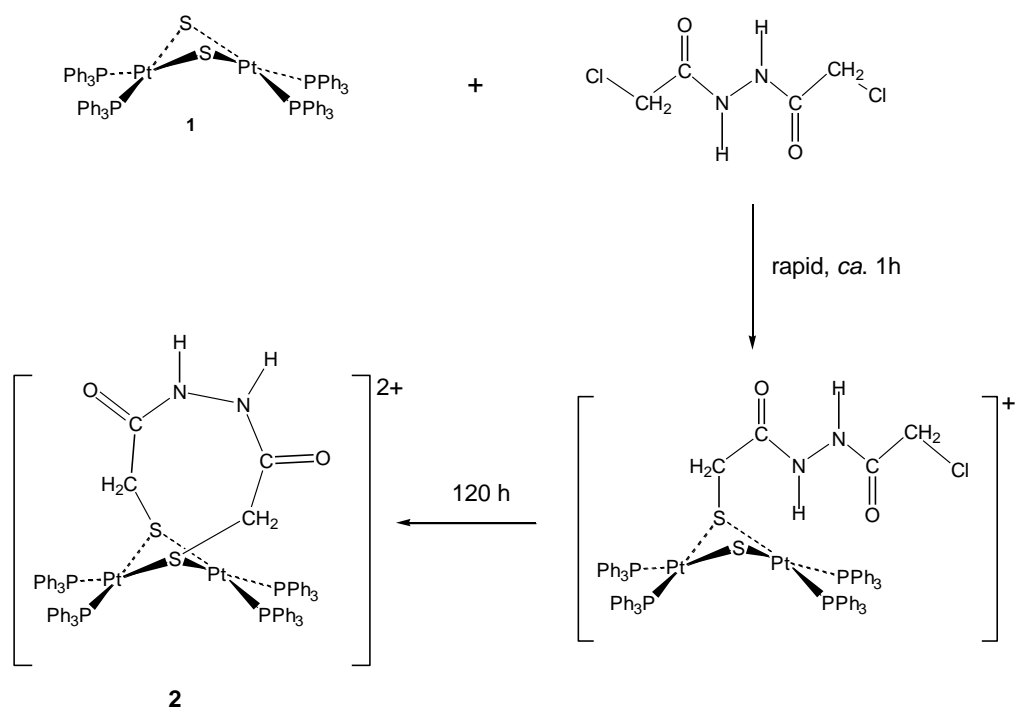
**Table 2** Selected bond lengths and atomic distances (Å) and bond angles (°) for [(Ph<sub>3</sub>P)<sub>4</sub>Pt<sub>2</sub>(μ-S){μ-*o*-SCH<sub>2</sub>C(O)NHC<sub>6</sub>H<sub>4</sub>NHC(O)CH<sub>2</sub>S}(μ-S)Pt<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>](BPh<sub>4</sub>)<sub>2</sub> **6**·(BPh<sub>4</sub>)<sub>2</sub> (Estimated standard deviations are in brackets).

Pt(1)-P(1)	2.282(3)	Pt(3)-P(5)	2.268(3)	S(2)-C(1)	1.821(13)
Pt(1)-P(2)	2.285(3)	Pt(3)-P(6)	2.284(3)	S(3)-C(4)	1.829(13)
Pt(2)-P(3)	2.273(3)	Pt(4)-P(7)	2.308(3)	C(1)-C(2)	1.526(18)
Pt(2)-P(4)	2.298(3)	Pt(4)-P(8)	2.273(3)	C(4)-C(3)	1.524(16)
Pt(1)-S(1)	2.330(3)	Pt(3)-S(3)	2.342(3)	C(2)-N(1)	1.232(16)
Pt(1)-S(2)	2.337(3)	Pt(3)-S(4)	2.325(2)	C(3)-N(2)	1.293(16)
Pt(2)-S(1)	2.311(3)	Pt(4)-S(3)	2.355(3)	N(1)-C(5)	1.430(16)
Pt(2)-S(2)	2.373(3)	Pt(4)-S(4)	2.321(3)	N(2)-C(6)	1.411(15)
S(1)···S(2)	3.070	S(3)···S(4)	3.058	C(2)-O(1)	1.265(17)
Pt(1)···Pt(2)	3.391	Pt(3)···Pt(4)	3.412	C(3)-O(2)	1.233(14)
P(1)-Pt(1)-P(2)	99.98(11)	S(4)-Pt(4)-S(3)	81.67(10)		
P(3)-Pt(2)-P(4)	100.83(10)	P(7)-Pt(4)-S(3)	86.71(10)		
P(1)-Pt(1)-S(2)	93.21(10)	P(8)-Pt(4)-S(4)	89.19(11)		
P(2)-Pt(1)-S(1)	84.73(10)	C(2)-C(1)-S(2)	123.5(9)		
S(1)-Pt(1)-S(2)	82.28(10)	C(3)-C(4)-S(3)	117.2(9)		
S(1)-Pt(2)-S(2)	81.89(9)	O(1)-C(2)-C(1)	113.3(12)		
P(3)-Pt(2)-S(1)	91.36(10)	O(2)-C(3)-C(4)	120.2(12)		
P(4)-Pt(2)-S(2)	86.29(10)	N(1)-C(2)-O(1)	119.7(14)		
P(5)-Pt(3)-P(6)	100.03(11)	O(2)-C(3)-N(2)	123.6(12)		
P(8)-Pt(4)-P(7)	102.56(11)	N(1)-C(2)-C(1)	120.4(11)		
P(5)-Pt(3)-S(3)	92.56(11)	N(2)-C(3)-C(4)	116.3(11)		
P(6)-Pt(3)-S(4)	85.61(11)	C(2)-N(1)-C(5)	131.7(12)		
S(4)-Pt(3)-S(3)	81.86(10)	C(3)-N(2)-C(6)	127.3(11)		

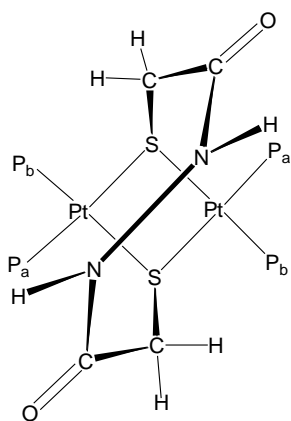
**Table 3** Crystal data and structure refinement for **5**·(BPh<sub>4</sub>)<sub>2</sub> and **6**·(BPh<sub>4</sub>)<sub>2</sub>

	<b>5</b> ·(BPh <sub>4</sub> ) <sub>2</sub>	<b>6</b> ·(BPh <sub>4</sub> ) <sub>2</sub>
Formula	C <sub>202</sub> H <sub>170</sub> B <sub>2</sub> N <sub>2</sub> O <sub>2</sub> P <sub>8</sub> Pt <sub>4</sub> S <sub>4</sub>	C <sub>204</sub> H <sub>170</sub> B <sub>2</sub> Cl <sub>6</sub> N <sub>2</sub> O <sub>2</sub> P <sub>8</sub> Pt <sub>4</sub> S <sub>4</sub>
Formula weight	3835.38	4072.10
Temperature (K)	123(2)	90(2)
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
<i>a</i> /Å	13.9301(7)	13.633(3)
<i>b</i> /Å	16.2595(9)	24.228(6)
<i>c</i> /Å	23.2219(13)	29.422(6)
$\alpha$ /°	99.096(3)	80.864(8)
$\beta$ /°	101.835(3)	80.823(8)
$\gamma$ /°	90.720(4)	81.647(8)
Volume (Å <sup>3</sup> )	5077.6(5)	9400(3)
<i>Z</i>	1	2
Calculated density (g cm <sup>-3</sup> )	1.254	1.439
Absorption coefficient (mm <sup>-1</sup> )	2.898	3.218
<i>F</i> (000)	1918	4064
Crystal size (mm <sup>3</sup> )	0.51 x 0.47 x 0.14	0.36 x 0.29 x 0.08
Reflections collected / unique	105166/21753 [ <i>R</i> <sub>int</sub> 0.0948]	180628/34993 [ <i>R</i> <sub>int</sub> 0.1026]
Max. and min. transmission	0.6871 and 0.3196	0.746 and 0.562
Data / restraints / parameters	21753 / 0 / 1009	34993 / 0 / 2098
Goodness of fit on <i>F</i> <sup>2</sup>	1.018	1.033
Final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> 0.0787, w <i>R</i> <sub>2</sub> 0.1954	<i>R</i> <sub>1</sub> 0.0627, w <i>R</i> <sub>2</sub> 0.1576
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> 0.1486, w <i>R</i> <sub>2</sub> 0.2252	<i>R</i> <sub>1</sub> 0.1183, w <i>R</i> <sub>2</sub> 0.1931
Largest diff. peak and hole	5.340 and -3.235 e Å <sup>-3</sup>	3.596 and -1.961 e Å <sup>-3</sup>

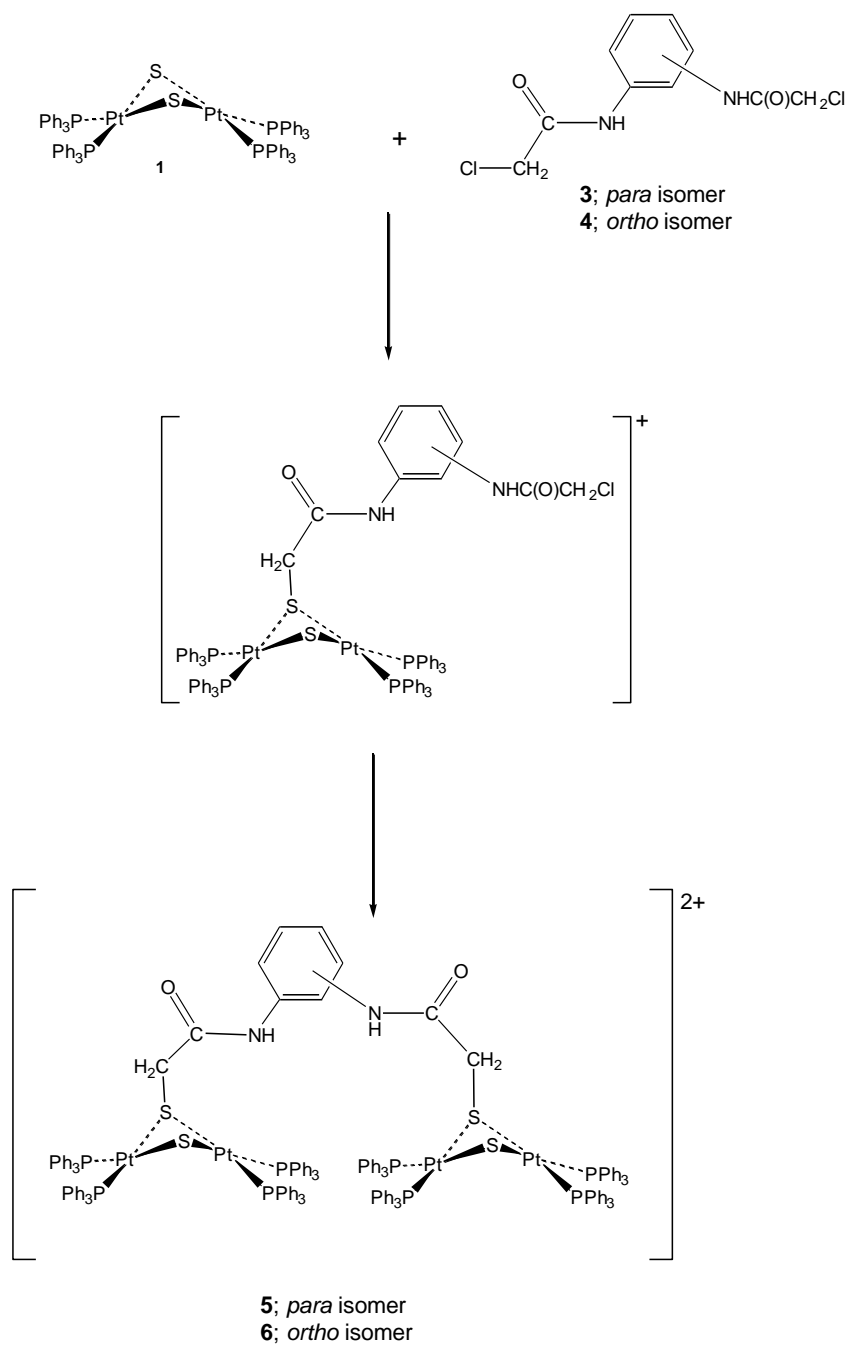




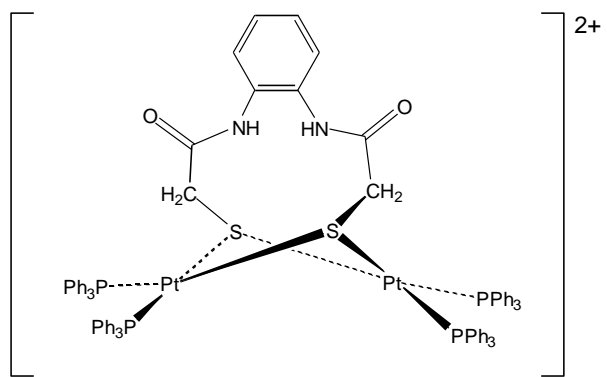
**Scheme 1** The stepwise formation of the hydrazide-derived intramolecular bridged dithiolate derivative  $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4]^{2+}$  **2**



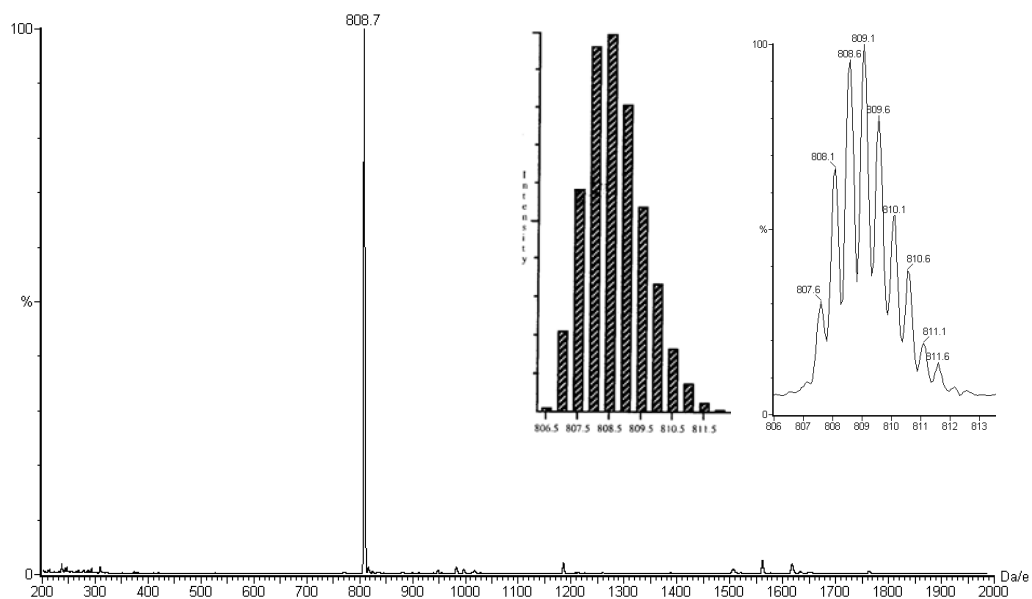
**Scheme 2** Plan view of the core of  $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4]^{2+}$  **2**, showing the inequivalence of the phosphorus donor atoms  $\text{P}_a$  and  $\text{P}_b$



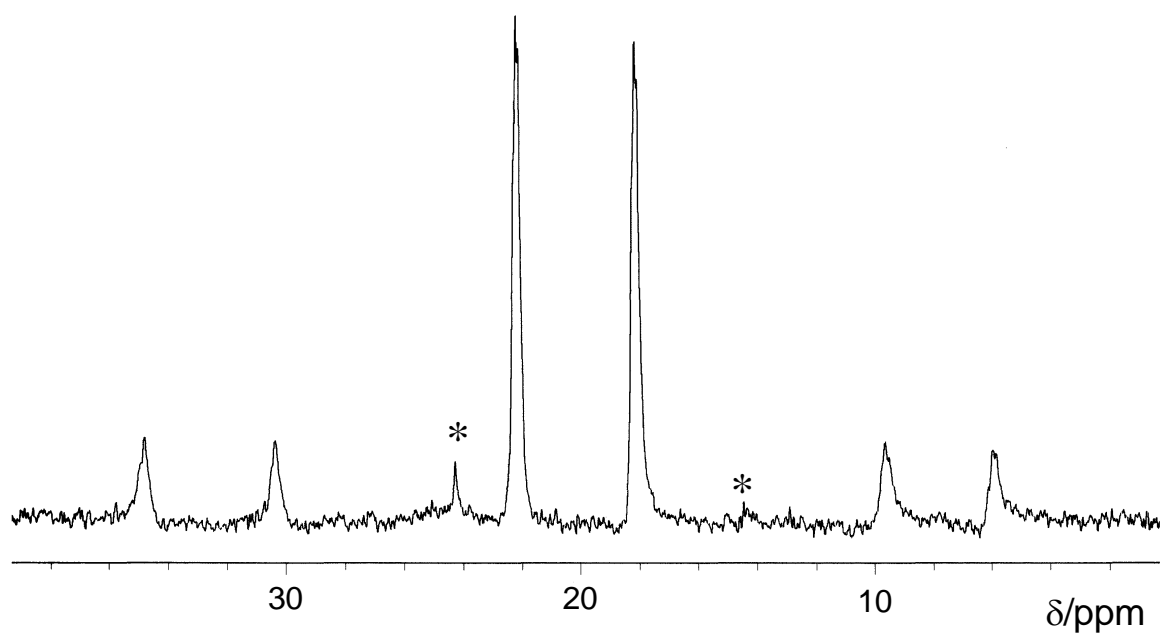
**Scheme 3** The two stage reaction for the formation of  $\text{Pt}_4$  aggregates **5** and **6** from the reactions of **1** with dialkylating agents **3** and **4**



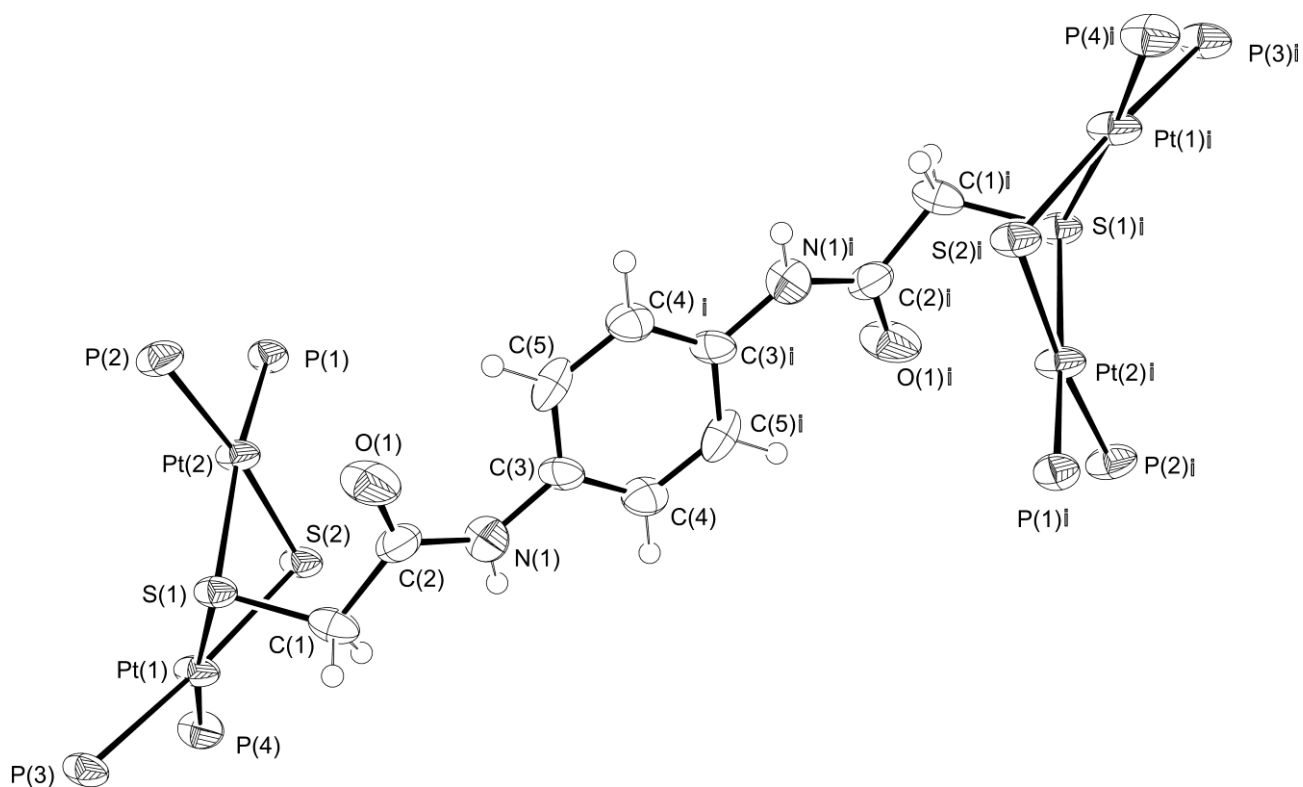
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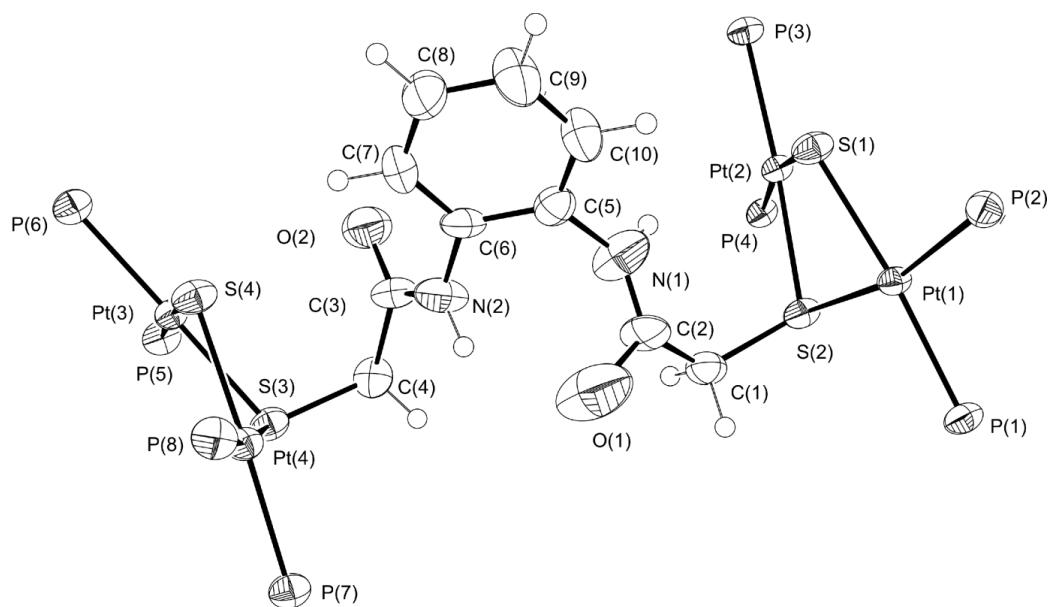
**Figure 1** ESI mass spectrum of the reaction mixture of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** with  $\text{ClCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{Cl}$  (120 hours, methanol, room temperature). The insets show the theoretical (left) and experimental (right) isotope patterns of the dication  $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4]^{2+}$  **2**



**Figure 2**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , room temperature) of the complex  $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4](\text{PF}_6)_2 \cdot 2 \cdot (\text{PF}_6)_2$  showing the presence of two inequivalent types of  $\text{PPh}_3$  ligands. The peaks marked \* are due to impurities.



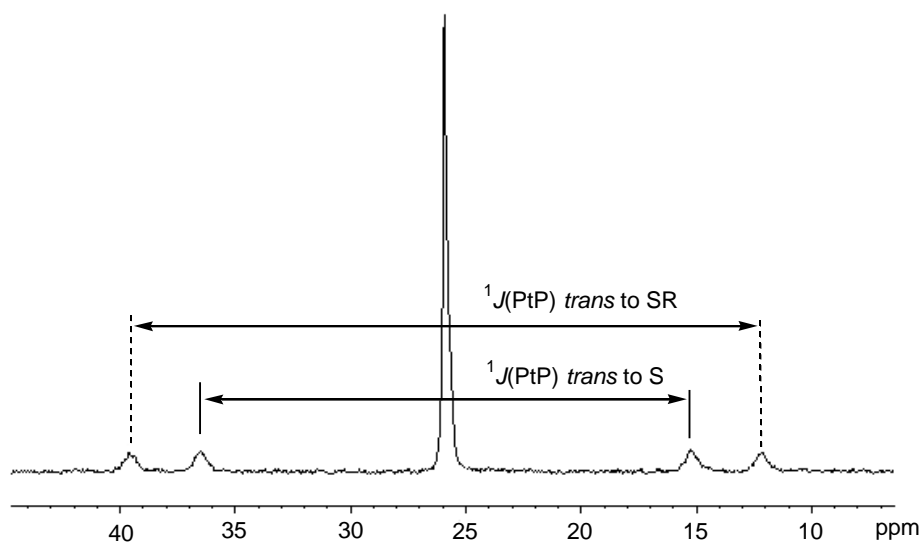
**Figure 3** Molecular structure of the cation of  $[(\text{Ph}_3\text{P})_4\text{Pt}_2(\mu\text{-S})\{\mu\text{-}p\text{-SCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{S-}\mu\}(\mu\text{-S})\text{Pt}_2(\text{PPh}_3)_4](\text{BPh}_4)_2 \cdot 5 \cdot (\text{BPh}_4)_2$  showing the atom numbering scheme with thermal ellipsoids at the 50% probability level. Phenyl rings of the  $\text{PPh}_3$  ligands are omitted.



**Figure 4** Molecular structure of the cation of  $[(\text{Ph}_3\text{P})_4\text{Pt}_2(\mu\text{-S})\{\mu\text{-S-}o\text{-CH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{S-}\mu\}\mu\text{-S})\text{Pt}_2(\text{PPh}_3)_4](\text{BPh}_4)_2 \cdot 6(\text{BPh}_4)_2$  showing the atom numbering scheme with thermal ellipsoids at the 50% probability level. Phenyl rings of the  $\text{PPh}_3$  ligands are omitted.



**Figure 5**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\text{Ph}_3\text{P})_4\text{Pt}_2(\mu\text{-S})\{\mu\text{-}o\text{-SCH}_2\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_2\text{S}\}(\mu\text{-S})\text{Pt}_2(\text{PPh}_3)_4](\text{BPh}_4)_2 \cdot 6(\text{BPh}_4)_2$  showing the overlapping phosphorus signals and the satellite peaks due to  $^{195}\text{Pt}$  coupling



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