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Dinuclear platinum complexes with designer thiolate ligands from the monoalkylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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Abstract

Alkylation reactions of the nucleophilic platinum(II) sulfide complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with functionalised alkylating agents have been investigated as a versatile synthetic route to dinuclear, cationic sulfide-thiolate complexes of the type $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$, extending the range of thiolate complexes that can be prepared using this methodology. A wide range of functional groups can be incorporated, using appropriate alkylating agents, and include ketone, ester, amide, hydrazone, semicarbazone, thiosemicarbazone, oxime, guanidine, urea and thiourea groups.

Keywords: Platinum complexes; Sulfido complexes; Thiolate complexes; Crystal structure; Alkylation reactions

Introduction

The sulfido complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** is a well known metalloligand with exceptional reactivity.[1,2,3] The sulfide centres in **1** are highly nucleophilic and readily react with a wide range of electrophiles and metal centres. Even mild electrophiles such as CH_2Cl_2 and $CHCl_3$ are able to alkylate one of the sulfido ligands,[4] with the alkylation reactions providing a facile route for the conversion of one or both of the sulfido ligands into coordinated thiolate (SR^-) ligands. In a recent study[5] using electrospray ionisation mass spectrometry (ESI MS)[6] as a screening technique, we explored the reaction landscape between **1** and a wide variety of alkylating agents, and demonstrated that it is possible to generate dinuclear platinum complexes containing a range of thiolate ligands. Although the alkylation of coordinated sulfide ligands should be a very widely applicable methodology for the synthesis of thiolate complexes, it has not been fully recognised for its potential

importance.[7] To date, only a limited number of dinuclear platinum complexes containing functionalised thiolate ligands have been synthesised using sulfide alkylation.[8,9,10,11,12] Further interest in these alkylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ comes from their own potential to act as (cationic) metalloligands. We recently showed that simple alkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ (R = n-Bu or CH_2Ph) are able to coordinate organo-mercury (RHg^+) and phosphine-gold(I) (Ph_3PAu^+) cations through the underivatised sulfide ligand.[13] While such metalloligands might be expected to have relatively poor donor abilities in comparison with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, in a recent report it was shown that they can lead to the formation of species with unusual quadruply-bridging sulfide, in the cores $[Ag_2Pt_2(\mu\text{-}SR)(\mu_4\text{-}S)]^{3+}$, when R is an azolium group.[14] We are attracted by the prospect that the incorporation of additional coordinating functionality on to the thiolate group, through alkylation reactions of sulfido ligands, could potentially be used to design metalloligands with a diverse range of ligand donor capabilities. In this contribution we report the synthesis and characterisation of thiolate complexes containing a wide range of C=O and C=NR functionalities.

Results and discussion

Syntheses and spectroscopic characterisation

Three different reactions were selected for the synthesis of the alkylating agents used in this study. The general reaction sequences, shown in Scheme 1, use (a) Schiff base formation involving $RC(O)CH_2X$ (R = Ph, Me or biphenyl; X = Cl or Br), (b) urea formation from 2-chloroethylisocyanate, or (c) chloroacetylation, and allow the incorporation of a wide range of functionalities derived from amine-containing substrates. Primarily, we have focused on compounds containing chloroalkyl groups (rather than bromo- or iodo- derivatives), because of their lesser tendency to effect dialkylation reactions, and the low nucleophilicity of

chloride will minimise side reactions involving loss of coordinated phosphine ligands that can occur with iodide.[5]

The alkylating agents, including phenacyl chloride and a selection of other ketone-containing compounds, were reacted with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** in methanol, leading to alkylated products with functionalised, bridging thiolate ligands, as shown in Scheme 2. Some of these complexes were previously identified in our earlier screening study.[5] Although metal complexes of the thiolate ligands $PhNHC(O)CH_2S^-$[15,16] and $MeO_2CCH_2S^-$[17,18,19] are well known, and the thiols $PhC(O)CH_2SH$[20] and $EtO_2CCH_2C(O)CH_2SH$[21] are reported, the other thiolate ligands (or the free thiols) contained in complexes **3e**-**3o** appear to be new ligands.

Reactions were monitored by positive ion electrospray ionisation mass spectrometry (ESI MS), which we have previously found to be a valuable technique in the investigation of the alkylation chemistry of **1**.[5] Complete alkylation was typically indicated by conversion of the orange methanol suspension of **1** to a clear, pale yellow solution and replacement of the characteristic $[\mathbf{1} + H]^+$ ion by the alkylated product cation $[\mathbf{3}]^+$ in the ESI MS of the reaction mixture. In all cases, selective alkylation of a single sulfido centre was observed, giving mono-thiolate complexes in high purity. Variations in reaction time and temperature were required for different alkylating agents in order to effect complete reaction. For the 2-chloroethyl derivatives $ClCH_2CH_2NHC(O)N(CH_2CH_2)_2S$ **2m** and $PyNHC(O)NHCH_2CH_2Cl$ **2n** the reactions with **1** proceeded more slowly than for the alkylating agents containing a CH_2Cl group activated in the β position by a CO or CN group. Thus, the synthesis of **3m** was completed after 24 hours of stirring at room temperature and 24 hours of refluxing in methanol at 65 ^oC. In contrast $PhC(=NNHTs)CH_2Cl$ **2j** gave the monoalkylated derivative **3j** after 20 minutes at room temperature. Products were isolated from the filtered reaction

solutions by the addition of excess NH_4PF_6 or $NaBPh_4$, and are stable solids, soluble in chlorinated hydrocarbon solvents such as CH_2Cl_2 and $CHCl_3$.

The attempted synthesis of $PhC(=NNHC(S)NH_2)CH_2Cl$ from phenacyl chloride and thiosemicarbazide was not successful because of a cyclisation reaction leading to the formation of a 1,3,4-thiadiazine-2-amine derivative.[22] An alternative attempted reaction of thiosemicarbazide with $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_4]^+$ **3a** was also unsuccessful, with no peak in the ESI mass spectrum attributable to the target product resulting from semicarbazone formation.

The mixed thiolate-sulfide complexes show the expected spectroscopic features for this class of complex. The ESI mass spectra at a low cone voltage (20 V) typically show the expected $[M]^+$ cation, while examination of the spectra of **3a** and **3b** at higher cone voltages (up to 100 V) revealed loss of 1 or 2 PPh_3 ligands, such fragmentation being typical for Pt-PPh_3 complexes.[6] It is noteworthy that the reaction between **1** and the guanidine-derived alkylating agent $PhC(=NNHC(NH)NH_2)CH_2Cl$ gave a dicationic product $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(NH_2)_2)Ph\}(PPh_3)_4]^{2+}$ **3h** resulting from spontaneous protonation of the highly basic guanidine group to form a guanidinium cation, isolated as its bis(hexafluorophosphate) salt.

Complexes **3** contain two inequivalent phosphorus centres, but in their $^{31}P\{^1H\}$ NMR spectra most complexes show superimposed central (non-^{195}Pt) lines because of coincidental chemical shifts. However, the satellite peaks due to ^{195}Pt coupling are well separated, as illustrated for complex **3o·PF$_6$** in Figure 1. The same phenomenon was observed in early studies in this system, in the complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]I$.[23] The $^1J(PtP)$ coupling constants reflect the differing *trans* influences[24] of thiolate versus sulfide ligands, with phosphines *trans* to the higher *trans*-influence sulfide showing coupling constants around 2600 Hz, while those *trans* to thiolate have values around 3300 Hz. A more detailed analysis

of the coupling constant data reveals that the compounds containing the $SCH_2C(O)$ group tend to have higher values of $^1J(PtP_B)$ for the phosphines *trans* to the thiolate ligand, indicating that these thiolates have slightly lower *trans* influences than their counterparts with $SCH_2C(NR)$ groups. Compounds with the SCH_2CH_2 functionality have the lowest $^1J(PtP)$ values for the phosphines *trans* to thiolates, indicating these ligands have slightly higher *trans* influences. The dicationic guanidine-based compound **3h** has a notably large $^1J(PtP_A)$ coupling constant for the phosphines *trans* to sulfide (2738 Hz), and a low $^1J(PtP_B)$ coupling constant for the phosphines *trans* to thiolate (3287 Hz).

The ^1H NMR spectra gave complicated multiple signals in the aromatic region, which could not be easily assigned, but the SCH_2 protons were easily identifiable as a broad signal between 2.6 and 4.0 ppm with satellite peaks due to coupling to ^{195}Pt, with $^3J(PtH)$ around 35 Hz. The observation of this resonance is a clear indication of sulfide alkylation. Figure 2 shows part of the ^1H NMR spectrum of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C(O)NHC(O)NHCH_2CH_3)(PPh_3)_4]PF_6$ **3o·PF$_6$** showing a triplet resonance, due to coupling of the CH_2 protons to two of the PPh_3 phosphorus atoms, together with broad satellites due to ^{195}Pt coupling of 36 Hz. The ^1H NMR signal for the NH_2 protons in the semicarbazones **3e** and **3f** and the thiosemicarbazone **3i** derivatives appeared broad, due to exchange. The same effect was observed for the OH proton of the oxime derivative **3g**.

X-ray structure determinations

X-ray structure determinations of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_4]BPh_4$ **3a·BPh$_4$** $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)Ph\}(PPh_3)_4]PF_6$ **3e·PF$_6$**, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(NH_2)_2)Ph\}(PPh_3)_4](PF_6)_2$ **3h·(PF$_6$)$_2$**, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2NHC(O)N(CH_2CH_2)_2S\}(PPh_3)_4]PF_6$ **3m·PF$_6$** and $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)NHC(O)NHCH_2CH_3\}(PPh_3)_4]PF_6$ **3o·PF$_6$** were carried out to confirm the

structures of the complexes and to provide comparison with structures of monoalkylated derivatives that have been previously reported. Selected bond lengths and angles are presented in Tables 1–5, and the molecular structures and atom numbering schemes are shown in Figures 3–7, respectively.

The structures reveal the typical hinged butterfly conformation of the $\{Pt_2S_2\}$ ring, with square-planar platinum(II) centres. Table 6 shows a comparison of key geometric parameters for the five new structures, together with $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]PF_6 \cdot MeOH$ **4a**[23] and $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CN)(PPh_3)_4]PF_6$ **4b**[9] as selected examples of monoalkylated complexes reported in the literature. As observed in $^{31}P\{^1H\}$ NMR spectra, the *trans*-influence is typically in operation, with phosphine ligands *trans* to the bridging sulfide having longer Pt-P bond distances compared to the phosphine ligands *trans* to the thiolate ligand. This is exemplified by complex **3a·BPh$_4$**, where the average Pt-P bond distance *trans* to sulfide [2.3059(8) Å] is longer than the average Pt-P bond distance *trans* to thiolate [2.2802(7) Å]. The only exception appears to be complex **3h·(PF$_6$)$_2$**, where all the Pt-P bond distances appear statistically the same, due to the poorer quality of the structure determination.

In all five complexes the alkyl substituents adopt the typical preferred *exo* orientation[23,25,26] and point away from the bulky triphenylphosphine ligands on the $\{Pt_2S_2\}$ core. However, there are subtle differences, as illustrated in Figure 8. For example in the phenacylthiolate complex **3a·BPh$_4$** (Figure 8a) the bulky phenyl ring adopts a position outside of the $\{Pt_2S_2\}$ core, thus placing the sterically non-demanding ketone group above the core. In contrast, the closely related semicarbazone complex **3e·PF$_6$** has the opposite arrangement, with the phenyl ring occupying a pocket formed by two PPh_3 ligands on Pt(1) and the semicarbazone group projecting out from the $\{Pt_2S_2\}$ core, Figure 8b.

The conformation of the semicarbazone ligand in **3e·PF$_6$** is the same as that observed in other crystallographically characterised compounds containing the PhC(=N-NHC(O)NH$_2$) group.[27,28,29] The N(2)-N(1)-C(2) plane of the semicarbazone moiety is twisted at an angle of 40.28^o from the plane of the phenyl ring as defined by C(23)-C(26)-C(21). This twist may be due to crystal packing or steric hindrance between the attached semicarbazone and the triphenylphosphine rings of the complex. The semicarbazone group is planar, with a hydrogen bond [2.285 Å] between one of the NH$_2$ protons and the C=N nitrogen. There is also an interaction between the other NH$_2$ proton and a fluorine of an adjacent PF$_6^-$ anion, with F···H 2.276 Å. A similar F···HN interaction [2.219 Å] is seen in complex **3m**·PF$_6$. No intermolecular hydrogen bonding between cationic complexes was observed for any of the other compounds, presumably because of the separation imposed by the bulky PPh$_3$ ligands.

The dihedral angles (Table 6), between the two coordination planes S-Pt(1)-S and S-Pt(2)-S, are typically around 133-138°, depending on the nature of the attached group. The urea-thiolate complex **3o·PF$_6$** has a significantly larger dihedral angle of 157.6°. The dihedral angles of **4a** (138^o) and **3m·PF$_6$** (138.6^o) are larger than **3a·BPh$_4$** (133.8^o) and **3e·PF$_6$** (133.1^o). The smaller dihedral angles in the latter may be due to repulsion between the sterically bulky phenyl group of the thiolate and the PPh$_3$ rings, resulting in greater bending of the {Pt$_2$S$_2$} core. The difference in dihedral angles of **3h·(PF$_6$)$_2$** (134.8^o) and **3o·PF$_6$** (158^o) show the same trend. The increased folding along the S···S axis results in shorter Pt···Pt separations in **3e·PF$_6$** (3.297 Å) and **3a·BPh$_4$** (3.283 Å) compared to **3m·PF$_6$** (3.325 Å) and **4a** (3.306 Å). The average Pt-S-Pt bond angles are typically around 90^o; the S-Pt-S bond angles (Table 6) also remain fairly constant among the complexes. The torsion which may have been created within the ring by alkylation can be accommodated because of the flexibility of the {Pt$_2$S$_2$} core, without the need for significant distortion of the platinum coordination environment.

Conclusions

This investigation has demonstrated the successful construction of a range of functionalised thiolate ligands in the dinuclear platinum complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$, utilising the high nucleophilicity of μ-sulfido ligands in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1**. Potentially a diverse range of functional groups can be incorporated into suitable alkylating agents for **1**, and we are interested in the prospect that complexes with $\{Pt_2S_2\}$ cores, already known to be potent metalloligands, can be modified to incorporate a range of other coordinating groups in multifunctional metalloligands. We plan to explore the coordination chemistry of such designer metalloligands. The alkylations reported herein selectively result in monoalkylation of a single sulfide ligand. The ability to access dialkylated derivatives lies in the appropriate choice of alkylating agent and an investigation into the factors that influence alkylation of the second sulfide will be the focus of future work.

Experimental

Materials

Phenacyl chloride **2a** (BDH), $NaBPh_4$ (BDH), NH_4PF_6 (Aldrich), thiomorpholine (Aldrich), 2-chloroethylisocyanate (Aldrich), methyl chloroacetate **2c** (Riedel de Häen) and ethyl 4-chloroacetoacetate **2d** (Aldrich) were used as supplied from the respective commercial source. Dichloromethane and methanol were AR grade and used as supplied. Petroleum spirits refers to the fraction of boiling range 40-60 ºC. The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** was prepared by the literature procedure from *cis*-$[PtCl_2(PPh_3)_2]$ and sodium sulfide nonahydrate (Aldrich) in benzene suspension.[30,31]

Instrumentation

Electrospray mass spectra were recorded in positive-ion mode using a VG Platform II instrument, typically using a cone voltage of 20 V. Isolated complexes (*ca.* 0.5 mg) were dissolved in a small quantity of CH_2Cl_2 in an Eppendorf tube, then diluted with methanol (*ca*. 1.5 mL) and centrifuged prior to MS analysis. Spectra were typically an average of at least 7 scans. Assignment of all major peaks was confirmed by recording the high-resolution isotope pattern of the ions and comparing with the theoretical pattern obtained using the *Isotope* program.[32] ^{1}H NMR spectra were either recorded in $CDCl_3$ solution at 400 MHz or 300 MHz on Bruker Avance NMR spectrometers and $^{31}P\{^1H\}$ NMR spectra were recorded at 121.49 MHz in $CDCl_3$, unless otherwise stated. Coupling constants *J* are in Hz. Microelemental analyses were obtained from the Microanalytical Laboratory, University of Otago. Melting points and IR spectra (as KBr disks, unless otherwise stated) were obtained using a Reichert Thermopan Melting Point Machine and Perkin Elmer Spectrum100 FT-IR respectively.

Synthesis of the alkylating agents

The following alkylating agents [Ts = *p*-$MeC_6H_4SO_2$, Py = 2-C_5H_4N] were synthesised by the literature procedure: $PhNHC(O)CH_2Cl$ **2b**,[33] $PhC(=NNHC(O)NH_2)CH_2Cl$ **2e**,[34] $CH_3C(=NNHC(O)NH_2)CH_2Cl$ **2f**,[35] $PhC(=NOH)CH_2Cl$ **2g**,[36] $PhC\{=NNHC(=NH)NH_2\}CH_2Cl$ **2h**,[37] $CH_3C(=NNHC(S)NH_2)CH_2Cl$ **2i**,[38] $PhC(=NNHTs)CH_2Cl$ **2j**,[39] $CH_3C(=NNHTs)CH_2Cl$ **2k**,[39] $C_6H_5C_6H_4C(=NNHC(O)NH_2)CH_2Br$ **2l**,[40] 2-$PyNHC(O)NHCH_2CH_2Cl$ **2n**,[41] and $CH_3CH_2NHC(O)NHC(O)CH_2Cl$ **2o**.[42]

Preparation of $ClCH_2CH_2NHC(O)N(CH_2CH_2)_2S$ 2m

Thiomorpholine [$HN(CH_2CH_2)_2S$, 200 mg, 0.0002 mmol] was added to a solution of $ClCH_2CH_2NCO$ (200 mg, 0.0002 mmol) in diethyl ether (30 mL), immediately producing a white precipitate of the product. After stirring for 5 min. the product was filtered and washed with ether (20 mL) and dried under vacuum to give $ClCH_2CH_2NHC(O)N(CH_2CH_2)_2S$ (370 mg, 93%). Found: C 40.3, H 6.3, N 13.4; $C_7H_{13}ClN_2OS$ requires C 40.3, H 6.3, N 13.4%. ESI MS: *m/z*: 230 ($[M + Na]^+$, 100%). ^{1}H NMR (400 MHz), δ 7.26 (1H, *s*, NH), 3.67 (4H, *m*, CH_2), 3.65 (2H, *t*, CH_2), 3.57 (2H, *m*, CH_2), 2.20 (4H, *m*, CH_2).

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_4]BPh_4$ 3a·BPh_4

Phenacyl chloride **2a** (0.022 g, 0.142 mmol) was added to an orange suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (0.099 g, 0.066 mol) in methanol (30 mL) and the mixture stirred at room temperature for 1 h during which time the mixture changed from an orange suspension to a cloudy yellow solution. The solution was filtered to remove solid impurities, and $NaBPh_4$ (0.068 g, 0.199 mmol) was added to the filtrate. The solid precipitate was filtered and washed successively with water (10 mL), methanol (10 mL), and diethyl ether (10 mL) and dried under vacuum giving a yellow powder (0.040 g, 32%). M.p. 250-254 °C. Found: C 63.8, H 4.5%. $C_{104}H_{87}BOP_4Pt_2S_2$ (M_r 1941.80) requires C 64.3, H 4.5%. ESI MS: *m/z* 1623 ($[\mathbf{3a}]^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 24.5 [*d*, $^1J(PtP_B)$ 3386, P_B], 23.9 [*d*, $^1J(PtP_A)$ 2630, P_A]. ^{1}H NMR (300 MHz), δ 7.48-6.88 (85H, *m*, 17Ph), 3.95 [2H, *t*, SCH_2, ^3J(PtH) 34, ^4J(PH) 3.5]. IR: ν(C=O) 1672 cm^{-1}.

Crystals (orange plates) of the complex suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)NHPh\}(PPh_3)_4]BPh_4$ 3b·BPh_4

$PhNHCOCH_2Cl$ **2b** (0.034 g, 0.199 mmol) was added to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (0.152 g, 0.101 mmol) in methanol (30 mL) and the mixture stirred for 2 h, during which time the solution changed from a cloudy orange colour to a clear, yellow solution. The reaction mixture was filtered to remove any remaining solids, and addition of $NaBPh_4$ (0.103 g, 0.300 mmol) to the filtrate gave a bright yellow precipitate. This was filtered and washed successively with distilled water (10 mL), methanol (10 mL), and diethyl ether (10 mL) to give **3b·BPh_4** (0.077 g, 40%). M.p. 240-243 °C. Found: C 63.3, H 4.5, N 0.7%. $C_{104}H_{88}NBOP_4Pt_2S_2$ (M_r 1956.81) requires C 63.8, H 4.5, N 0.7%. ESI MS: *m/z* 1637 ([**3b**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 25.4 [*d*, $^1J(PtP_A)$ 2586, P_A], 25.1 [*d*, $^1J(PtP_B)$ 3332, P_B]. ^1H NMR (300 MHz), δ 8.18 (1H, *s*, NH), 7.82-5.87 (85H, *m*, 17Ph), 2.63 [2H, SCH_2, ^3J(PtH) 30]. IR: ν(NH) 3442; ν(C=O) 1686 cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CO_2Me\}(PPh_3)_4]BPh_4$ 3c·BPh_4

To $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (0.102 g, 0.068 mmol) in methanol (30 mL) was added methyl chloroacetate **2c** (5 drops, excess), and the mixture stirred at room temperature overnight, giving a cloudy yellow solution. After filtration, $NaBPh_4$ (0.067 g, 0.200 mmol) was added to the filtrate, giving a yellow precipitate, which was filtered, washed with water (10 mL), methanol (10 mL), and diethyl ether (10 mL) to give **3c·BPh_4** as a bright yellow solid (0.126 g, 54%). M.p. 207-210 °C. Found: C 62.4, H 4.5. $C_{99}H_{85}BO_2P_4Pt_2S_2$ (M_r 1895.73) requires C 62.7, H 4.5%. ESI MS: *m/z* 1577 ([**3c**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 25.4 [*d*, $^1J(PtP_B)$ 3365, P_B], 25.3 [*d*, $^1J(Pt\text{-}P_A)$ 2575, P_A]. ^1H NMR (300 MHz), δ 7.48-6.88 (80H, *m*, 16Ph), 3.34 (3H, *s*, CH_3), 2.62 [2H, SCH_2, ^3J(PtH) 39]. IR: ν(C=O) 1729 cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2COCH_2CO_2Et\}(PPh_3)_4]BPh_4$ 3d·BPh_4

To a suspension of **1** (0.099 g, 0.066 mmol) in methanol (30 mL) was added ethyl 4-chloroacetoacetate **2d** (5 drops, excess), and the mixture stirred at room temperature for 24 h to give a pale yellow cloudy solution, which was filtered. $NaBPh_4$ (0.067 g, 0.196 mmol) was added to the filtrate, and the resulting precipitate filtered and washed successively with water (10 mL), methanol (10 mL), diethyl ether (10 mL) and dried under vacuum giving **3d·BPh_4** as a yellow powder (0.064 g, 50%). M.p. 221-225 °C. Found: C 62.9, H 4.7%. $C_{102}H_{89}BO_3P_4Pt_2S_2$ (M_r 1951.79) requires C 62.8, H 4.6%. ESI-MS: *m/z* 1633 ([**3d**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 24.7 [*d*, $^1J(PtP_B)$ 3385, P_B], 23.9 [*d*, $^1J(PtP_A)$ 2610, P_A]. ^1H NMR (300 MHz), δ 7.49-6.88 (80H, *m*, 16Ph), 4.15 (2H, *q*, C**H**$_2$CH$_3$), 3.24 [2H, SCH_2, ^3J(PtH) 37], 2.56 (2H, *s*, COC**H**$_2$), 1.27 (3H, *t*, CH_3). IR: ν(C=O) 1740 cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)Ph\}(PPh_3)_4]PF_6$ 3e·PF_6

$PhC(=NNHC(O)NH_2)CH_2Cl$ **2e** (16.9 mg, 0.0798 mmol) was added to **1** (100 mg, 0.0665 mmol) in methanol (30 mL). The mixture was stirred at room temperature for 1 h to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (150 mg, 0.92 mmol) was added, followed by distilled water (60 mL) to induce precipitation. The product was filtered, washed with water (20 mL) and diethyl ether (20 mL) and dried under vacuum to give **3e·PF_6** as a pale yellow powder (109 mg, 90%). M.p. 192-194 ^oC. Found: C 52.5, H 3.9, N 2.5. $C_{81}H_{70}F_6N_3OP_5Pt_2S_2$ (M_r 1824.59) requires: C 53.3, H 3.9, N 2.3%. ESI MS: *m/z* 1679 ([**3e**] $^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 22.7 [*br s*, $^1J(PtP_A)$ 2634, ^1J(Pt-P_B) 3379]. ^1H NMR (400 MHz), δ 8.54 (1H, *s*, NH), 7.41-6.80 (65H, *m*, 13Ph), 3.95 [2H, *br*, SCH_2, ^3J(PtH) not discernible]. IR: ν_{max} 1701 (w), 1638(w) cm^{-1}.

Pale yellow crystals of **3e·PF_6** suitable for X-ray crystallographic analysis were obtained by vapour diffusion of diethyl ether into a dichloromethane solution.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)CH_3\}(PPh_3)_4]PF_6$ 3f·PF_6

$CH_3C(=NNHC(O)NH_2)CH_2Cl$ **2f** (11.9 mg, 0.0798 mmol) was added to **1** (100 mg, 0.0665 mmol) in methanol (30 mL). The mixture was stirred at room temperature for 1 h to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (150 mg, 0.92 mmol) was added, followed by distilled water (60 mL). The product was filtered, washed with water (20 mL) and diethyl ether (20 mL) and dried under vacuum to give **3f·PF_6** (96 mg, 82%) as a pale yellow powder. M.p. 188-190 ^oC. Found: C 51.4, H 3.9, N 2.3. $C_{76}H_{68}F_6N_3OP_5Pt_2S_2$ (M_r 1762.52) requires C 52.8, H 3.9, N 2.4%. ESI MS: *m/z* 1616 ([**3f**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 23.6 [*br s*, $^1J(PtP_A)$ 2607, $^1J(PtP_B)$ 3332]. ^1H NMR (400 MHz), δ 8.35 (1H, *s*, NH), 7.43-6.50 (60H, *m*, 12Ph), 3.39 [2H, *t*, SCH_2, $^3J(PtH)$ 34, $^4J(PH)$ 4.5], 0.49 (3H, s, CH_3). IR: ν(C=O) 1695 cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NOH)Ph\}(PPh_3)_4]PF_6$ 3g·PF_6

$PhC(=NOH)CH_2Cl$ **2g** (13.5 mg, 0.0798 mmol) was added to **1** (100 mg, 0.0665 mmol) in methanol (30 mL). The mixture was stirred at room temperature for 1 h to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (150 mg, 0.92 mmol) was added to the filtrate followed by distilled water (60 mL). Complex **3g·PF_6** (94 mg, 79%) was obtained as a pale yellow powder after filtration, washing with water (20 mL) and diethyl ether (20 mL), and vacuum drying. M.p. 164-166 ^oC. Found: C 53.2, H 3.9, N 0.8. $C_{80}H_{68}F_6NOP_5Pt_2S_2$ (M_r 1782.55) requires C 53.9, H 3.9, N 0.8%. ESI MS: *m/z* 1636 ([**3g**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 22.7 [*br s*, $^1J(PtP_A)$ 2635, $^1J(PtP_B)$ 3332]. ^1H NMR (300 MHz), δ 7.52-6.80 (65H, *m*, 13Ph), 3.89 [2H, *t*, SCH_2, $^3J(PtH)$ 35]. IR: ν_{max} 1629 (w) cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(NH_2)_2)Ph\}(PPh_3)_4](PF_6)_2$ $\mathbf{3h{\cdot}(PF_6)_2}$

$PhC(=NNHC(NH)NH_2)CH_2Cl$ (16.8 mg, 0.0798 mmol) was added to **1** (100 mg, 0.0665 mmol) in methanol (30 mL). The mixture was stirred at room temperature for 15 min. to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (150 mg, 0.92 mmol) was added, followed by distilled water (60 mL). The solid was filtered, washed with water (20 mL) and diethyl ether (20 mL) and dried under vacuum to give $\mathbf{3h{\cdot}(PF_6)_2}$ (68 mg, 61%) as a pale yellow powder. M.p. 167-170 ^oC. Found: C 49.4, H 3.8, N 2.8. $C_{81}H_{73}F_{12}N_4P_6Pt_2S_2$ (M_r 1970.59) requires C 49.4, H 3.6, N 2.8%. ESI MS: *m/z* 838 ([**3h**]$^{2+}$, 100%). $^{31}P\{^1H\}$ NMR, δ 22.4 [*s*, $^1J(PtP_B)$ 2738] and 21.2 [*s*, $^1J(PtP_A)$ 3287]. ^1H NMR (300 MHz), δ 12.20 (1H, *br*, NH), 7.62-6.95 (65H, *m*, 13Ph), 3.35 (2H, *br*, SCH_2). IR: ν_{max} 1679, 1614 cm^{-1}.

Light yellow crystals of $\mathbf{3h{\cdot}(PF_6)_2}$ suitable for X-ray crystallographic analysis were obtained by vapour diffusion of pentane into a dichloromethane solution.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(S)NH_2)CH_3\}(PPh_3)_4]PF_6$ $\mathbf{3i{\cdot}PF_6}$

$CH_3C(=NNHC(S)NH_2)CH_2Cl$ **2i** (10.6 mg, 0.0639 mmol) was added to **1** (80 mg, 0.053 mmol) in methanol (30 mL). The mixture was stirred at room temperature for 1 h to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (100 mg, 0.61 mmol) was added, followed by distilled water (60 mL). The solid was filtered, washed with water (40 mL) and diethyl ether (40 mL) and dried under vacuum to give $\mathbf{3i{\cdot}PF_6}$ (48 mg, 56%) as a pale yellow powder. M.p. 188-191 ^oC. Found: C 50.9, H 4.0, N 2.8. $C_{78}H_{68}F_6N_3P_5Pt_2S_3$ (M_r 1778.58) requires C 51.3, H 3.9, N 2.4%. ESI MS: *m/z* 1617 ([**3i**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 22.5 [*br s*, $^1J(PtP_A)$ 2602 and $^1J(PtP_B)$ 3322]. ^1H NMR (400 MHz), δ 7.53-6.80 (60H, *m*, 12Ph), 3.34 [2H, *t*, SCH_2, $^3J(PtH)$ 32, $^4J(PH)$ 4.5], 0.97 (NH), 0.64 (3H, *s*, CH_3). IR: ν_{max} 1620 (w) cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHTs)Ph\}(PPh_3)_4]PF_6$ 3j·PF_6

PhC(═NNHTs)CH_2Cl **2j** (25.8 mg, 0.0798 mmol) was added to **1** (100 mg, 0.0665 mmol) in methanol (30 mL). The mixture was stirred at room temperature for 20 min. to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (150 mg, 0.92 mmol) was added, followed by distilled water (60 mL). The product was filtered, washed with water (40 mL) and diethyl ether (40 mL) and dried under vacuum to give **3j·PF_6** (84 mg, 66%) as a pale yellow powder. M.p. 168-170^{o}C. Found: C 53.7, H 4.0, N 1.7. $C_{87}H_{75}F_6N_2OP_5Pt_2S_3$ (M_r 1935.74) requires C 54.0, H 3.9, N 1.5%. ESI MS: *m/z* 1787.3 ([**3j**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 22.6 [*br s*, $^1J(PtP_A)$ 2648, $^1J(PtP_B)$ 3375]. ^1H NMR (400 MHz), δ 9.59 (1H, *s*, NH), 7.73-6.51 (*m*, 13Ph & Ts), 3.63 (2H, *br*, SCH_2), 2.46 (3H, *s*, CH_3). IR: ν_{max} 1632 (w, br) cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHTs)CH_3\}(PPh_3)_4]PF_6$ 3k·PF_6

CH_3C(═NNHTs)CH_2Cl **2k** (21 mg, 0.0798 mmol) was added to **1** (100 mg, 0.0665 mmol) in methanol (30 mL). The mixture was stirred at room temperature for 25 min. to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (150 mg, 0.92 mmol) was added, followed by distilled water (60 mL). The product was isolated by filtration, washed with water (40 mL) and diethyl ether (40 mL) to give **3k·PF_6** (86 mg, 69%) as a pale yellow powder. M.p. 170-173 ^{o}C. Found: C 52.2, H 4.0, N 1.6. $C_{87}H_{73}F_6N_2O_2P_5Pt_2S_3$ (M_r 1874.68) requires C 52.6, H 3.9, N 1.5%. ESI MS: *m/z* 1735 ([**3k**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 23.6 [*br s*, $^1J(PtP_A)$ 2613] and 24.6 [*br s*, $^1J(PtP_B)$ 3330]. ^1H NMR (400 MHz), δ 7.50-7.03 (*m*, 12Ph & Ts), 3.8 (3H, *s*, CH_3), 3.21 [2H, *br*, SCH_2, ^3J(PtH) *ca*. 33, ^4J(PtH) 4.3], 2.48 (3H, *s*, CH_3). IR: ν_{max} 1619 (w, br), 1597 (w) cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)C_6H_4C_6H_5\}(PPh_3)_4]PF_6$ $\mathbf{3l{\cdot}PF_6}$

$C_6H_5C_6H_4C(=NNHC(O)NH_2)CH_2Br$ **2l** (13.3 mg, 0.040 mmol) was added to **1** (50 mg, 0.033 mmol) in methanol (20 mL). The mixture was stirred at room temperature for 25 min. to give a pale yellow solution. The solution was filtered to removed traces of solid matter and excess NH_4PF_6 (80 mg, 0.49 mmol) was added, followed by distilled water (30 mL). The product was filtered, washed with water (40 mL) and diethyl ether (40 mL) and dried under vacuum to give $\mathbf{3l{\cdot}PF_6}$ (37 mg, 59%) as a pale yellow powder. M.p. 188-190 ^oC. Found: C 54.6, H 4.0, N 2.6. $C_{87}H_{74}F_6N_3OP_5Pt_2S_2$ (M_r 1900.68) requires C 55.0, H 3.9, N 2.2%. ESI MS: *m/z* 1753 ([**3l**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 22.7 [*br s*, $^1J(PtP_A)$ 2619, $^1J(PtP_B)$ 3381]. ^1H NMR (300 MHz), δ 8.68 (1H, *s*, NH), 7.07-7.40 (*m*, 13Ph), 3.39 (2H, *br*, SCH_2). IR: ν_{max} 1698 (w) cm^{-1}.

Preparation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2NHC(O)N(CH_2CH_2)_2S\}(PPh_3)_4]PF_6$ $\mathbf{3m{\cdot}PF_6}$

The thiomorpholine-derived chloride **2m** (13.3 mg, 0.0639 mmol) was added to **1** (80 mg, 0.053 mmol) in methanol (20 mL). The mixture was stirred at room temperature for 24 h to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (100 mg, 0.61 mmol) was added, followed by distilled water (40 mL). The product was isolated by filtration, washed with water (40 mL) and diethyl ether (40 mL) and vacuum dried to give $\mathbf{3m{\cdot}PF_6}$ (75.3 mg, 79%) as a pale yellow powder. M.p. 249-252 ^oC. Found: C 51.8, H 4.1, N 1.5. $C_{79}H_{74}F_6N_2OP_5Pt_2S_3$ (M_r 1822.66) requires C 52.1, H 4.1, N 1.5%. ESI MS: *m/z* 1675 ([**3m**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 25.4 [*br s*, $^1J(PtP_A)$ 2670, $^1J(PtP_B)$ 3232]. ^1H NMR (400 MHz), δ 7.41-6.72 (60H, *m*, 12Ph), 6.76 (1H, *t*, NH), 3.55 (4H, *t*, CH_2), 3.41 (2H, *m*, CH_2), 2.31 (4H, *t*, CH_2), 1.36 [2H, *t*, SCH_2, $^4J(PH)$ 5.3]. IR: ν(C=O) 1638 cm^{-1}, ν(NH) 3455 (br) cm^{-1}.

Pale yellow crystals of **3m·PF$_6$** suitable for X–ray crystallographic analysis were obtained by diffusion of pentane into a dichloromethane solution.

Preparation of [Pt$_2$(μ-S){μ-SCH$_2$CH$_2$NHC(O)NHPy}(PPh$_3$)$_4$]PF$_6$ 3n·PF$_6$

PyNHC(O)NHCH$_2$CH$_2$Cl **2n** (12.8 mg, 0.0639 mmol) was added to **1** (80 mg, 0.053 mmol) in methanol (20 mL). The mixture was stirred at room temperature for 24 h. and refluxed at 65 ^{o}C for another 24 h to give a pale yellow solution. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (100 mg, 0.61 mmol) was added, followed by distilled water (40 mL). The product was isolated by filtration, washed with water (40 mL) and diethyl ether (40 mL) and dried under vacuum to give **3n·PF$_6$** (55 mg, 57%) as a pale yellow powder. M.p. 150-153 ^{o}C. Found: C 52.4, H 4.6, N 2.8. $C_{80}H_{71}F_6N_3OP_5Pt_2S_2$ (M_r 1813.59) requires C 53.0, H 4.0, N 2.3%. ESI MS: *m/z* 1667 ([**3n**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 25.0 [*br s*, $^1J(PtP_A)$ 2597, $^1J(PtP_B)$ 3281]. ^{1}H NMR (300 MHz), δ 8.38 (*s*, CH$_2$N**H**), 7.40-7.07 (60H, *m*, 12Ph), 2.74 (2H, *br m*, NHC**H**$_2$, 2.25 (2H, *br m*, SCH$_2$). IR: ν(CO) 1678 cm^{-1}.

Preparation of [Pt$_2$(μ-S){μ-SCH$_2$C(O)NHC(O)NHCH$_2$CH$_3$}(PPh$_3$)$_4$]PF$_6$ 3o·PF$_6$

CH$_3$CH$_2$NHC(O)NHC(O)CH$_2$Cl **2o** (66 mg, 0.40 mmol) was added to **1** (50 mg, 0.033 mmol) in methanol (20 mL) and the mixture stirred for 15 h. The solution was filtered to remove traces of solid matter and excess NH_4PF_6 (80 mg, 0.49 mmol) was added, followed by distilled water (30 mL). The product was filtered, washed with water (40 mL) and diethyl ether (40 mL) and dried under vacuum to give **3o·PF$_6$** (15 mg, 26%) as a pale yellow powder. M.p. 166-168 ^{o}C. Found C 51.3, H 4.0, N 2.0. $C_{77}H_{70}F_6N_2O_2P_5Pt_2S_2$ (M_r 1778.54) requires C 52.0, H 4.0, N 1.6%. ESI MS: *m/z* 1630 ([**3o**]$^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 24 [*br s*, $^1J(PtP_A)$ 2002, $^1J(PtP_B)$ 3379]. ^{1}H NMR (400 MHz), δ 7.42-7.08 (60H, *m*, 12Ph), 7.76 (1H, *t*, CONH),

6.67 (1H, *s*, NH), 3.18 (2H, *m*, CH_2), 2.85 [2H, *t*, SCH_2, ^3J(PtH) 36, ^4J(PH) 4.2], 1.03 (3H, *t*, CH_3). IR: ν(CO) 1710 cm^{-1}.

Pale yellow crystals of **3o·PF_6** suitable for X-ray crystallographic analysis were obtained by vapour diffusion of diethyl ether into a dichloromethane solution.

X-ray structure determinations

All data were obtained on a Bruker SMART CCD diffractometer at the University of Auckland and were corrected for absorption using a multi-scan method.[43] Structures were solved by the direct methods option of SHELXS-97[44] to give the location of the platinum atoms. All other non-hydrogen atoms were located from a series of difference maps. Full-matrix least-squares refinement (SHELXL-97)[45] was based on F_o^2 with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions, except as noted otherwise below. The crystal data and structure refinement parameter details are given in Table 7.

The crystal of **3e·PF_6** did not diffract very strongly, so the data were weaker than usual. A final peak in the penultimate difference map was assigned as the oxygen atom of a water molecule, hydrogen bonded to the C=O of the main molecule and to an F atom of the anion. The H atoms of the water molecule were not included in the refinement.

The structure of **3h·(PF_6)$_2$** was solved by direct methods and developed routinely to give the core of the dication. Subsequent difference maps revealed peaks that could be assigned to the side-chain attached to one S atom, but development of this part of the model was complicated by partial disorder arising from overlap of the side-chain in the reverse orientation by attachment to the other S atom, as indicated in Figure 9. This could not be resolved so the minor disordered fragment was not included in the refinement. Further disorder involved the anions. The cation charge requires 12 anions in the unit cell for neutrality. These were made up from six reasonably ordered PF_6^- anions in a general position.

Two more were rotationally disordered lying on a 3-fold axis coincident with the axial P-F bonds, so the equatorial F atoms were modelled over 9 equivalent sites. Two further PF_6^- anions were located on a 3-bar axis and were translationally disordered over 3 sites but could be modelled sensibly. At this stage a difference map revealed an isolated peak of *ca* 7 e $Å^{-3}$ on a three-fold axis, surrounded at a distance of 2.9 Å by C-H bonds. This refined sensibly as an F^- anion, providing the other two negative charges needed. An alternative interpretation of the electron density would be to assign four anions in total to the 3-bar site, and to refine the isolated peak as the O atom of an H_2O of crystallisation, but this was thought to be less likely. In the final refinement, the side-chain atoms and the disordered PF_6^- anion's F atoms, were treated isotropically and only the hydrogen atoms associated with the phenyl rings were included. This model led to a satisfactory refinement (R_1 = 0.0569) but there were still residual electron density peaks up to 4 e $Å^{-3}$ (mostly associated with the disordered side-chain) and significant "solvent accessible voids" which indicates that the overall structure determination was not completely resolved. The basic features are unambiguous, but parameters involving the disordered sections will not be reliable.

In complex **3o·PF$_6$** the substituent on the sulfide centre is disordered so that it is equally distributed across both symmetry-related S atoms, generating 2-fold pseudo symmetry. This could be modelled in space group C2/c, Hydrogen atoms were not included for the organic fragment, only for the phenyl rings.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 776311 (**3a**), 776313 (**3e**), 776312 (**3h**), 776314 (**3m**), and 776315 (**3o**). Copies of this information can be obtained free of charge from The Director, CCDC, 12

Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 1 Selected bond lengths and atomic distances (Å) and bond angles (°) for $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_4]BPh_4$ **3a·BPh$_4$** (Estimated standard deviations are in parentheses).

Bond lengths and interatomic distances (Å)

Pt(1)-P(1)	2.2903(7)	Pt(2)-P(3)	2.2700(7)
Pt(1)-P(2)	2.3186(7)	Pt(2)-P(4)	2.2931(8)
Pt(1)-S(1)	2.3580(7)	Pt(2)-S(1)	2.3180(7)
Pt(1)-S(2)	2.3594(7)	Pt(2)-S(2)	2.3837(7)
Pt(1)···Pt(2)	3.283	S(1)···S(2)	3.087
S(2)-C(1)	1.857(3)	O(1)-C(2)	1.219(4)

Bond angles (°)

S(1)-Pt(1)-S(2)	81.74(2)	S(1)-Pt(2)-S(2)	82.06(3)
P(1)-Pt(1)-S(1)	85.53(3)	P(3)-Pt(2)-S(1)	91.07(3)
P(2)-Pt(1)-S(2)	91.03(3)	P(4)-Pt(2)-S(2)	88.02(3)
Pt(2)-S(1)-Pt(1)	89.18(2)	Pt(1)-S(2)-Pt(2)	87.59(2)
C(1)-S(2)-Pt(1)	101.00(11)	C(1)-S(2)-Pt(2)	100.42(11)

Table 2 Selected bond lengths and atomic distances (Å) and bond angles (°) for $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)Ph\}(PPh_3)_4]PF_6$ **3e·PF$_6$** (Estimated standard deviations are in parentheses).

Bond lengths and interatomic distances (Å)

Pt(1)-P(2)	2.310(3)	Pt(1)-P(1)	2.315(3)
Pt(2)-P(3)	2.281(3)	Pt(2)-P(4)	2.316(3)
Pt(1)-S(1)	2.379(3)	Pt(1)-S(2)	2.344(3)
Pt(2)-S(1)	2.401(3)	Pt(2)-S(2)	2.333(3)
S(1)-C(1)	1.853(10)	C(1)-C(2)	1.486(15)
C(3)-N(3)	1.328(15)	C(3)-N(2)	1.388(14)
N(1)-N(2)	1.359(13)	C(2)-C(21)	1.525(16)
C(3)-O(1)	1.245(15)	C(2)-N(1)	1.298(13)
Pt(1)···Pt(2)	3.297	S(1)···S(2)	3.071

Bond angles (°)

S(2)-Pt(1)-S(1)	81.14(9)	Pt(1)-S(1)-Pt(2)	87.23(8)
S(2)-Pt(2)-S(1)	80.89(9)	Pt(2)-S(2)-Pt(1)	89.65(9)
N(1)-C(2)-C(1)	126.1(11)	C(1)-S(1)-Pt(2)	102.2(3)
O(1)-C(3)-N(2)	118.6(13)	C(1)-S(1)-Pt(1)	104.7(3)
N(3)-C(3)-N(2)	116.7(12)	C(1)-C(2)-C(21)	121.0(9)
C(2)-N(1)-N(2)	119.9(10)	O(1)-C(3)-N(3)	124.7(12)
N(1)-N(2)-C(3)	119.0(11)	C(2)-C(1)-S(1)	113.7(7)

Table 3 Selected bond lengths (Å) and bond angles (°) for $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(NH_2)_2)Ph\}(PPh_3)_4](PF_6)_2$ **3h·(PF$_6$)$_2$** (Estimated standard deviations are in parentheses).

Bond lengths and interatomic distances (Å)

Pt(1)-P(2)	2.291(2)	Pt(1)-P(1)	2.293(2)
Pt(2)-P(3)	2.295(2)	Pt(2)-P(4)	2.297(2)
Pt(1)-S(1)	2.363(2)	Pt(1)-S(2)	2.353(2)
Pt(2)-S(1)	2.354(2)	Pt(2)-S(2)	2.353(2)
S(1)-C(1)	1.934(17)	C(1)-C(2)	1.687(15)
C(3)-N(3)	1.26(2)	C(3)-N(2)	1.398(19)
N(1)-N(2)	1.357(16)	C(2)-C(11)	1.608(18)
C(3)-N(4)	1.41(2)	C(2)-N(1)	1.215(17)
Pt(1)···Pt(2)	3.305	S(1)···S(2)	3.064

Bond angles (°)

S(2)-Pt(1)-S(1)	81.01(8)	Pt(1)-S(1)-Pt(2)	88.96(7)
S(2)-Pt(2)-S(1)	81.20(7)	Pt(2)-S(2)-Pt(1)	89.23(7)
N(1)-C(2)-C(1)	126.1(14)	C(1)-S(1)-Pt(2)	105.6(5)
N(4)-C(3)-N(2)	116.5(15)	C(1)-S(1)-Pt(1)	96.9(5)
N(3)-C(3)-N(2)	117.5(16)	C(1)-C(2)-C(11)	102.7(11)
C(2)-N(1)-N(2)	117.4(13)	N(4)-C(3)-N(3)	126.0(17)
N(1)-N(2)-C(3)	121.0(12)	C(2)-C(1)-S(1)	113.7(11)

Table 4 Selected bond lengths (Å) and bond angles (°) for $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2NHC(O)N(CH_2CH_2)_2S\}(PPh_3)_4]PF_6$ **3m·PF$_6$**. (Estimated standard deviations are in parentheses).

Bond lengths and interatomic distances (Å)

Pt(1)-P(2)	2.2907(17)	Pt(2)-P(3)	2.2694(18)
Pt(1)-P(1)	2.2981(18)	Pt(2)-P(4)	2.3081(17)
Pt(1)-S(2)	2.3433(17)	Pt(2)-S(2)	2.3252(16)
Pt(1)-S(1)	2.3621(16)	Pt(2)-S(1)	2.3720(17)
S(1)-C(1)	1.827(7)	C(3)-O(1)	1.246(9)
C(1)-C(2)	1.516(10)	C(2)-N(1)	1.466(9)
C(3)-N(1)	1.348(10)	C(3)-N(2)	1.381(10)
Pt(1)···Pt(2)	3.325	S(1)···S(2)	3.077

Bond angles (°)

P(2)-Pt(1)-P(1)	98.10(6)	P(3)-Pt(2)-P(4)	99.82(6)
S(2)-Pt(1)-S(1)	81.68(6)	S(2)-Pt(2)-S(1)	81.84(6)
Pt(1)-S(1)-Pt(2)	89.23(6)	Pt(2)-S(2)-Pt(1)	90.83(6)
C(1)-S(1)-Pt(1)	104.9(2)	C(1)-S(1)-Pt(2)	103.1(2)
C(2)-C(1)-S(1)	109.0(5)	C(5)-S(3)-C(6)	94.9(6)
N(1)-C(2)-C(1)	113.1(6)	O(1)-C(3)-N(1)	120.6(7)
O(1)-C(3)-N(2)	120.9(7)	C(3)-N(1)-C(2)	119.5(6)
N(1)-C(3)-N(2)	118.5(7)		

Table 5 Selected bond lengths (Å) for $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C(O)NHC(O)NHCH_2CH_3)(PPh_3)_4]PF_6$ **3o·PF$_6$** (Estimated standard deviations are in parentheses).

Bond lengths and interatomic distances (Å)

Pt(1)-P(2)	2.2756(10)	Pt(1)-P(1)	2.2954(13)
Pt(1)-S(1)	2.3304(14)	Pt(1)-S(1a)	2.3371(11)
S(1)-C(1)	1.782(8)	N(1)-C(3)	1.422(11)
C(1)-C(2)	1.506(12)	C(3)-O(2)	1.194(11)
C(2)-O(1)	1.220(10)	C(3)-N(2)	1.332(12)
C(2)-N(1)	1.365(11)	N(2)-C(4)	1.465(11)
Pt(1)···Pt(2)	3.479	S(1)···S(2)	3.034

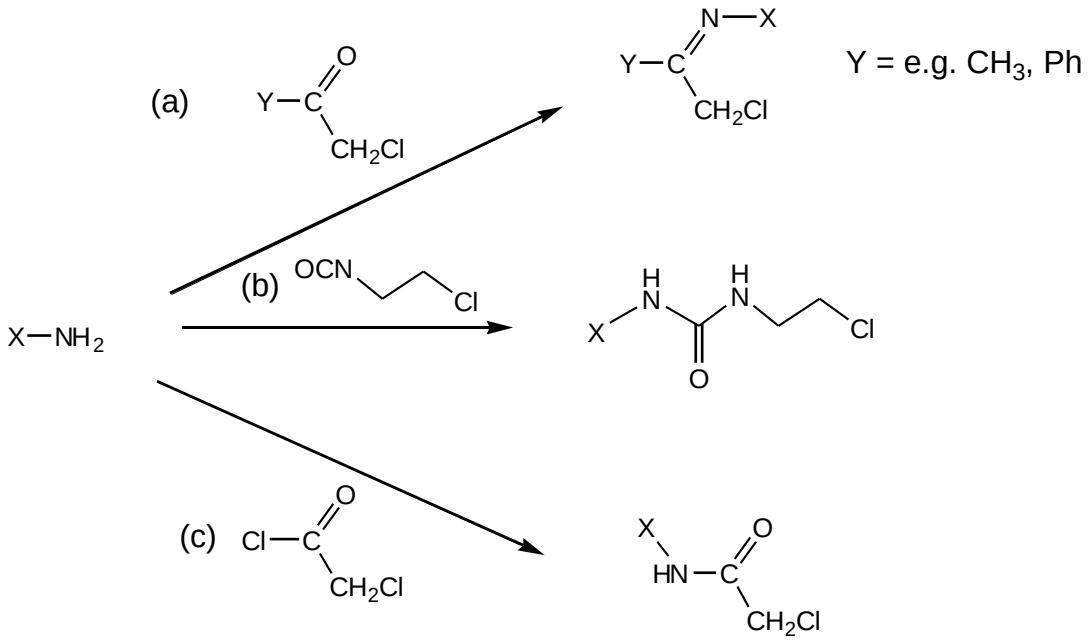
Table 6 A comparison of the geometric parameters [distances (Å) and angles (°)] for the complexes **3a·BPh_4**, **3e·PF_6**, **3h·$(PF_6)_2$**, and **3m·PF_6** together with $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]PF_6\cdot MeOH$ **4a** and $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CN)(PPh_3)_4]PF_6$ **4b** (Estimated standard deviations are in parentheses where reported)

	3a·BPh_4	**3e·PF_6**	**3h·$(PF_6)_2$**	**3m·PF_6**	**4a**	**4b**
Mean Pt-S	2.3380(7)	2.339(3)	2.353(2)	2.3343(17)	2.320(6)	2.367(5)
Mean Pt-SR	2.3716(7)	2.390(3)	2.359(2)	2.3671(17)	2.363(6)	2.3448(17)
Pt···Pt	3.283	3.297	3.305	3.325	3.306(1)	3.311
S···S	3.087	3.071	3.064	3.077	3.058(8)	3.169
Mean Pt-S-Pt	88.39(2)	88.44(8)	89.10(7)	90.03(6)	89.9(2)	89.30(12)
Mean S-Pt-S	81.90(3)	81.02(9)	81.11(7)	81.76(6)	81.6(2)	84.57(12)
Dihedral angle[¶]	133.8	133.1	134.8	138.6	138	144

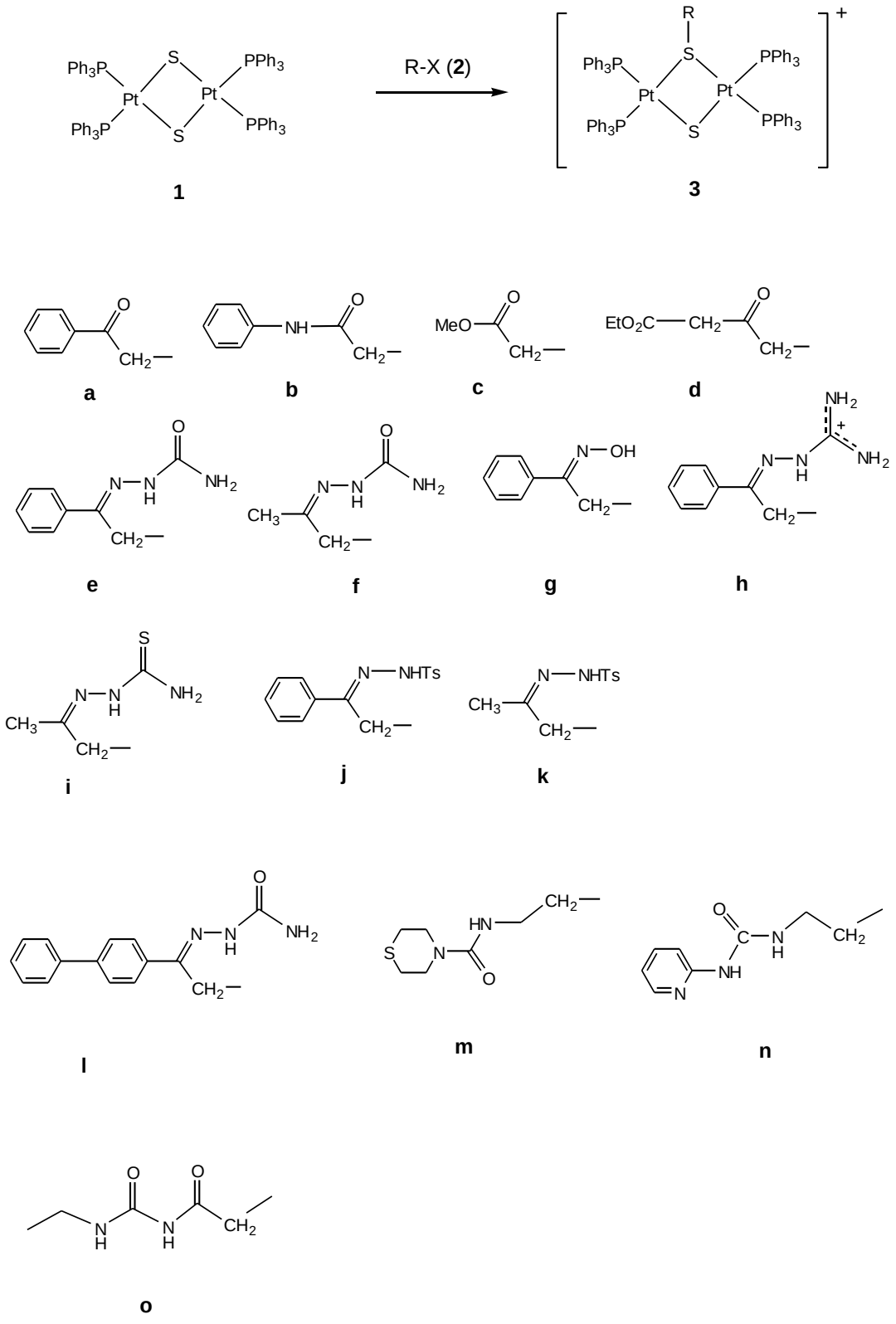
[¶] Dihedral angle = angle between the S(1)-Pt(1)-S(2) and S(1)-Pt(2)-S(2) planes

	3a·BPh_4	**3e·PF_6·H_2O**	**3h·$(PF_6)_2$**	**3m·PF_6·CH_2Cl_2**	**3o·PF_6**
Formula	$C_{104}H_{87}BOP_4Pt_2S_2$	$C_{81}H_{72}F_6N_3O_2P_5Pt_2S_2$	$C_{81}H_{72}F_{10.33}N_4P_{5.67}Pt_2S_2$	$C_{80}H_{75}Cl_2F_6N_2OP_5Pt_2S_3$	$C_{77}H_{69}F_6N_2O_2P_5Pt_2S_2$
Formula weight	1941.73	1842.57	1927.56	1906.53	1777.49
Temperature (K)	84(2)	89(2)	89(2)	89(2)	93(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Trigonal	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	P-3	$P2_1/c$	C2/c
a/Å	14.0766(2)	18.1793(1)	25.8410(2)	12.9507(1)	17.2956(6)
b/Å	19.8231(2)	21.0437(3)	25.8410(2)	22.4127(3)	18.8826(6)
c/Å	30.9538(4)	19.8683(3)	21.5233(3)	28.2565(3)	21.4712(7)
β/°	96.51(1)	92.995(1)	90	99.411(1)	90.067(1)
γ/°	90	90	120	90	90
Volume ($Å^3$)	8581.71(25)	7590.43(16)	12446.8(2)	8091.35(15)	7012.2(4)
Z	4	4	6	4	4
Density calcd (Mg m^{-3})	1.503	1.612	1.543	1.565	1.684
Absorption coeff.(mm^{-1})	3.430	3.906	3.595	3.755	4.224
F(000)	3888	3648	5712	3776	3512
Crystal size (mm)	0.21 x 0.21 x 0.10	0.26 x 0.10 x 0.08	0.30 x 0.18 x 0.14	0.28 x 0.24 x 0.20	0.49 x 0.42 x 0.32
Theta range for data collection (°)	1.22 to 27.17	1.41 to 26.30	1.82 to 26.39	1.59 to 26.37	2.36 to 31.76
Reflections collected	85356	43725	74050	47739	29848
Unique	18858 [R_{int} =0.0391]	15323[R_{int} = 0.1060]	16991[R_{int} = 0.0453]	16445[R_{int} = 0.0477]	10648 [R_{int} = 0.0237]
Max. and min. transmission	0.7254 and 0.5328	0.7452 and 0.4299	0.628 and 0.558	0.5205 and 0.4195	0.345 and 0.231
Goodness of fit on F^2	1.175	1.083	1.060	1.156	1.019
Final R indices [$I>2\sigma(I)$]	R_1 0.0293, wR_2 0.0517	R_1 0.0727, wR_2 0.1259	R_1 0.0569, wR_2 0.1495	R_1 0.0540, wR_2 0.1148	R_1 0.0375, wR_2 0.0835
R indices (all data)	R_1 0.0372, wR_2 0.0540	R_1 0.1353, wR_2 0.1469	R_1 0.0786, wR_2 0.1659	R_1 0.0665, wR_2 0.1206	R_1 0.0582, wR_2 0.0974
Largest diff. peak and hole (e $Å^{-3}$)	0.606 and -0.878	2.057 and -2.359	4.194 and -1.653	2.396 and -1.936	2.84 and -2.24

Table 7 Crystal and refinement data for the structures reported herein



Scheme 1 General procedures used in the synthesis of alkylating agents from an alkyl- or aryl-amine X-NH_2



Scheme 2 The synthesis of monoalkylated complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ **3** and the range of functionalised substituents R

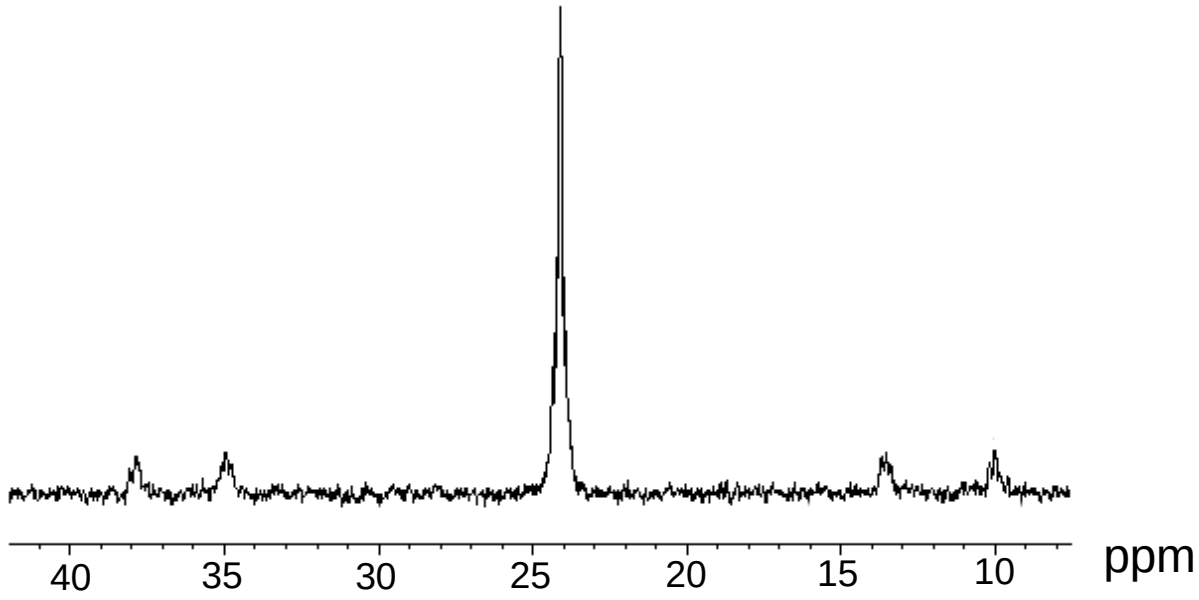


Figure 1 The $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C(O)NHC(O)NHCH_2CH_3)(PPh_3)_4]PF_6$ **3o·PF$_6$** showing the near equivalence of the central peaks, with two sets of satellites due to different ^{195}Pt coupling constants

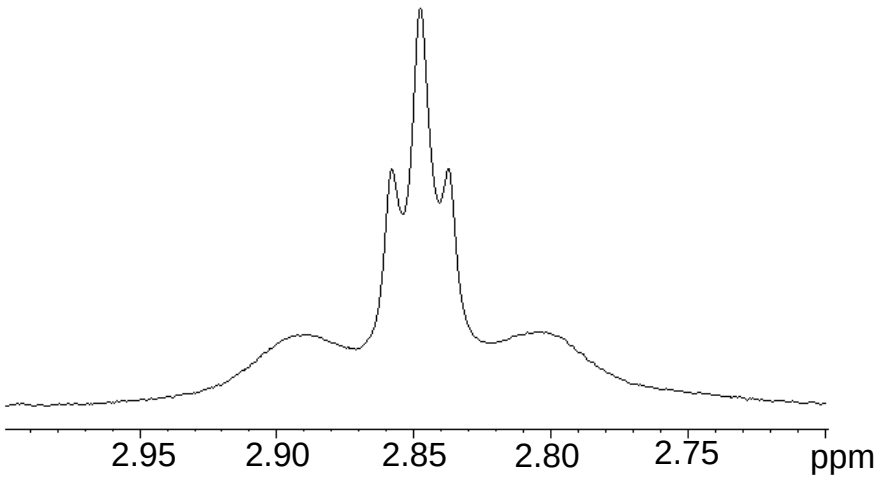


Figure 2 Part of the ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C(O)NHC(O)NHCH_2CH_3)(PPh_3)_4]PF_6$ **3o·PF$_6$** showing the triplet feature for the SCH_2 protons, with associated broad satellites due to coupling to ^{195}Pt.

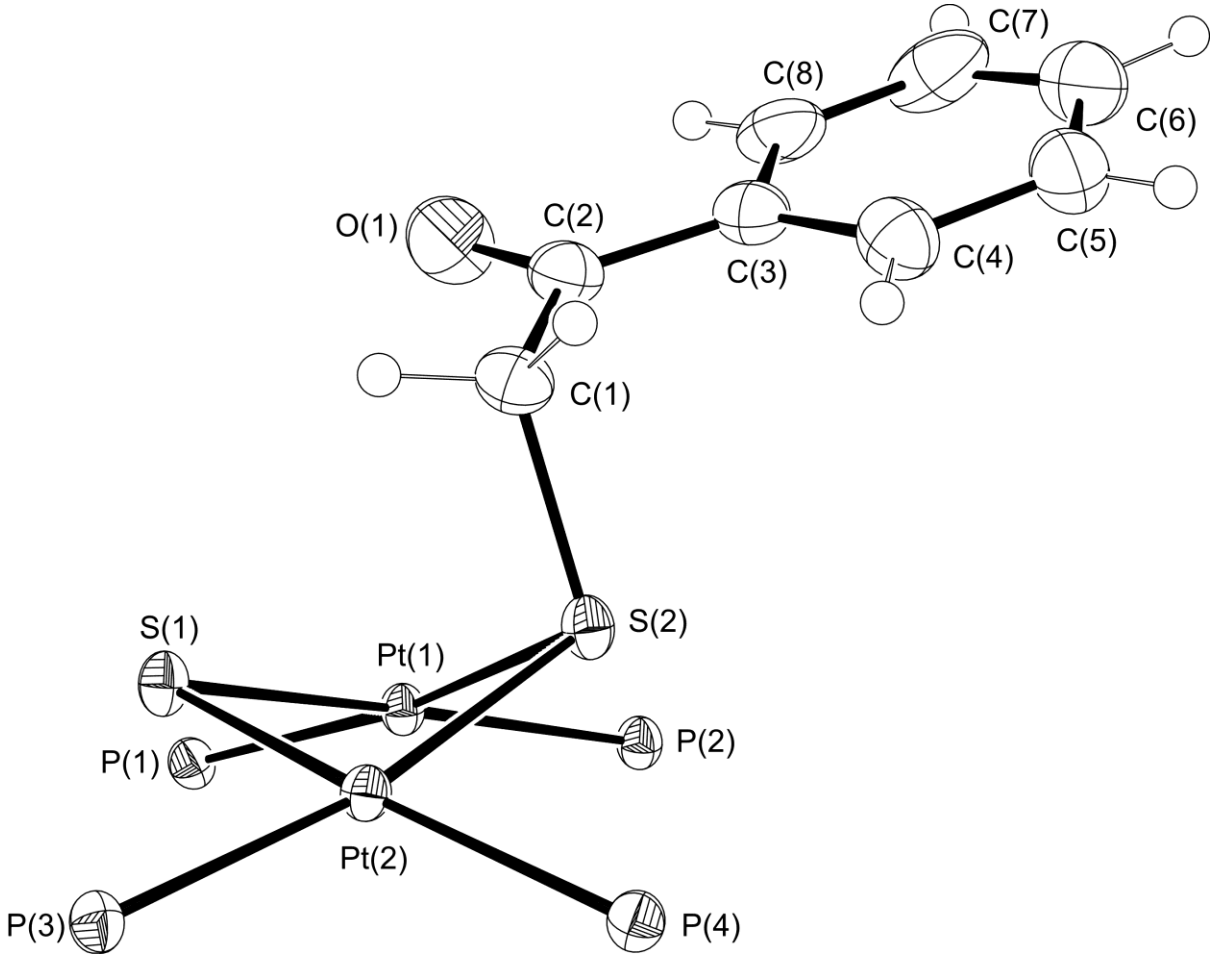


Figure 3 Molecular structure of the complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_4]BPh_4$ **3a·BPh$_4$** showing the atom numbering scheme, with thermal ellipsoids at the 50% probability level. The BPh_4^- counterion and the phenyl rings of the PPh_3 ligands have been omitted for clarity.

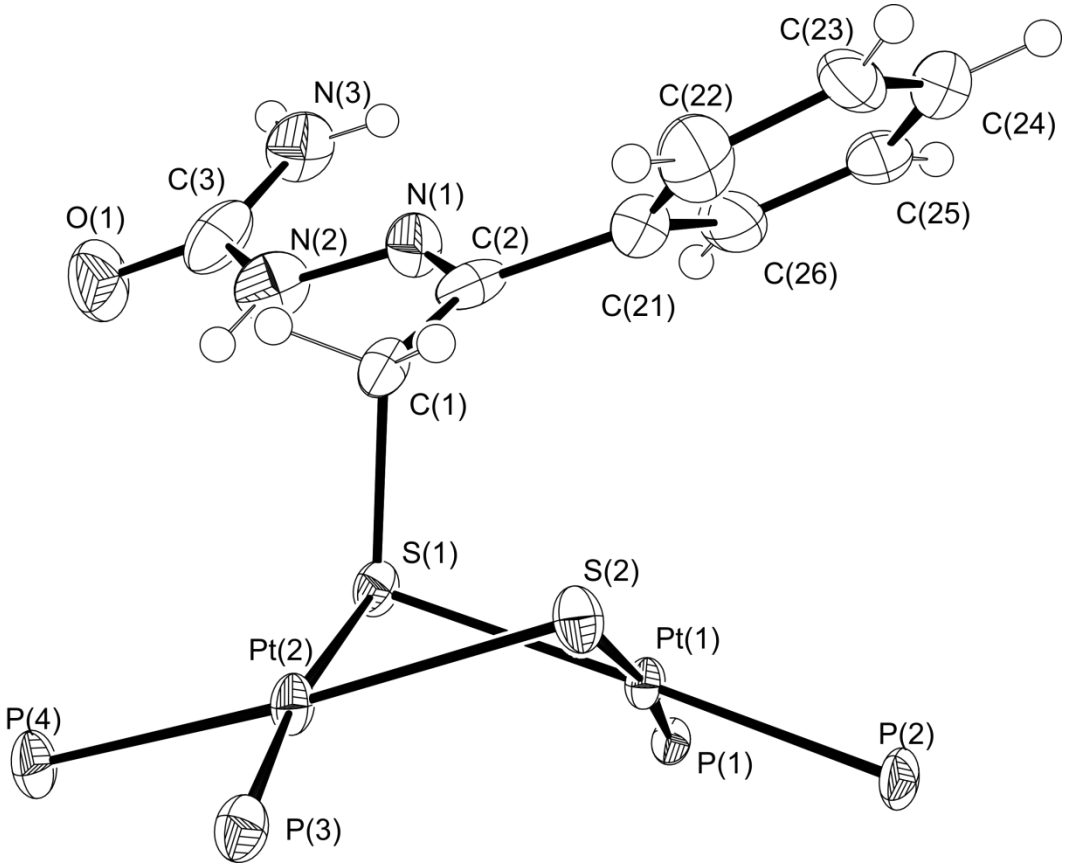


Figure 4 Molecular structure of the complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)Ph\}(PPh_3)_4]PF_6$ **3e·PF$_6$** showing the atom numbering scheme, with thermal ellipsoids at the 50% probability level. The PF_6^- counterion and the phenyl rings of the PPh_3 ligands have been omitted for clarity.

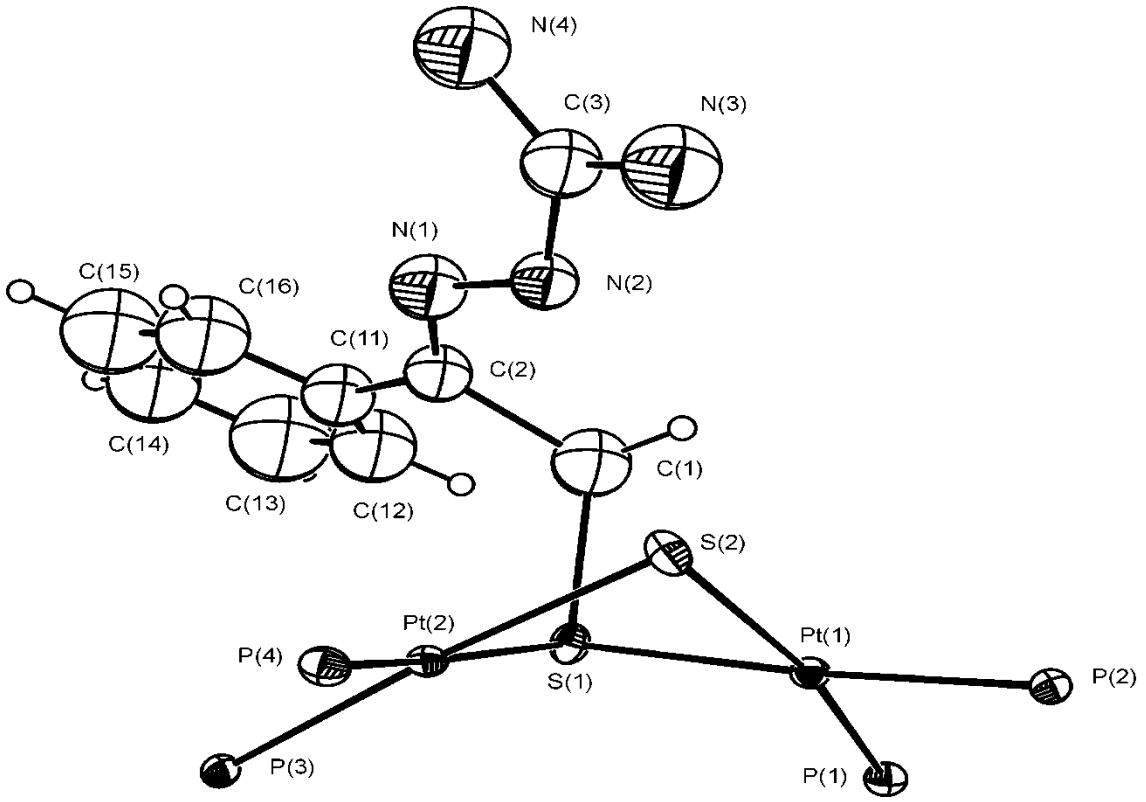


Figure 5 Molecular structure of the complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(NH_2)_2)Ph\}(PPh_3)_4](PF_6)_2$ **3h·(PF$_6$)$_2$** showing the atom numbering scheme, with thermal ellipsoids at the 50% probability level. The PF_6^- counterion and the phenyl rings of the PPh_3 ligands have been omitted for clarity.

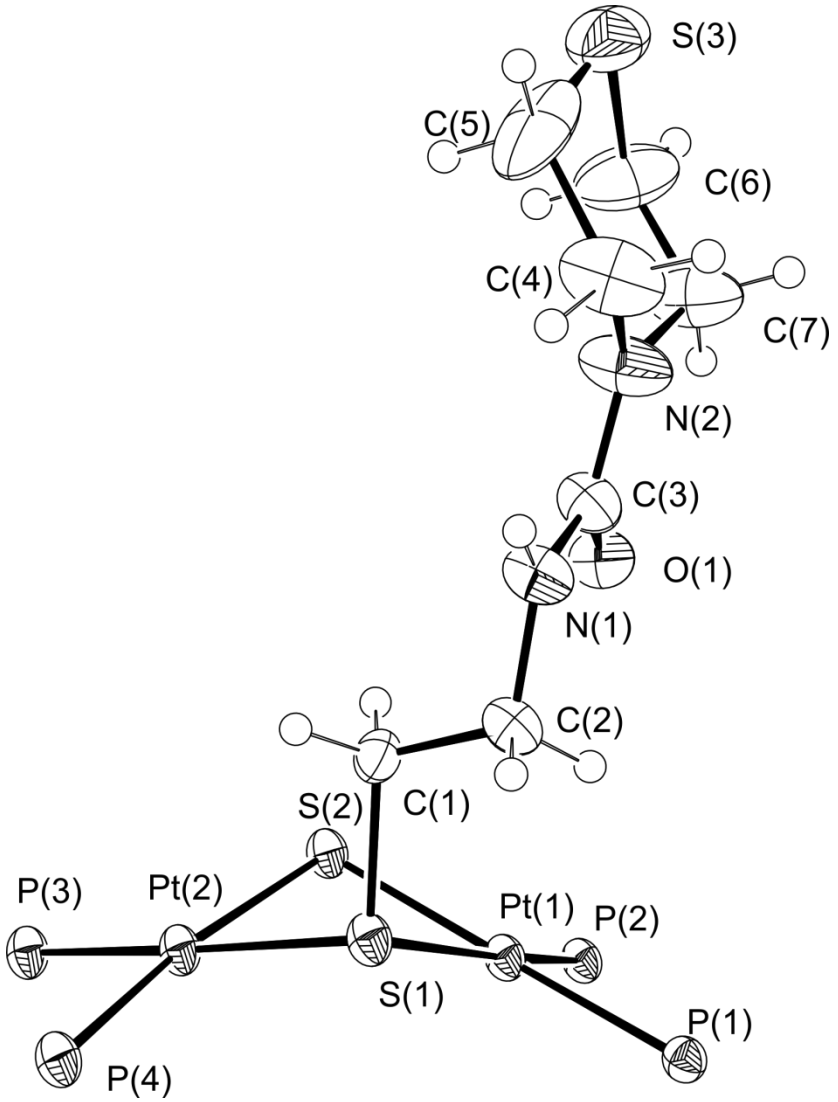


Figure 6 Molecular structure of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2NHC(O)N(CH_2CH_2)_2S\}(PPh_3)_4]PF_6$ **3m·PF$_6$** showing the atom numbering scheme, with thermal ellipsoids at the 50% probability level. The PF_6^- counterion, CH_2Cl_2 and the phenyl rings of the PPh_3 ligands have been omitted for clarity.

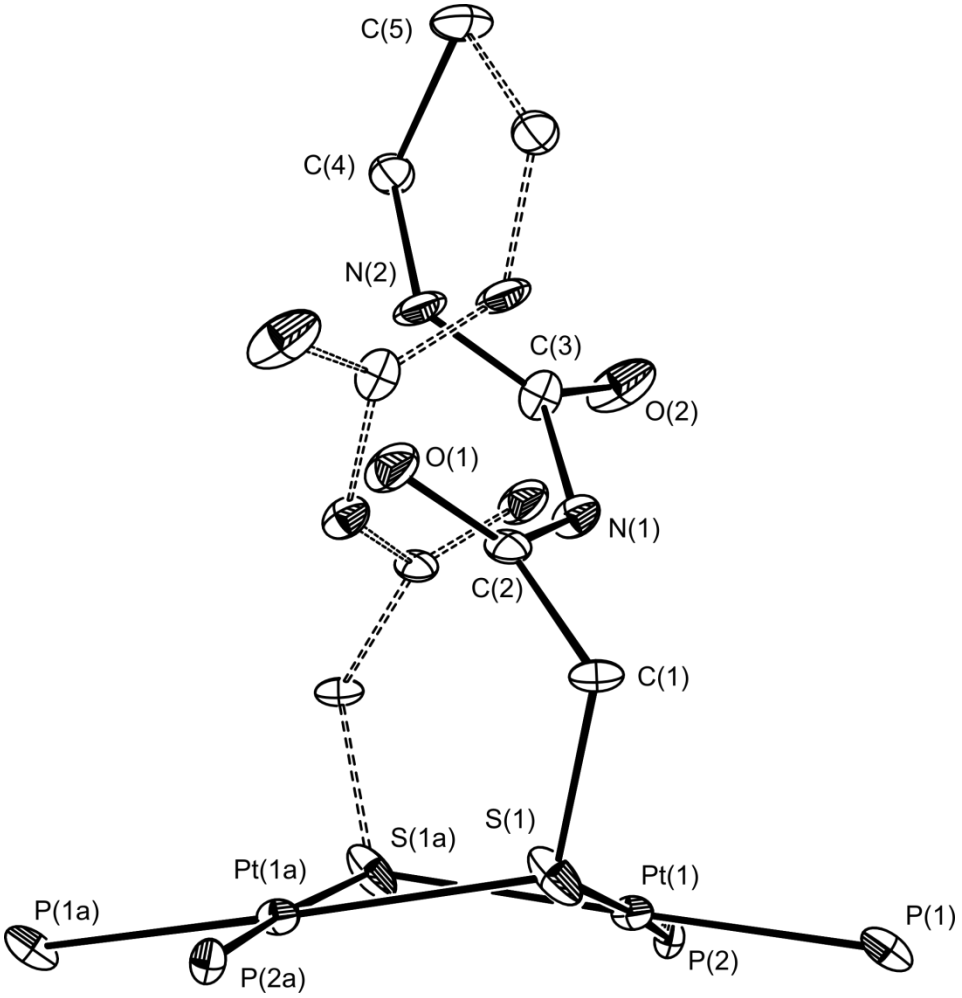


Figure 7 Molecular structure of the complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)NHC(O)NHCH_2CH_3\}(PPh_3)_4]PF_6$ **3o·PF$_6$** showing the atom numbering scheme, with thermal ellipsoids at the 50% probability level and the pseudo symmetry generated disordered substituent on the second sulfur atom. The PF_6^- counterion and the phenyl rings of PPh_3 ligands have been omitted for clarity.

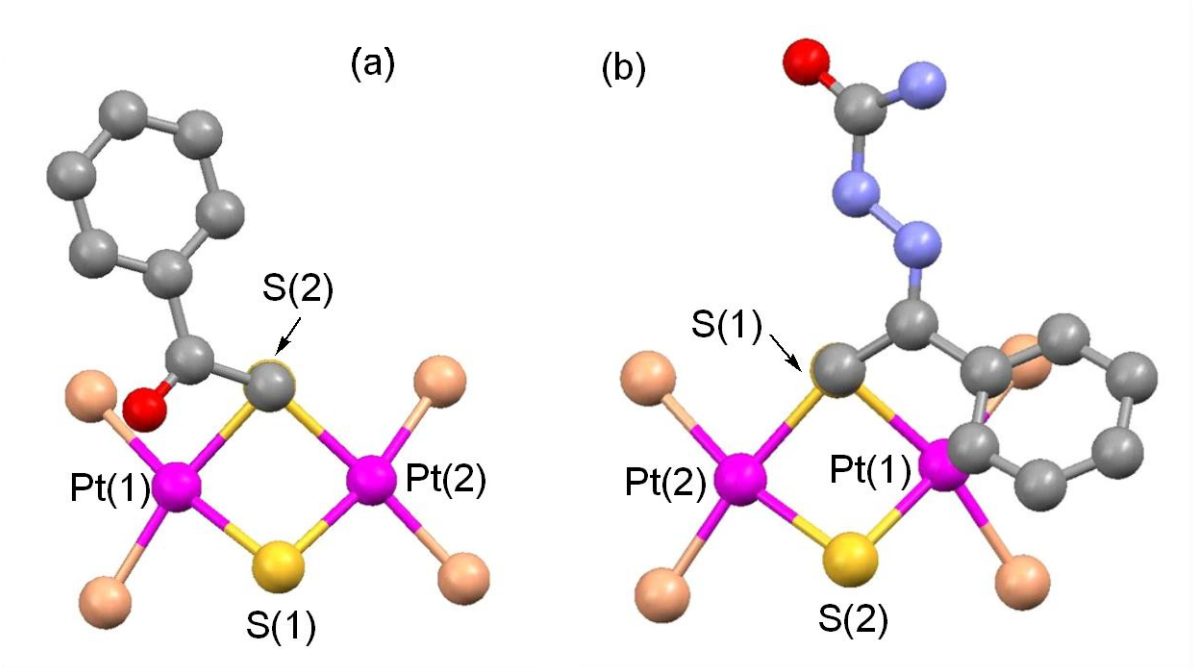


Figure 8 Plan views of (a) $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_4]BPh_4$ **3a·BPh$_4$** and (b) $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)Ph\}(PPh_3)_4]PF_6$ **3e·PF$_6$** looking down the S-C bonds, showing the arrangements of the thiolate substituents relative to the $\{Pt_2S_2\}$ cores.

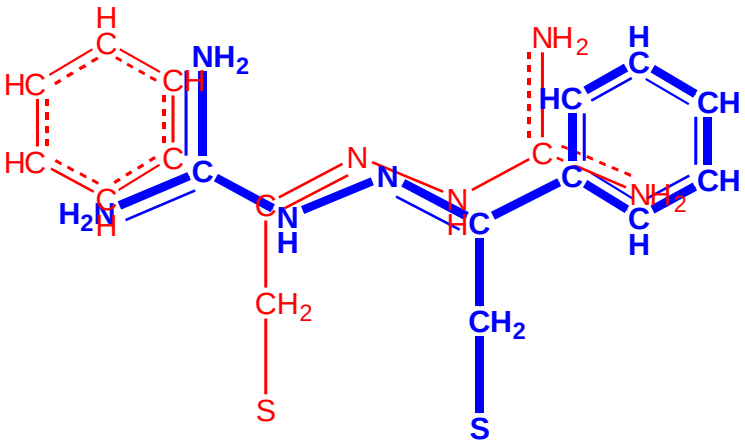


Figure 9 A diagram showing partial disorder of the thiolate ligand (bold, blue) in complex **3h·(PF$_6$)$_2$** arising from overlap of the side-chain attached to the other sulfur atom in the reverse orientation (red), giving a similar packing motif.

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