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PAPER

A novel structural rearrangement reaction of dialkylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ involving Pt–C bond formation†

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Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the dialkylating agents $ClCH_2C(O)CH_2Cl$ or $ClCH_2C(=NNHC(O)NH_2)CH_2Cl$ gives the dicationic di-μ-thiolate complexes $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4]^{2+}$ or $[Pt_2\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)CH_2S\}(PPh_3)_4]^{2+}$, isolated as BPh_4^- salts and characterised by ESI mass spectrometry, NMR spectroscopy and single-crystal X-ray crystallography. Treatment of the complex $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4]^{2+}$, which contains a [6.6.4] bicyclic system, with hydroxide ions results in deprotonation of a CH_2 group and rearrangement of the resulting monocation, giving $[Pt_2(\mu\text{-}SCH_2C(O)CHS\}(PPh_3)_4]^+$, isolated as its PF_6^- salt. An X-ray structure determination shows the complex to have a novel rearranged [6.5.5] bicyclic system containing a Pt–S–Pt–S–C five-membered ring with a Pt–C bond. The alkyl ligand has a high *trans*-influence, manifest in a long *trans* Pt–P bond and small ^1J(PtP) coupling constant to the *trans* PPh_3 ligand. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the 2,4-dinitrophenyl-hydrazone derivative of 1,3-dichloroacetone leads to the closely related complex $[Pt_2\{\mu\text{-}SCH_2C\text{-}(=NNHAr)CHS\}(PPh_3)_3Cl]$ [Ar = $C_6H_3(NO_2)_2$] in which a PPh_3 ligand is substituted by a chloride.

Introduction

The dinuclear platinum complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** has both a long history, and a very rich chemistry, as a result of the highly electron-rich and nucleophilic bridging sulfido ligands.[1] Analogues with selenide ligands,[2,3] or a variety of alternative phosphine[4–6] and arsine[7] ligands have also been described, and in many cases show an even more diverse reactivity.[8] Alkylation of metal–sulfido complexes is potentially a very general means of synthesising a metal–thiolate complex;[9,10] alkylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was realised in very early studies[11–14] and has continued to be developed as a versatile means of synthesising dinuclear platinum thiolate complexes[15] and of particular note is the ability to generate a wide variety of functionalised thiolate ligands at platinum by appropriate choice of alkylating agent. In some cases it may be possible to obtain thiolate ligands not easily accessible by other methodologies. This methodology has been employed in the synthesis of thiolate ligands containing, for example, fluorinated substituents,[16] or semicarbazone, urea, oxime and other groups.[17] The use of a dialkylating agent allows extension of the methodology to generate complexes containing a dithiolate ligand,[18] and the catalytic potential of this methodology for the synthesis of organosulfur compounds has been commented upon.[19] Additional longstanding interest in the chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ comes from its ability to act as a potent metalloligand towards a diverse range of metal centres, including main group[1,20,21] and transition metals,[1,22–26] as well as the actinide uranium.[27] The presence of a μ_2-sulfido ligand in monoalkylated complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ also allows these derivatives to act as cationic metalloligands, though to date this chemistry has not been extensively exploited.[28,29]

In the vast majority of studies on complexes with $\{Pt_2(\mu\text{-}S)_2\}$ cores, the core remains intact, though in a few cases partial desulfurisation of the core to a $\{Pt_2S\}$ unit,[30–32] or complete disintegration of the core to mononuclear platinum complexes, can occur. Examples of the latter include the reactivity with CH_2Cl_2 (giving complexes with $PtSCH_2S$ four-membered rings),[33–35] with hexafluorobenzene[36] and with protic acids.[37] However, we are unaware of any examples of studies involving complexes with $\{Pt_2S_2\}$ cores where an *expansion* of the four-membered $\{Pt_2S_2\}$ core occurs.

We have previously carried out a preliminary investigation into the alkylation and arylation chemistry landscape of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ using electrospray ionisation mass spectrometry (ESI MS) as an efficient, rapid screening methodology.[38] In this contribution we report studies on the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards the dialkylating agents $ClCH_2C(O)CH_2Cl$ and $ClCH_2C(=NNHR)CH_2Cl$ (R = $C(O)NH_2$ or 2,4-dinitrophenyl), which result in novel dinuclear dithiolate complexes with an expanded $\{Pt_2S_2C\}$ core. The reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with related monoalkylating agents such as $PhC(=NNHC_6H_3(NO_2)_2)CH_2Br$ has recently been reported.[17,39]

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Results and discussion

Synthesis and characterisation of dicationic dialkylated species

The reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** towards excess 1,3-dichloroacetone in methanol has previously been explored using electrospray ionisation mass spectrometry (ESI MS) and found to produce predominantly $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4]^{2+}$ **2**.[38] Two other species are formed in this reaction; one is a methanol adduct, tentatively assigned as the hemiketal $[Pt_2\{\mu\text{-}SCH_2C(OH)(OMe)CH_2S\}(PPh_3)_4]^{2+}$ **3**, while the second species is a monocation formed by deprotonation of $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4]^{2+}$, presumably one of the CH_2 protons. Macroscopic reaction followed by addition of a small quantity of aqueous HCl to reprotonate any monocationic species, followed by addition of excess $NaBPh_4$ gave an off-white precipitate shown by ESI MS to be predominantly $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4](BPh_4)_2$ **2**·$(BPh_4)_2$, still containing some methanol adduct. The $^{31}P\{^1H\}$ NMR spectrum of **2**·$(BPh_4)_2$ showed a single resonance at δ 19.3 showing ^1J(PtP) 3021 Hz, consistent with a highly symmetric structure, and in the ^1H NMR spectrum a broad resonance at δ 2.84 is assigned to the SCH_2 protons. Although satisfactory elemental analytical data could not be obtained (despite several attempts on different preparations of the complex) its formulation as **2** was confirmed by a single-crystal X-ray diffraction study (Fig. 1). The structure determination was of poor quality because of weakly diffracting crystals but it unambiguously confirms dialkylation of the $\{Pt_2S_2\}$ core. The structure is similar to other dialkylated derivatives, having the SCH_2 groups in axial positions on the puckered four-membered $\{Pt_2S_2\}$ ring. The bridging $CH_2C(O)CH_2$ group is inclined towards one of the Pt centres [Pt(2)], giving unequal Pt···C(3) distances. The distances between Pt(2) and the two CH_2 carbons C(1) and C(3) are 3.28(2) and 3.25(2) Å respectively. There is clearly no interaction between Pt(2) and the two CH_2 carbon atoms (*vide infra*) and the Pt(2)···O(1) separation in **2** is also too large for there to be any interaction, unlike other dicationic dialkylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ such as $[Pt_2\{\mu\text{-}SCH_2C(O)Ph\}_2(PPh_3)_4]^{2+}$, where relatively short Pt···O contacts occur.[40]

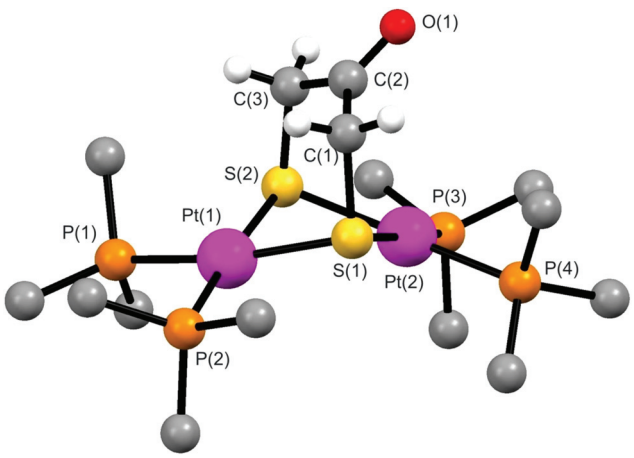


Fig. 1 Molecular structure of the core of the complex $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4]^{2+}$ **2**, with only the *ipso* carbon atoms of the PPh_3 ligands shown.

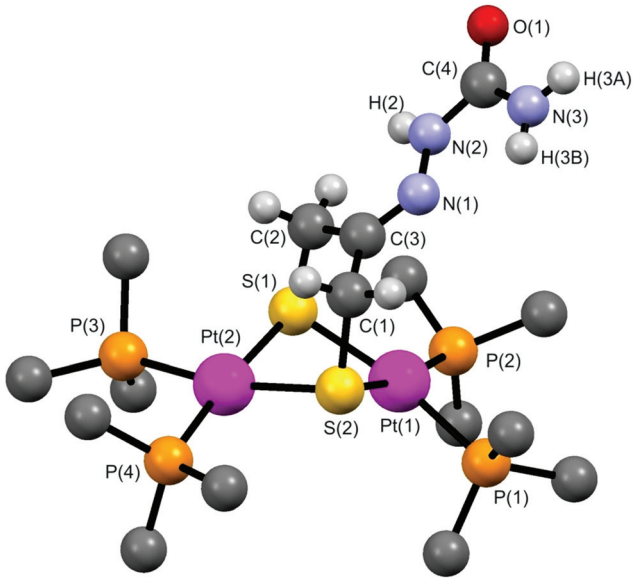


Fig. 2 Molecular structure of the core of the complex $[Pt_2\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)CH_2S\}(PPh_3)_4]^{2+}$ **4**, with only the *ipso* carbon atoms of the PPh_3 ligands shown.

Table 1 Selected bond lengths (Å) and angles (°) for $[Pt_2\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)CH_2S\}(PPh_3)_4](BPh_4)_2\cdot CH_2Cl_2$ [**4**·$(BPh_4)_2$·CH_2Cl_2]

Pt(1)–P(1)	2.2942(14)	Pt(1)–P(2)	2.2745(15)
Pt(2)–P(3)	2.2884(14)	Pt(2)–P(4)	2.2884(14)
Pt(1)–S(1)	2.3525(14)	Pt(1)–S(2)	2.3772(14)
Pt(2)–S(1)	2.3672(13)	Pt(2)–S(2)	2.3451(14)
S(2)–C(1)	1.827(6)	S(1)–C(2)	1.827(6)
C(1)–C(3)	1.511(7)	C(2)–C(3)	1.484(8)
C(3)–N(1)	1.287(7)	N(1)–N(2)	1.379(6)
N(2)–C(4)	1.389(8)	C(4)–O(1)	1.236(8)
C(4)–N(3)	1.328(8)		
P(2)–Pt(1)–S(1)	93.98(5)	P(1)–Pt(1)–S(2)	88.83(5)
P(4)–Pt(2)–S(2)	94.66(5)	P(3)–Pt(2)–S(1)	86.67(5)
S(1)–Pt(1)–S(2)	79.65(5)	S(2)–Pt(2)–S(1)	80.01(5)
C(2)–S(1)–Pt(1)	102.7(2)	C(2)–S(1)–Pt(2)	104.3(2)
C(1)–S(2)–Pt(2)	100.8(2)	C(1)–S(2)–Pt(1)	100.1(2)
Pt(2)–S(2)–Pt(1)	90.81(5)	Pt(1)–S(1)–Pt(2)	90.88(4)
N(1)–C(3)–C(2)	124.9(5)	N(1)–C(3)–C(1)	114.5(5)
C(2)–C(3)–C(1)	120.6(5)		

In a similar fashion, ESI MS-monitored reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the semicarbazone derivative of 1,3-dichloroacetone $[ClCH_2C(=NNHC(O)NH_2)CH_2Cl]$ rapidly gave the dialkylated complex $[Pt_2\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)CH_2S\}(PPh_3)_4]^{2+}$ **4**, *m/z* 810.7. There was no evidence for deprotonated species (presumably due to the semicarbazone group being less strongly electron-withdrawing than the parent ketone), or methanol adduct as found for 1,3-dichloroacetone itself. The cation was isolated as the BPh_4^- salt **4**·$(BPh_4)_2$ by addition of excess $NaBPh_4$.

The X-ray crystal structure of complex **4** was also determined, and the structure of the core is shown in Fig. 2, while selected bond lengths and angles are given in Table 1. The Pt–S bond lengths of the $\{Pt_2S_2\}$ core (dihedral angle between PtS_2 planes 136.5°) span the range 2.3451(14) to 2.3772(14) Å and the S–C bond lengths are S(2)–C(1) 1.827(6) and S(1)–C(2) 1.827(6) Å.

Similar to **2**, the semicarbazone ligand of **4** is tilted towards one of the platinum atoms such that the angles between the S(1)–C(2)–C(1)–S(2) and C(1)–C(2)–C(3)–N(1) planes is 45.1°, and the Pt···C(3) distances are 3.196(7) and 3.739(7) Å. One of the $C(O)NH_2$ hydrogens [H(3B)] is involved in an intramolecular hydrogen bond with the imine nitrogen N(1) forming a five-membered ring, with N(1)···H(3B) 2.245(7) Å. The semicarbazone forms an intermolecular hydrogen-bonded dimer in the crystal, through interaction of N(2)–H(2) with O(1), giving an N···O separation of 2.87(1) Å.

The asymmetry of the semicarbazone group is shown in the $^{31}P\{^{1}H\}$ NMR spectrum of **4**·$(BPh_4)_2$ which showed two overlapping singlets for the two PPh_3 environments; P(2) and P(3) (which are on the same side of the Pt_2S_2 core as the semicarbazone group) and P(1) and P(4) (which are on the opposite side). The lack of free rotation about the C═N bond maintains the inequivalence of these two sets of PPh_3 ligands in solution. Accordingly, two slightly different ^{1}J(PtP) couplings (3043 and 2992 Hz) are seen for the two pairs of PPh_3 ligands. The CH_2 groups also give two broadened triplets in the ^{1}H NMR spectrum of **4**·$(BPh_4)_2$ at δ 2.38 and 2.73; this is consistent with the observation of two CH_2 environments in $ClCH_2C(=NNHC(O)NH_2)$-CH_2Cl and CH_3 environments in $CH_3C(=NNHC(O)NH_2)$-CH_3.[41]

Synthesis and characterisation of rearranged products with novel five-membered {Pt_2S_2C} rings

When a pale yellow reaction mixture of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and 1,3-dichloroacetone, generating $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}$-$(PPh_3)_4]^{2+}$ **2** *in situ*, is subsequently treated with a strong base (aqueous NaOH), it immediately turns deep yellow, and positive-ion ESI MS shows complete deprotonation of the starting cation $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4]^{2+}$ **2**, with concomitant loss of the associated methanol adduct **3**. A parallel reaction, replacing hydroxide by a weaker base (pyridine, 1 mol equivalent) did not result in deprotonation of the parent dication. Precipitation of the deprotonated product as its BPh_4^- salt (by addition of excess $NaBPh_4$) yielded a yellow solid which showed predominantly the deprotonated species in its ESI mass spectrum, together with a small amount (*ca.* 10% relative intensity) of the reprotonated dication. Spectroscopic data on this compound did not allow the unambiguous assignment of a sensible structure, so attempts were made to characterise the complex crystallographically. The BPh_4^- salt did not yield good crystals, however the corresponding PF_6^- salt **5**·PF_6 (prepared by addition of excess NH_4PF_6 to another reaction mixture) yielded orange crystals suitable for crystallographic characterisation, and which gave satisfactory microanalytical data.

The X-ray structure (Fig. 3) revealed a novel rearranged product containing a $[Pt_2\{\mu\text{-}SCH_2C(O)CHS\}(PPh_3)_4]^+$ cation and a PF_6^- counteranion, together with two molecules of CH_2Cl_2. Selected bond lengths and angles for **5**·PF_6 are given in Table 2. The organic ligand of **5** is formally trianionic, and its formation is a consequence of a novel structural rearrangement process. In the starting bicyclic complex **2**, the four-membered {Pt_2S_2} core is intact [relative to the parent complex $Pt_2(\mu\text{-}S)_2(PPh_3)_4$], such that there are one four-membered and two six-membered rings *i.e.* a [6.6.4] bicyclic system. In **5**, there are two five-membered and one-six membered rings, *i.e.* a [6.5.5] system.

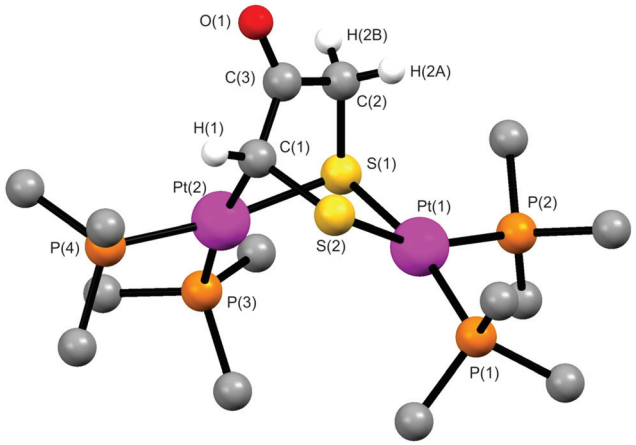


Fig. 3 Molecular structure of the core of the complex $[Pt_2\{\mu\text{-}SCH_2C(O)CHS\}(PPh_3)_4]^+$ **5**, with only the *ipso* carbon atoms of the PPh_3 ligands shown.

Table 2 Selected bond lengths (Å) and angles (°) for $[Pt_2\{\mu\text{-}SCH_2C(O)CHS\}(PPh_3)_4]PF_6\cdot 2CH_2Cl_2$ [**5**·PF_6·$2CH_2Cl_2$]

Pt(2)–C(1)	2.090(3)	Pt(2)–P(4)	2.2902(16)
Pt(2)–P(3)	2.3510(13)	Pt(2)–S(1)	2.3684(16)
Pt(1)–P(2)	2.3051(15)	Pt(1)–P(1)	2.3034(13)
Pt(1)–S(2)	2.3323(13)	Pt(1)–S(1)	2.3589(14)
S(1)–C(2)	1.823(3)	S(2)–C(1)	1.823(3)
O(1)–C(3)	1.207(4)	C(1)–C(3)	1.483(4)
C(2)–C(3)	1.511(4)		
C(1)–Pt(2)–P(4)	90.64(8)	C(1)–Pt(2)–P(3)	170.41(8)
P(4)–Pt(2)–P(3)	98.58(3)	C(1)–Pt(2)–S(1)	79.20(8)
P(4)–Pt(2)–S(1)	168.96(3)	P(3)–Pt(2)–S(1)	91.80(3)
P(1)–Pt(1)–P(2)	99.23(4)	P(1)–Pt(1)–S(2)	89.54(5)
P(2)–Pt(1)–S(2)	159.39(3)	P(1)–Pt(1)–S(1)	167.80(3)
P(2)–Pt(1)–S(1)	87.44(4)	S(2)–Pt(1)–S(1)	87.57(5)
C(2)–S(1)–Pt(1)	101.28(11)	C(2)–S(1)–Pt(2)	98.95(10)
Pt(1)–S(1)–Pt(2)	97.58(3)	C(1)–S(2)–Pt(1)	107.51(10)
C(3)–C(1)–S(2)	113.4(2)	C(3)–C(1)–Pt(2)	107.12(19)
S(2)–C(1)–Pt(2)	105.40(14)	C(3)–C(2)–S(1)	109.2(2)
O(1)–C(3)–C(1)	123.0(3)	O(1)–C(3)–C(2)	120.3(3)
C(1)–C(3)–C(2)	116.7(2)		

Complex **5** contains a μ-thiolate ligand S(1) that coordinates to both platinums, and linked through a $CH_2C(O)$ group to a CHS moiety. This thiolate bonds solely to Pt(1) through its sulfur S(2) (forming a terminal thiolate bond), and to Pt(2) through the CH moiety, forming a Pt–C bond with a Pt–C bond distance of 2.090(3) Å. This appears to be somewhat short for Pt–C bonds involving an electron-withdrawing group attached to the Pt–C carbon, *e.g.* 2.126(8) and 2.12(1) Å for the respective Pt–C bonds in the complexes $[PtCl\{CHMe(CO_2{}^tBu)\}(Ph_2PCH_2$-$CH_2PPh_2)]$[42] and $[PtCl\{CHCl(CO_2Me)\}(Ph_2PCHMeCHMe$-$PPh_2)]$.[43]

Platinum Pt(2) is only very slightly distorted from a regular square-planar geometry, with an angle of 5.12° between the Pt(2)–P(3)–P(4) and Pt(2)–S(1)–C(1) planes. This can be additionally quantified by the Houser τ_4 parameter[44] for Pt(2) of 0.15, where a perfect square-plane and tetrahedron have τ_4

values of 0 and 1 respectively. In contrast, the geometry at Pt(1) is more distorted; the corresponding angle between the planes Pt(1)–S(1)–S(2) and Pt(1)–P(1)–P(2) is 21.08°, and the Houser τ_4 parameter is 0.23. As expected, the Pt···Pt [3.556(2) Å] and S···S [3.246(2) Å] distances of **5** are significantly increased compared to compound **4** with a $\{Pt_2S_2\}$ core [Pt···Pt 3.363(1), S···S 3.029(3) Å]. The Pt(1)–S(1)–Pt(2) bond angle (involving the sulfide) in **5** [97.58(3)°] is notably larger than Pt–S–Pt bond angles in complexes with $\{Pt_2S_2\}$ cores [*e.g.* **4**, Pt(2)–S(2)–Pt(1) 90.81(6), Pt(1)–S(1)–Pt(2) 90.88(6)], on account of a five- *versus* four-membered ring.

The differing *trans*-influences[45] of the donor ligands of **5** are reflected in the range of Pt–P bond distances. Thus, the high *trans*-influence carbon donor effects a significant lengthening of the *trans* Pt(2)–P(3) bond [2.3510(13) Å], this being the longest Pt–P bond in the complex. Lengthening of the Pt(2)–P(3) bond effects a mutual shortening of the other Pt–P bond on the same platinum [Pt(2)–P(4) 2.2902(16) Å], which is slightly shorter than the other Pt–P bond *trans* to the μ-sulfido ligand Pt(1)–P(1) [2.3034(13) Å]. The remaining triphenylphosphine P(2) is *trans* to the thiolate sulfur S(2) with a Pt(1)–P(2) bond distance of 2.3051(15) Å.

The Pt(1)–S(2) terminal thiolate bond [2.3323(13) Å] is shorter than the Pt–S bonds to the μ-sulfido ligand [Pt(1)–S(1) 2.3589(14) and Pt(2)–S(1) 2.3684(16) Å], and these can be compared with an average Pt–S bond distance of 2.346(6) Å in the dication **2** (*vide supra*). The C═O bond distance of **5** is 1.207(4) Å, which compares favourably to C═O bond distances of 1.207(12) and 1.227(14) Å] in the cyclic dimer **6**.[46]

The $^{31}P\{^1H\}$ NMR spectrum of **5**·PF_6 showed four inequivalent PPh_3 ligands, each appearing as a doublet due to coupling to the other phosphine ligand on the same platinum; $Pt(PPh_3)_2$ units were identified on the basis of ^1J(PtP) coupling constant data, ^2J(PP) couplings and visual inspection. This is a marked contrast with complexes where the $\{Pt_2S_2\}$ core is intact, such as in the starting dialkylated complex **2**; in such species the phosphine ligands are either identical, or have similar (often overlapping) chemical shifts of the central (non-^{195}Pt) resonances. Thus phosphorus atoms P(1) and P(2) appear as a distinct AB pair of doublets (with lower intensity outer lines) at δ 16.1 and 17.2 respectively, while phosphorus atoms P(3) (δ 22.8) and P(4) (δ 15.5) are better separated, giving doublets with approximately equal intensity peaks. ^2J(PP) couplings are 19.2 Hz [for P(3) and P(4)] and 25.5 Hz [for P(1) and P(2)]. Phosphorus P(3) is *trans* to the high *trans*-influence carbon donor, and the value of ^1J(PtP) (2084 Hz) is smallest for this phosphine (which has the longest Pt–P bond in the X-ray structure determination). The coupling constant is similar to that of other complexes with PPh_3 *trans* to a $CH_2C(O)$ group, such as *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ (2075.2 Hz)[43] and *cis*-$[PtCl\{CH_2C(O)CH_3\}(PPh_3)_2]$ (1973 Hz).[47] The corresponding *cis* phosphine, P(4), has the largest ^1J(PtP) coupling of 3775 Hz. This coupling is significantly larger than that typically observed for PPh_3 ligands *trans* to bridging thiolates, which are typically around 3300 Hz. The other pair of PPh_3 ligands [P(1) and P(2)] are assigned on the assumption that a terminal thiolate has a higher *trans*-influence than a bridging thiolate, placing phosphorus P(1) [^1J(PtP) 3159 Hz] *trans* to the bridging thiolate and P(2) [^1J(PtP) 2728 Hz] *trans* to the terminal thiolate.

The ^{1}H NMR spectrum of **5**·PF_6 showed, in addition to the typical complex set of PPh_3 resonances, three unique CH resonances – a broad doublet at δ 3.22, a complex multiplet at δ 2.94, and a doublet of doublets at δ 2.17. The presence of three aliphatic protons is consistent with the protons of the CH_2 group being inequivalent due to the molecular symmetry. The protons at δ 3.22 and 2.17 showed a strong mutual correlation in a COSY spectrum (identifying them as the CH_2 protons), while the proton at δ 2.94 showed no correlations (and is thus assigned as the Pt–CH proton). Irradiation of the CH_2 proton at δ 2.17 collapsed the signal at δ 3.22 to a singlet, while irradiation of the δ 3.22 signal collapsed the δ 2.17 peak to a doublet. This allows the geminal ^2J(HH) coupling [16.9 Hz], and the ^4J(PH) coupling for the CH proton at δ 2.22 [8.1 Hz] to be determined. Examination of the crystal structure of **5**·PF_6 suggests that one of the hydrogens H(2B) is almost coplanar with P(1) [through C(2), S(1) and Pt(1)] and this hydrogen can be tentatively assigned to the resonance at δ 2.17. IR spectroscopy shows a progressive decrease in CO stretching frequency from $ClCH_2C(O)CH_2Cl$ (1745 cm^{-1}) to the dicationic $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4]^{2+}$ **2** (1697 cm^{-1}), to the deprotonated monocation $[Pt_2\{\mu\text{-}SCH_2C(O)CHS\}(PPh_3)_4]^+$ **5** (1676 cm^{-1}).

The corresponding reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with a slight excess of the 2,4-dinitrophenylhydrazone of 1,3-dichloroacetone, *viz.* $ClCH_2C(═NNHAr)CH_2Cl$ (Ar = 2,4-dinitrophenyl) was also investigated, and proceeds similarly. Reaction in methanol resulted in dissolution of the Pt complex and formation of a clear, bright yellow solution, containing predominantly $[Pt_2\{\mu\text{-}SCH_2C(═NNHAr)CH_2S\}(PPh_3)_4]^{2+}$ **7** (*m*/*z* 869.5) together with various minor ions. Precipitation with $NaBPh_4$ yielded a yellow solid, which showed the same ESI MS data and a single resonance [δ 19.3, ^1J(PtP) 3009 Hz] in the $^{31}P\{^1H\}$ NMR spectrum, indicative of the symmetric dithiolate complex $[Pt_2\{\mu\text{-}SCH_2C(═NNHAr)CH_2S\}(PPh_3)_4]^{2+}$ (though one ^{195}Pt satellite was somewhat broader than the other, probably due to slight inequivalence of the PPh_3 ligands effected by the 2,4-dinitrophenylhydrazone group, akin to the semicarbazone **4**, *vide infra*). However, upon drying under vacuum, it quickly transformed to a bright red solid; the same process occurs under ambient conditions, albeit more slowly. Recrystallisation by vapour diffusion of diethyl ether and trimethylamine base into a dichloromethane solution gave a small number of well-formed crystals suitable for an X-ray structure determination, which showed the crystals to be the neutral rearranged complex $[Pt_2\{\mu\text{-}SCH_2C(═NNHAr)CHS\}(PPh_3)_3Cl]$ **8**.

The molecular structure of the core of **8** is shown in Fig. 4 and selected bond lengths and angles are summarised in Table 3. The complex is closely related to the ketone analogue **5**, except that one of the PPh_3 ligands (*trans* to the alkyl carbon) is substituted by chloride. The geometries about the Pt centres are only slightly distorted from regular square-planar, with Houser τ_4 values of 0.09 and 0.11 for Pt(1) and Pt(2) respectively. The Pt(1)–S(1) and Pt(2)–S(1) bond distances [2.376(3) and 2.338(3) Å] are longer than the Pt(1)–S(2) distance 2.305(3) Å], as expected. Because the terminal thiolate S(2) has a higher *trans*-influence than the doubly-bridging S(1), the Pt(1)–P(1) bond distance [2.295(3) Å] is significantly longer than the Pt(1)–P(2) bond distance [2.273(3) Å]. The Pt–C bond distance of **8** [2.034(10) Å] is significantly shorter than the Pt–C bond

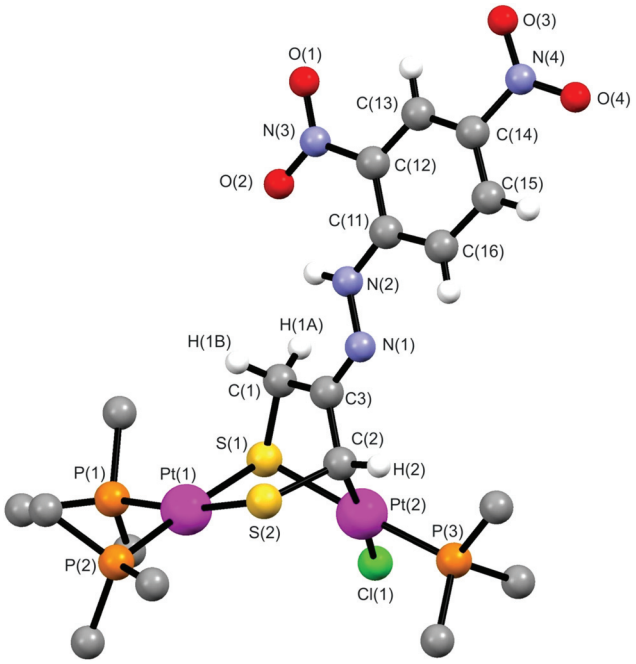


Fig. 4 Molecular structure of the core of the complex $[Pt_2\{\mu\text{-}SCH_2C(=NNHAr)CHS\}(PPh_3)_3Cl]$ **8**, with only the *ipso* carbon atoms of the PPh_3 ligands shown.

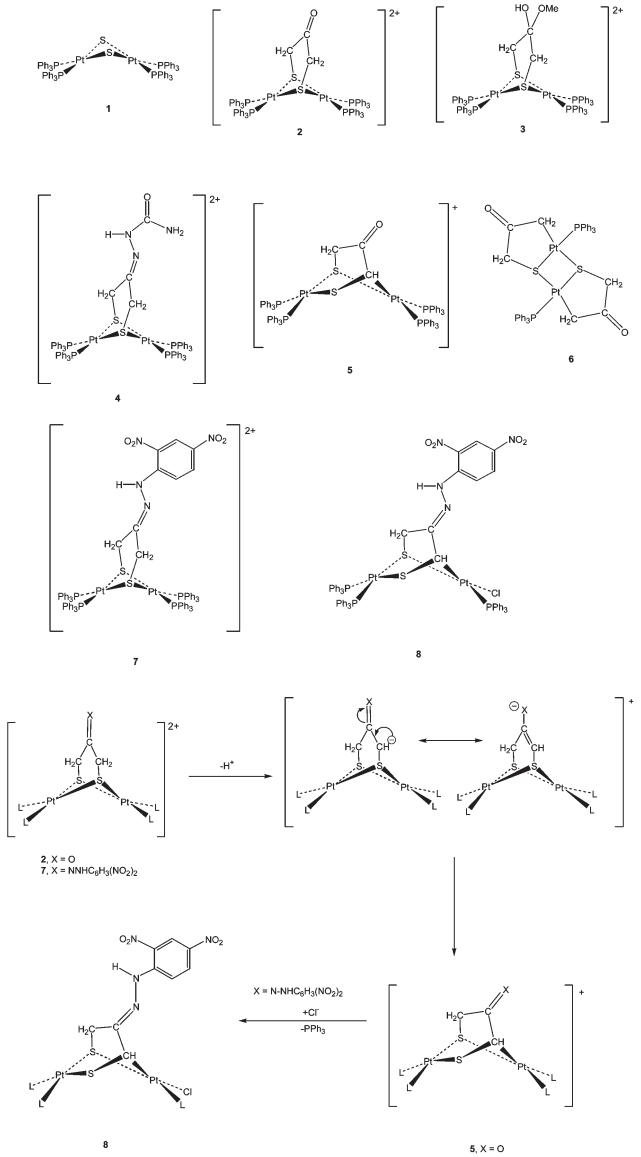
Table 3 Selected bond lengths (Å) and angles (°) for $[Pt_2\{\mu\text{-}SCH_2C(=NNHAr)CHS\}(PPh_3)_3Cl]\cdot CH_2Cl_2$ [**8**·CH_2Cl_2]

Pt(1)–S(1)	2.376(3)	Pt(1)–S(2)	2.305(3)
Pt(2)–S(1)	2.338(3)	Pt(1)–P(1)	2.295(3)
Pt(1)–P(2)	2.273(3)	Pt(2)–P(3)	2.238(3)
Pt(2)–Cl(1)	2.402(3)	Pt(2)–C(2)	2.034(10)
S(1)–C(1)	1.823(11)	S(2)–C(2)	1.872(11)
C(1)–C(3)	1.502(15)	C(2)–C(3)	1.485(15)
C(3)–N(1)	1.284(13)	N(1)–N(2)	1.404(12)
P(2)–Pt(1)–P(1)	97.42(10)	P(2)–Pt(1)–S(2)	88.77(10)
S(2)–Pt(1)–S(1)	89.15(10)	P(1)–Pt(1)–S(1)	84.99(9)
C(1)–S(1)–Pt(1)	100.8(3)	C(1)–S(1)–Pt(2)	96.9(4)
Pt(1)–S(1)–Pt(2)	99.45(10)	P(3)–Pt(2)–Cl(1)	95.21(11)
C(2)–Pt(2)–P(3)	93.3(3)	C(2)–Pt(2)–S(1)	80.4(3)
S(1)–Pt(2)–Cl(1)	91.03(10)	S(2)–C(2)Pt(2)	108.8(5)

distance in **5** [2.090(3) Å] because in **8** it is *trans* to a lower *trans*-influence chloride ligand.

A possible reaction sequence for the formation of the ring expanded products **5** and **8** is shown in Scheme 1. Initial dialkylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to form $[Pt_2\{\mu\text{-}SCH_2C(=X)CH_2S\}(PPh_3)_4]^{2+}$ (**2**, X = O; **7**, X = NNHAr) is then followed by base-induced deprotonation of a CH_2 group to give a (resonance-stabilised) monocation, which contains a carbanionic CH group. This in turn causes a bridging thiolate ligand to rearrange to a terminal bonding mode, with concomitant formation of a Pt–C bond. In the final step involving the dinitrophenylhydrazone system, the high *trans*-influence and *trans*-effect of the carbon-based ligand effects substitution of PPh_3 by chloride, giving the observed complex **8**.

In conclusion, we have synthesised and structurally characterised novel ring-expanded derivatives of the metalloligand



Scheme 1 Proposed reaction sequence for the formation of the organoplatinum dinuclear complexes **5** and **8** (L = PPh_3) by deprotonation and rearrangement of the dialkylated dications $[Pt_2\{\mu\text{-}SCH_2C(=X)CH_2S\}(PPh_3)_4]^{2+}$ [X = O or $NNHC_6H_3(NO_2)_2$].

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ which contain a Pt–C bond. This transformation is made possible by the presence of acidic SCH_2 groups, and opens up the possibility for other novel chemistry initiated by deprotonation of other cationic thiolate complexes; we are currently investigating these possibilities.

Experimental

IR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer, as KBr disks. Melting points were recorded using a Reichert hotstage apparatus and are uncorrected. Elemental analyses were obtained by the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Low resolution ESI mass spectra were recorded on a VG Platform II instrument and high resolution spectra on a Bruker MicrOTOF instrument, the latter

calibrated using a methanol solution of sodium formate. Solutions of approximate concentration *ca.* 0.1 mg mL^{-1} were prepared by dissolving a small quantity of sample in a few drops of either dichloromethane or acetonitrile, followed by dilution to *ca.* 1.5 mL with methanol. Confirmation of species was facilitated by comparison of observed and calculated isotope distribution patterns, the latter obtained from instrument-based software or the *Isotope* program.[48] Reported *m/z* values are of the most abundant isotopomer in the isotope envelope of the ion. NMR spectra were recorded in $CDCl_3$ solution unless otherwise stated. $^{31}P\{^1H\}$ spectra were recorded on Bruker DRX 300 MHz spectrometer at 121.5 MHz. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 400 MHz and 100 MHz respectively on a Bruker DRX spectrometer.

The compounds 1,3-dichloroacetone (Aldrich; CAUTION – highly toxic, potent lachrymator and vesicant) and semicarbazide hydrochloride (BDH) were used as supplied from commercial sources. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was prepared from *cis*-$[PtCl_2(PPh_3)_2]$ and $Na_2S{\cdot}9H_2O$ in benzene suspension, following the literature procedure.[13,49] The dinitrophenylhydrazone of 1,3-dichloroacetone was prepared by the standard procedure for this type of compound, using 2,4-dinitrophenylhydrazine in acidified ethanol.[50]

Synthesis of $ClCH_2C(=NNHC(O)NH_2)CH_2Cl$

This was prepared by a minor modification of the literature procedure,[51] starting from semicarbazide hydrochloride and 1,3-dichloroacetone in ethanol-water. Sodium hydrogen carbonate was used as the base in place of sodium acetate, and the reaction mixture was briefly boiled before cooling at −18 °C overnight to precipitate the product. Found: C 26.4; H 4.1; N 23.0. Calculated for $C_4H_7N_3Cl_2O$ (M_r 184.02) C 26.1; H 3.8; N 22.8%. M.p. 117–119 °C. IR ν_{max} 3462, 3314, 3223, 1720 cm^{-1}. ESI MS $[M + H]^+$, *m/z* 184. ^1H NMR, δ 4.2 (s, 2H, CH_2), 4.3 (s, 2H, CH_2), 9.8 (s, 2H, NH_2). $^{13}C\{^1H\}$ NMR, δ 158.8 (s, CO), 141.4 (s, CN), 46.0 (s, CH_2), 343.1 (s, CH_2).

Synthesis of $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4](BPh_4)_2$ **2**·$(BPh_4)_2$

1,3-Dichloroacetone (20 mg, 0.158 mmol) was added to a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (120 mg, 0.0798 mmol) in methanol (25 mL) and the reaction mixture stirred at room temperature for 1 h giving a clear pale yellow solution. HCl (2 drops, 2 mol L^{-1}) was added, immediately turning the solution colourless. The solution was filtered to remove a trace of insoluble matter, and solid $NaBPh_4$ (200 mg, 0.585 mmol) added to the filtrate, immediately yielding a precipitate. The solid was filtered and dried under vacuum to give $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2S\}(PPh_3)_4](BPh_4)_2$ **2**·$(BPh_4)_2$ as a white powder (69 mg, 39%). Found: C 65.8; H 4.7%. $C_{123}H_{104}B_2OP_4Pt_2S_2$ (M_r 2196.81, uncorrected for methanol adduct **3**) requires C 67.2; H 4.8%. M.p. 151–154 °C. IR ν(C=O) 1696 cm^{-1}. ESI MS $[M]^{2+}$ *m/z* 778.5 (100%), $[M + MeOH]^{2+}$ *m/z* 794.5 (25%). $^{31}P\{^1H\}$ NMR (d^6-acetone), δ 19.3 [s, ^1J(PtP) 3021]. ^1H NMR (d^6-acetone), δ 7.59–6.75 (m, Ph), 2.84 (br s, SCH_2, overlapping water peak).

Synthesis of $[Pt_2\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)CH_2S\}(PPh_3)_4]$-$(BPh_4)_2$ 4·$(BPh_4)_2$

To a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (100 mg, 0.067 mmol) in methanol (25 mL) was added $ClCH_2C(=NNHC(O)NH_2)CH_2Cl$ (15 mg, 0.080 mmol) and the mixture stirred at room temperature for 1 h. The resulting colourless solution was filtered and $NaBPh_4$ (40 mg, 0.117 mmol) added to the filtrate giving a white precipitate. The product was filtered, washed with water (50 mL) and diethyl ether (40 mL) and dried to give **4**·$(BPh_4)_2$ (111 mg, 74%). Found: C 65.1; H 5.0; N 1.8. $C_{124}H_{107}N_3B_2OP_4Pt_2S_2$ (M_r 2255.01) requires C: 66.1; H 4.8; N 1.9%. M.p. 175–177 °C. IR ν_{max} 3479, 3054, 1694, 1480, 1436, 1096 cm^{-1}. ESI MS $[M]^{2+}$ *m/z* 808. ^1H NMR (CD_2Cl_2), δ 2.38 [t, CH_2, J(PH) 5.6, J(PtH) not discernible], 2.73 [t, CH_2, J(PH) 4.2, J(PtH) not discernible], 6.9–7.5 (m, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ 19.2 [s, br, ^1J(PtP) 3043 and 2992].

Synthesis of $[Pt_2\{\mu\text{-}SCH_2C(O)CHS\}(PPh_3)_4]PF_6$ 5·PF_6

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (100 mg, 0.067 mmol) and 1,3-dichloroacetone (10.1 mg, 0.080 mmol) in methanol (25 mL) was stirred giving a clear, pale yellow solution after 1 h, which was monitored by ESI MS. Aqueous sodium hydroxide solution (0.1 mol L^{-1}, 1 mL) was added, rapidly giving a bright yellow solution; monitoring by ESI MS showed complete formation of the monocation formed by deprotonation of $[Pt_2\{\mu\text{-}SCH_2C(O)CH_2\}(PPh_3)_4]^{2+}$. The solution was filtered to remove traces of insoluble matter, and NH_4PF_6 (43 mg, 0.264 mmol) added to the filtrate, followed by water (10 mL). The yellow precipitate was filtered, washed with water (2 × 10 mL) and diethyl ether (2 × 10 mL) and dried to give $[Pt_2\{\mu\text{-}SCH_2C(O)CHS\}(PPh_3)_4]PF_6$ **5**·PF_6 (83 mg, 73%). Vapour diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature gave X-ray quality crystals. Found: C 50.1; H 4.0. $C_{75}H_{63}F_6OP_5Pt_2S_2{\cdot}2CH_2Cl_2$ (M_r 1872.29) requires C 49.4; H 3.6%. M.p. 180–182 °C. IR ν_{max} 1676, 1481, 1436, 1096, 838 cm^{-1}. ESI MS $[M]^+$ *m/z* 1562 (100%). ^1H NMR ($CDCl_3$), δ 2.17 [1H, dd, CH_2, ^2J(HH) 16.9, ^4J(PH) 8.1], 2.94 [1H, m, Pt–CH], 3.22 [1H, d, CH_2, ^2J(HH) 16.9], 6.94–7.50 (m, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 15.5 [d, P(4), ^1J(Pt(2)P(4)) 3775, ^2J(PP) 19.2], 16.1 [d, P(2), ^1J(Pt(1)P(2)) 3159, ^2J(PP) 25.5], 17.2 [d, P(1), ^1J(Pt(1)P(1) 2728, ^2J(PP) 25.5] and 22.8 [d, P(3), ^1J(Pt(2)P(3)) 2084, ^2J(PP) 19.2]; refer to Fig. 3 for numbering of P atoms.

Synthesis of $[Pt_2\{\mu\text{-}SCH_2C(=NNHAr)CHS\}(PPh_3)_3Cl]$ **8** (Ar = 2,4-dinitrophenyl)

$ClCH_2C(=NNHAr)CH_2Cl$ (38 mg, 0.124 mmol) was added to a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (147 mg, 0.098 mmol) in methanol (40 mL), and the reaction mixture stirred at room temperature. An immediate colour change from orange to bright yellow was observed, and the solution was filtered to remove traces of solid impurities. $NaBPh_4$ (94 mg, 0.275 mmol) was added to the filtrate, immediately producing a yellow precipitate. The product was filtered, washed with distilled water (10 mL), methanol (10 mL), and diethyl ether (10 mL) to give $[Pt_2\{\mu\text{-}SCH_2C(=NNHAr)CH_2S\}(PPh_3)_4](BPh_4)_2$ **1** (107 mg,

Table 4 Crystallographic data for complexes **4**·$(BPh_4)_2$·CH_2Cl_2, **5**·PF_6·$2CH_2Cl_2$ and **8**·CH_2Cl_2

	4·$(BPh_4)_2$·CH_2Cl_2	**5**·PF_6·$2CH_2Cl_2$	**8**·CH_2Cl_2
Empirical formula	$C_{125}H_{109}B_2Cl_2N_3OP_4Pt_2S_2$	$C_{77}H_{67}Cl_4F_6OP_5Pt_2S_2$	$C_{64}H_{54}Cl_3N_4O_4P_3Pt_2S_2$
Formula weight	2339.85	1873.26	1596.67
Temperature (K)	93(2)	90(2)	93(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
a (Å)	17.8478(5)	19.577(13)	13.1803(8)
b (Å)	18.5906(5)	14.693(10)	15.482(1)
c (Å)	18.8511(5)	26.924(18)	19.2062(14)
α (°)	83.448(2)	90	112.021(2)
β (°)	70.165(2)	110.392(7)°	106.941(2)
γ (°)	71.444(2)	90	90.752(3)
Volume (Å^3)	5577.7(3)	7259(8)	3442.4(4)
Z, calculated density (g cm^{-3})	2, 1.393	4, 1.714	2, 1.540
Absorption coefficient (mm^{-1})	2.699	4.226	4.352
F(000)	2360	3688	1564
Crystal size (mm)	0.35 × 0.10 × 0.02	0.34 × 0.18 × 0.10	0.12 × 0.05 × 0.01
Reflections collected/unique	139 903/29 702 [R_{int} 0.1078]	91 680/17 315 [R_{int} 0.0403]	35 154/11 716 [R_{int} 0.0609]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Empirical
Max. and min. transmission	0.746 and 0.567	1.000 and 0.652	0.958 and 0.623
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	29 702/20/1270	17 315/0/874	11 716/531/719
Goodness-of-fit on F^2	1.025	1.019	1.157
Final R indices [$I > 2\sigma(I)$]	R_1 0.0535, wR_2 0.1008	R_1 0.0244, wR_2 0.0539	R_1 0.0614, wR_2 0.1608
R indices (all data)	R_1 0.1059, wR_2 0.1112	R_1 0.0314, wR_2 0.0565	R_1 0.0911, wR_2 0.1716
Largest diff. peak and hole (eÅ^{-3})	1.744 and −1.433	1.245 and −1.539	5.28 and −3.24

45%), which turned red upon air- or vacuum-drying. [The yellow colour could be regenerated by addition of a trace of HCl to a (bright red) solution of the compound.]

Recrystallisation was carried out by diffusion of diethyl ether and trimethylamine into a dichloromethane solution at room temperature. Initially, some pale pink needles crystallised out; these were removed, tentatively assigned as $[Me_3NH][BPh_4]$ (negative ion ESI MS m/z 319) and discarded. Continued crystallisation produced red-orange crystalline material; the bulk of these crystals were unsuitable for X-ray crystallography, but amongst these were a small number of very small, well-formed orange-yellow crystals. The compound was characterised solely by an X-ray structure determination.

X-ray structure determinations of 2·$(BPh_4)_2$·CH_2Cl_2, 4·$(BPh_4)_2$·CH_2Cl_2, 5·PF_6·$2CH_2Cl_2$ and 8·CH_2Cl_2

Data were acquired on a Bruker SMART APEX II diffractometer equipped with a CCD area detector, using Mo-Kα radiation (λ 0.71073 Å). The software SMART was used for collection of data frames, indexing reflections and to determine lattice parameters, and SAINT was used for integration of the intensity of reflections and for scaling.[52] SADABS was used for empirical absorption correction.[53] Structures were solved and refined full-matrix least-squares based on F_o^2 with anisotropic thermal parameters for non-hydrogen atoms, using the SHELX suite of programs.[54] Crystallographic data are summarised in Table 4.

[Pt_2{μ-$SCH_2C(O)CH_2S$}$(PPh_3)_4$]$(BPh_4)_2$ 2·$(BPh_4)_2$·CH_2Cl_2. Crystals (obtained by vapour diffusion of diethyl ether into a dichloromethane solution at room temperature) were poor quality, so only a weak data set was obtained (less than half reflections observed). Refinement with only the heavier atoms anisotropic gave R_1 = 0.117 so served to confirm connectivity, but more detailed discussion of bond parameters is unwarranted.[55]

[Pt_2{μ-$SCH_2C(=NNHC(O)NH_2)CH_2S$}$(PPh_3)_4$]$(BPh_4)_2$ 4·$(BPh_4)_2$·CH_2Cl_2. The structure was solved by direct methods; the Pt, S and P atoms were located followed by other atoms. All non-hydrogen atoms were refined as anisotropic. The structure contains a molecule of disordered CH_2Cl_2. Remaining residual peaks in the final electron density map could not be resolved and were removed from the refinement using SQUEEZE.[56] Solvent-accessible voids of about 487 Å^3 were involved.

[Pt_2{μ-$SCH_2C(O)CHS$}$(PPh_3)_4$]PF_6 5·PF_6·$2CH_2Cl_2$. The structure was solved by direct methods. The Pt, S and P atoms were located first, followed by C(1) and other atoms; all non-hydrogen atoms were refined as anisotropic.

[Pt_2{μ-$SCH_2C(=NNHAr)CHS$}$(PPh_3)_3Cl$] 8·CH_2Cl_2. Crystals obtained were very small yellow-orange needles (*vide supra*). The structure was solved by direct methods and normal development revealed the main molecule, together with one well-behaved molecule of CH_2Cl_2 in the lattice. This refined to R_1 = 0.077. There remained several large residual peaks close to the Pt atoms, presumably because of the limitations in the data set arising from the very small crystal used. In addition there were significant peaks presumably associated with more lattice solvent, and a PLATON[53] analysis indicated large solvent-accessible voids (*ca.* 596 Å^3). It was clear that the remaining solvent would not be able to be modelled in a sensible way, so the SQUEEZE[53] routine of PLATON was used to eliminate it. Final refinement using data that had been modified by SQUEEZE converged with R_1 = 0.0614 (8014 data with $I > 2\sigma(I)$), wR_2 = 0.1716 for all 11716 data.

CCDC 844720, 844719, 844718 and 844717 contain the supplementary crystallographic data for **2**·$(BPh_4)_2$, **4**·$(BPh_4)_2$·CH_2Cl_2, **5**·PF_6·$2CH_2Cl_2$ and **8**·CH_2Cl_2 respectively.

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