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Synthesis and characterisation of adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with organo-palladium and platinum-hydride substrates

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Abstract

The reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards a range of palladium(II) complexes containing organometallic ligands (cyclopalladated *N*-donor ligands, η^3-allyl, phenyl) have been explored, leading to the formation of a series of cationic, trinuclear sulfido-bridged aggregates containing $\{Pt_2PdS_2\}$ cores. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ also reacts with the platinum(II) hydride complex *trans*-$[PtHCl(PPh_3)_2]$ giving the adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]^+$. X-ray crystal structure determinations on the complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]PF_6$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]PF_6$ are reported, and show the expected bis μ_3-sulfido aggregates with three square-planar metal centres.

Keywords: Platinum complexes; Palladium complexes; Trinuclear complexes; Sulfido ligands; Electrospray mass spectrometry; Crystal structure

Introduction

The metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ displays considerable and varied reactivity towards a wide variety of metal- and organic-based electrophiles.[1] A range of palladium adducts of $\{Pt_2S_2\}$ metalloligands have been previously reported,[2,3,4,5,6] but few are organometallic derivatives. The pentafluorophenyl adducts $[Pt_2(\mu\text{-}S)_2L_4Pd(C_6F_5)_2]$ [L = PPh_3, PMe_2Ph or L_2 = $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$] have been prepared by reaction of the appropriate $\{Pt_2S_2\}$ metalloligand with the labile palladium precursor $[Pd(C_6F_5)_2(NCMe)_2]$.[7] The cyclo-octa-1,5-diene (cod) adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4M(cod)]^{2+}$ (M = Pd, Pt) have been prepared by reaction with $[MCl_2(cod)]$ substrates, resulting in displacement of chloride ligands and coordination of the $M(cod)^{2+}$

group.[8] The related triplatinum complex $[Pt_2(\mu\text{-}S)_2(dppp)_2Pt(cod)]^{2+}$ [dppp = $Ph_2P(CH_2)_3PPh_2$] has interestingly been found to undergo deprotonation of a CH_2 group instead of the more usual nucleophilic attack of solvent-derived methoxide ion at a coordinated alkene.[9]

In developing the chemistry of $\{Pt_2S_2\}$ metalloligands, the technique of electrospray ionisation mass spectrometry (ESI MS)[10] has proved to be extremely useful, being rapid and only requiring only miniscule amounts of material. Information on the range of species present in solution is then used to target subsequent macroscopic syntheses.[11,12,13,14] We have recently used ESI MS to screen the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards a range of palladium(II) and platinum(II) halide substrates.[8] In this contribution we report on the application of this methodology to the synthesis of some organo-palladium(II) complexes, including complexes containing cyclometallated ligands. Previously we have reported analogous derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with gold(III) centres containing various cycloaurated *N,C*-donor ligands.[15,16]

Results and discussion

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ reacts readily with a series of chloride- and acetate-bridged dinuclear palladium(II) substrates containing cyclopalladated ligands (*C,N*) $[PdCl(dmamp)]_2$ (dmamp = dimethyaminomethyphenyl) and substituted analogues, $[PdCl(phimid)]_2$ (phimid = 2-phenylimidazolyl), $[PdCl(bzpy)]_2$ (bzpy = 2-benzylpyridyl) and $[Pd(OAc)(\eta^2\text{-}C_6H_4PPh_2{=}NPh\text{-}C,N)]_2$, in methanol to give solutions containing the trimetallic aggregates $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(C,N)]^+$ **1-4** respectively. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ also reacts readily with the palladium η^3-allyl complex $[PdCl(\eta^3\text{-}C_3H_5)]_2$, the 2-pyridyl

complex *trans*-[PdBr(C_5H_4N)($PMePh_2$)$_2$] and the phenyl derivative *trans*-[PdBrPh(PPh_3)$_2$] in methanol to give the mixed-metal aggregates [Pt_2(μ-S)$_2$(PPh_3)$_4$Pd(η^3-C_3H_5)]$^+$ **5**, [Pt_2(μ-S)$_2$(PPh_3)$_4$Pd(NC_5H_4)($PMePh_2$)]$^+$ **6** and [Pt_2(μ-S)$_2$(PPh_3)$_4$PdPh(PPh_3)]$^+$ **7** respectively. Precipitation of the cations was achieved by addition of excess NH_4PF_6, yielding the appropriate salts in reasonably good yields. The complexes are all stable and soluble in chlorinated hydrocarbon solvents such as CH_2Cl_2 and $CHCl_3$, and represent an addition to the wide range of trinuclear complexes containing {M_3(μ-S)$_2$} cores (M = Pt, Pd).[3,17,18,19,20]

Using the same methodology, reaction of [Pt_2(μ-S)$_2$(PPh_3)$_4$] with *trans*-[PtHCl(PPh_3)$_2$] gave the new platinum-hydride adduct [Pt_2(μ-S)$_2$(PPh_3)$_4$PtH(PPh_3)]$^+$, though the reaction proceeded slowly, and a considerable amount of unreacted [Pt_2(μ-S)$_2$(PPh_3)$_4$] remained (as the bright yellow methanol solvate[21]). Refluxing the reaction mixture resulted in moderate conversion of the reactants, and the complex **8**·PF_6 was isolated from the reaction filtrate by precipitation with NH_4PF_6 as a cream powder in modest (34%) yield.

The complexes - with one exception - all show a single intense $[M]^+$ ion in their positive-ion ESI MS spectra at low cone voltages (e.g. 20 V). The exception is complex **6** which shows an M^{2+} ion due to protonation of the pyridine nitrogen, however, microelemental analytical data support the formulation of the isolated product as being unprotonated, with a single hexafluorophosphate anion overall. At high cone voltages (e.g. 100 V) complex **6** showed the base peak at *m/z* 1887 for the $[M]^+$ ion, together with $[M - PMePh_2]^+$ at *m/z* 1687. The selective loss of the palladium-bound phosphine is consistent with the greater lability of palladium(II) compared to platinum(II). The other

monocations are generally stable up to moderate cone voltages of 60-80 V, with the first fragmentations being either a loss of PPh_3 from the $\{Pt_2S_2PdL\}$ core (L = supporting palladium ligand), or the loss of the palladium supporting ligand and a PPh_3 resulting in $[Pt_2S_2(PPh_3)_2Pd(Ph_2PC_6H_4)]^+$ through cyclometallation of a PPh_3 ligand. To illustrate this, the effect of increasing cone voltage on complex **1c**·PF_6 is shown in Figure 1.

The ^{31}P NMR spectra of complexes **1a**, **1b**, **2** and **3** give a single phosphorus signal with the characteristic satellites due to coupling to ^{195}Pt. Even though the organo-palladium centres in these complexes are not symmetrical with respect to the $\{Pt_2S_2\}$ ring the asymmetry is not sufficient to give rise to two distinct sets of phosphorus signals, though in each case one of the ^{195}Pt satellites is broader than the other, suggesting slightly different coupling constants. However, the chiral derivative **1c** appears to show four distinct P environments (though still with considerable overlapping of peaks) as a result of all four PPh_3 ligands being inequivalent in this complex. The presence of the chiral CHMe group therefore appears to have a significant effect on the environments of the PPh_3 phosphorus atoms. The pyridyl and phenyl complexes **6** and **7** also show distinct Pt-PPh_3 resonances for the $Pt_2S_2(PPh_3)_4$ core, with two different couplings to ^{195}Pt (e.g. 3081 and 3121 Hz for **7**). Complex **4** also shows inequivalent PPh_3 groups [with *J*(PtP) couplings of 3073 and 3152 Hz] together with a slightly broad singlet at δ 43.2 due to the iminophosphorane PPh_2 group, this chemical shift being indicative of phosphorus in a five-membered ring.[22] Complexes **6**, **7** and **8**, containing an additional phosphine ligand on the adducted metal, also show an additional resonance for this phosphine, with the Pt-hydride complex **8** showing the expected satellites [^1JPtP 4094 Hz]. The observation of

distinct resonances indicates that these complexes are not undergoing any fluxional exchange process involving the adducted metal at room temperature.

The ^{1}H NMR spectra of the complexes show the expected features, with characteristic resonances for the palladium-bound ligands being observed in addition to a suite of complex signals for the various aromatic protons. For example, the complex **1a** showed the expected singlet peaks due to the CH_2 and NCH_3 protons of the palladium adduct, at δ 3.87 and 2.37, respectively. In the chiral analogue **1c**, the two *N*-methyl groups are inequivalent singlets (δ 2.67 and 2.01), with the chiral CHMe group giving the characteristic quartet and doublet features for the CH and Me protons respectively.

The ^{1}H NMR spectrum of **3** shows a complex set of signals due to the triphenylphosphine protons along with other signals due to the benzylpyridyl protons, which were fully assigned *via* the use of ^{1}H,^{1}H-COSY experiments. A variable temperature ^{1}H NMR study on **3** showed a sharp singlet at 330 K for the CH_2 protons at δ 4.38. Upon cooling this gradually broadens (e.g. at 233 K) and then resolves into two broad singlets at 223 K, consistent with the known fluxional processes in the palladium-benzylpyridyl ring system.[23]

The platinum-hydride complex **8** shows the characteristic signal for the hydride at δ -12.50 in the ^{1}H NMR spectrum, as a doublet of triplets (due to phosphorus coupling), together with platinum satellites [$^{1}J_{PtH}$ 1295 Hz]. These values compare favourably with the chemical shift and $^{1}J_{PtH}$ of -12.06 and 1075 Hz respectively, in the trinuclear complex $[CH_3C\{CH_2SPtH(PPh_3)\}_3]$.[24]

X-ray structure determinations

The structures of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]PF_6$ (**7**·PF_6) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]PF_6$ (**8**·PF_6) were determined. The structure of the cation **7** is shown in Figure 2 with the atom numbering scheme, and selected bond lengths and angles in Table 1. The structure of **8** is shown in Figure 3, with selected bond lengths and angles in Table 2. The structures confirm the identity of the complexes as adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $PdPh(PPh_3)^+$ and $PtH(PPh_3)^+$ moieties.

Complex **7** has the expected trimetallic assembly with two Pt and one Pd centre triply-bridged by two sulfido ligands. The S-M-S bond angles are very similar for Pd(1) [78.68(3)°], Pt(1) [80.01(3)°] and Pt(2) [79.86(3)°]. The palladium centre has the expected approximately square-planar geometry, though the presence of asymmetrically-sized ligands [PPh_3 and Ph] on Pd(1) results in a widening of the S(2)-Pd(1)-P(5) bond angle to 105.30(3)°. The asymmetry also causes variation in the Pt-S-M (M = Pd, Pt) angles, e.g. for S(1): Pt(2)-S(1)-Pd(1) 81.24(3); Pd(1)-S(1)-Pt(1) 83.99(3); Pt(2)-S(1)-Pt(1) 86.40(3)°. The same order in bond angles is observed for the angles about S(2): Pt(2)-S(2)-Pd(1) 79.67(3); Pd(1)-S(2)-Pt(1) 82.81(3); Pt(2)-S(2)-Pt(1) 86.28(3)°. In each case the largest angle is between the two $Pt(PPh_3)_2$ groups, as expected. The dihedral angle, between the least-squares planes defined by the Pt coordination spheres, is 126.9°, which is typical for such adducts.[16] The corresponding dihedral angle between the Pd(1) and Pt(2) coordination planes is 114.4°. Finally, the high *trans*-influence[25] σ-phenyl ligand causes a marked lengthening of the *trans* Pd(1)-S(2) bond [2.4157(8) Å] relative to the Pd(1)-S(1) bond [2.3531(9) Å], *trans* to the PPh_3 ligand on palladium. Similar effects have been seen in adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with cycloaurated gold(III) moieties,

such as **9**, where the Au-S bond *trans* to C [2.386(4) Å] is again significantly longer than the Au-S bond *trans* to N [2.366(4) Å].[16] For comparison, the palladium(II) dithiophosphinate complex [Pd(S_2PPh_2)(Ph)(PPh_3)] also shows longer and shorter Pd-S bond distances [2.4571(11) and 2.4029(10) Å] *trans* to higher and lower *trans*-influence Ph and PPh_3 ligands, respectively.[26]

The same general trends are also observed in the structure of **8**; the structure contains three approximately square-planar Pt centres, triply bridged by two sulfido ligands in a similar asymmetric fashion to **7** [e.g. Pt(3)-S(1)-Pt(2) 82.77(12); Pt(3)-S(1)-Pt(1) 81.54(11); Pt(2)-S(1)-Pt(1) 89.04(11)°]. The dihedral angle between the $Pt(PPh_3)_2$ coordination planes is 135.6°. The hydride ligand was not found, but its presence can easily be inferred by both the presence of a 'vacant' coordination position on Pt(3), and by the significant asymmetry of the Pt(3)-S bond distances, with Pt(3)-S(2) [2.427(4) Å] being considerably longer than Pt(3)-S(1) *trans* to P(5) [2.350(4) Å], consistent with the presence of a high *trans*-influence hydride on Pt(3). The complex [$CH_3C\{CH_2SPtH(PPh_3)\}_3$] also contains the $PtH(PPh_3)S_2$ coordination sphere, and provides a useful comparison with **8**;[24] the Pt-S bonds *trans* to hydride are significantly longer [e.g. 2.387(5) Å] compared to those *trans* to phosphine [2.344(4) Å]. Complex **8** also shows a widening of the S(2)-Pt(3)-P(5) bond angle involving the adduct $PtH(PPh_3)$ group, to 106.07(12)°.

Experimental

Instrumentation

ESI mass spectra were recorded in positive-ion mode on a VG Platform II instrument, using methanol as the mobile phase and solvent, and a cone voltage of 20 V unless otherwise stated. Samples of isolated hexafluorophosphate salts were prepared for analysis by dissolution in a few drops of CH_2Cl_2, followed by dilution with methanol. Assignment of ions was aided by use of the ISOTOPE simulation program.[27]

NMR spectra were recorded on a Bruker AC300P spectrometer at 300.13 MHz (^{1}H) or 121.51 MHz (^{31}P) in $CDCl_3$ solution, and were referenced relative to residual $CHCl_3$ (^{1}H) or external 85% H_3PO_4 (^{31}P).

Materials

Reactions were carried out in LR grade methanol. Products were recrystallised from dichloromethane and diethyl ether that were dried and distilled (from CaH_2 and sodium-benzophenone ketyl respectively) under a nitrogen atmosphere prior to use. Petroleum spirits refers to the fraction of boiling point 40-60 ºC.

The compounds NH_4PF_6 (Aldrich) and (*S*)-(+)-di-μ-chlorobis[{2-(1-dimethylamino)ethyl}phenyl-*C*,*N*]dipalladium(II), $[PdCl(\eta^2\text{-}C_6H_4CHMeNMe_2\text{-}C^2,N)]_2$ (Precious Metals Online) were used as received. The following complexes were prepared by the literature procedure, or a minor variation thereof: $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$,[28] $[PdCl(\eta^2\text{-}C_6H_4CH_2NMe_2\text{-}C,N)]_2$,[29] $[PdCl(\eta^2\text{-}C_6H_3(OMe\text{-}3)CH_2NMe_2\text{-}C,N)]_2$,[30] $[PdCl(phimid)]_2$,[31] $[PdCl(2\text{-benzylpyridyl})]_2$,[23] $[PdCl(\eta^3\text{-}C_3H_5)]_2$,[32] *trans*-$[PdBr(C_5H_4N)(PMePh_2)_2]$,[33] *trans*-

[PdBrPh(PPh_3)$_2$][34] and *trans*-[PtHCl(PPh_3)$_2$].[35] [Pd(OAc)(η^2-$C_6H_4PPh_2$=NPh-*C,N*)]$_2$ was prepared from palladium(II) acetate and Ph_3P=NPh following the method of Vicente *et al*.[36]

Synthesis of [$Pt_2(\mu$-S)$_2$(PPh_3)$_4$Pd(η^2-$C_6H_4CH_2NMe_2$-*C,N*)]PF_6 1a·PF_6

[$Pt_2(\mu$-S)$_2$(PPh_3)$_4$] (204 mg, 0.136 mmol) and [PdCl(η^2-$C_6H_4CH_2NMe_2$-*C,N*)]$_2$ (40 mg, 0.072 mmol) were stirred in methanol (30 mL) at room temperature for 19 h. The resulting clear yellow solution was filtered to remove a trace of insoluble matter. NH_4PF_6 (300 mg, 1.84 mmol) was added, followed by water (40 mL) to precipitate a cream solid. This was filtered and washed successively with water (2 x 20 mL) and petroleum spirits (10 mL), and dried under vacuum giving **1a**·PF_6 as a cream powder (179 mg, 70%). Found: C, 50.9; H, 3.7; N, 0.8. $C_{81}H_{72}F_6NP_5PdPt_2S_2$ (M_r 1889) requires C, 51.5; H, 3.8; N, 0.7%. ESI MS, [**1a**]$^+$ *m/z* 1743. $^{31}P\{^1H\}$ NMR, δ 18.6 (*s*, $^1J_{PtP}$ 3135). ^1H NMR, δ 7.37-5.76 (*m*, aryl-H), 3.88 (*s*, CH_2) and 2.37 (*s*, CH_3).

Synthesis of [$Pt_2(\mu$-S)$_2$(PPh_3)$_4$Pd(η^2-C_6H_3(OMe-3)CH_2NMe_2-*C,N*)]PF_6 1b·PF_6

Following a similar procedure for **1a**, [$Pt_2(\mu$-S)$_2$(PPh_3)$_4$] (415 mg, 0.277 mmol) and [PdCl(η^2-C_6H_3(OMe-3)CH_2NMe_2-*C,N*)]$_2$ (89 mg, 0.145 mmol) in 30 mL methanol, with NH_4PF_6 (300 mg, 1.84 mmol) gave **1b**·PF_6 (382 mg, 72%) as a cream powder. Found: C, 50.0; H, 3.9; N, 0.8. $C_{82}H_{74}NF_6OP_5PdPt_2S_2$ (M_r 1919) requires C, 51.3; H, 3.9; N, 0.7%. ESI MS, [**1b**]$^+$ *m/z* 1773. $^{31}P\{^1H\}$ NMR, δ 18.2 (*m*, $^1J_{PtP}$ 3112). ^1H NMR, δ 7.37-6.46 (*m*, aryl-H), 3.82 (*s*, CH_2), 3.39 (*s*, OCH_3) and 2.29 (*s*, NMe_2).

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(\eta^2\text{-}C_6H_4CHMeNMe_2\text{-}C,N)]PF_6$ 1c·PF_6

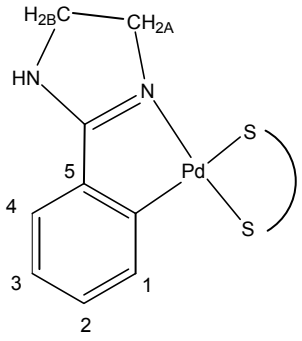
Following a similar procedure for **1a**, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (416 mg, 0.277 mmol) and (S)-(+)-$[PdCl(\eta^2\text{-}C_6H_4CHMeNMe_2\text{-}C,N)]_2$ (85 mg, 0.147 mmol) in 30 mL methanol, with NH_4PF_6 (300 mg, 1.84 mmol) gave **1c**·PF_6 (384 mg, 73%) as a cream powder. Found: C, 51.4; H 4.0; N, 0.7. $C_{82}H_{74}NF_6P_5PdPt_2S_2$ (M_r 1903) requires C, 51.8; H, 3.9; N, 0.7%. ESI MS, $[\mathbf{1c}]^+$ *m/z* 1757. $^{31}P\{^1H\}$ NMR, δ 20.2 (*m*, $^1J_{PtP}$ 3172 and 3115) and 17.5 (*m*, ^1JPtP 3091). ^1H NMR, δ 7.38-5.68 (*m*, aryl-H), 3.55 (*q*, C**H**Me, J_{HH} 6.3), 2.67 (*s*, NMe), 2.01 (*s*, NMe), and 1.71 (*d*, CH**Me**, J_{HH} 6.3).

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(\eta^2\text{-}C_6H_4C_3H_5N_2\text{-}C,N)]PF_6$ 2·PF_6

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (98 mg, 0.0652 mmol) and $[PdCl(\eta^2\text{-}C_6H_4C_3H_5N_2\text{-}C,N)]_2$ (37 mg, 0.0653 mmol) were stirred in methanol (30 mL) at room temperature for 24 h. Insoluble material was removed by filtration through Celite and washed successively with methanol until the washing were colourless. The washings and filtrate were combined to give a clear red solution. NH_4PF_6 (15 mg, 0.092 mmol) was added and the resulting suspension stirred for a further 30 min. Water (20 mL) was added to complete precipitation of the brick red powder, which was filtered, washed with water (2 x 5 ml), methanol (2 x 5 mL) and diethyl ether (2 x 5 mL) and dried *in vacuo*. Recrystallisation from CH_2Cl_2/ diethylether gave **2**·PF_6 as a brown powder of the dichloromethane solvate (84 mg, 62%). Found: C, 48.0; H, 3.7; N, 2.2. $C_{81}H_{69}F_6N_2P_5PdPt_2S_2{\cdot}2CH_2Cl_2$ (M_r 2070) requires C, 48.2; H, 3.6; N, 1.4%. ESI MS, $[\mathbf{2}]^+$ *m/z* 1754. $^{31}P\{^1H\}$ NMR, δ 19.2 (*s*, $^1J_{PtP}$ 3116). ^1H NMR, δ 8.22 (*d*, 1H, $^3J_{4,3}$ 7.3, H-4), 7.55 (*t*, 1H, $^3J_{3,2/4}$ 7.4, H-3), 7.34-6.96 (*m*, 60H, PPh_3), 6.77 (*t*, 1H, $^3J_{2,1/3}$ 7.4, H-2), 6.10 (*d*, 1H, $^3J_{1,2}$ 7.3, H-1), 5.69 (*s*, NH), 3.73 (*t*,

2H, $^{3}J_{B,A}$ 9.4, CH_{2B}), and 3.04 (*t*, 2H, $^{3}J_{A,B}$ 9.4, CH_{2A}). $^{13}C\{^{1}H\}$ NMR, δ 134.9-128 (*m*, aryl-C), 56.4 (*d*, CH_{2B}), and 43.5 (*d*, CH_{2A}).

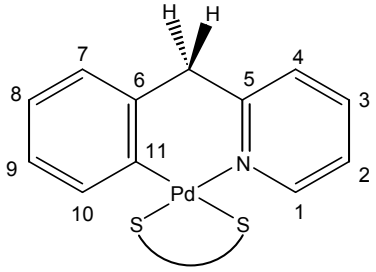
NMR numbering scheme, S-S = $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$:



Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(\eta^2\text{-}C_6H_4CH_2C_5H_4N\text{-}C,N)]PF_6$ 3·PF_6

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (100 mg, 0.066 mmol) and $[PdCl(2\text{-benzylpyridyl})]_2$ (44 mg, 0.066 mmol) were stirred in methanol (30 mL) at room temperature for 24 h to give a clear yellow solution. NH_4PF_6 (20 mg, 0.123 mmol) was added and the suspension stirred for a further 1 h resulting in the formation of a yellow-brown precipitate, which was filtered and washed successively with water (2 x 10 mL), methanol (2 x 5 mL), and diethyl ether (10 mL) and dried under vacuum giving **3**·PF_6 (104 mg, 81%). Found: C, 52.0; H, 3.7; N, 0.8. $C_{84}H_{90}F_6NP_5PdPt_2S_2$ (M_r 1943) requires C, 51.9; H, 4.7; N, 0.7%. ESI MS, $[\mathbf{3}]^+$ *m/z* 1774. $^{31}P\{^{1}H\}$ NMR, δ 18.8 (*m*, $^{1}J_{PtP}$ 3106). ^{1}H NMR, δ 7.71 (*t*, 1H, $^{3}J_{2,1/3}$ 7.3, H-2), 7.51 (*d*, 1H, $^{3}J_{1,2}$ 7.7, H-1), 7.32-6.98 (*m*, 60H, PPh_3), 7.18 (*d*, 1H, $^{3}J_{7,8}$ 7.2, H-7), 7.14 (*d*, 1H, $^{3}J_{4,3}$ 4.7, H-4), 6.91 (*t*, 1H, $^{3}J_{8,7/9}$ 7.2, H-8), 6.69 (*t*, 1H, $^{3}J_{3,2/4}$ 6.2, H-3), 6.44 (*t*, 1H, $^{3}J_{9,8/10}$ 7.0, H-9), 5.98 (*d*, 1H, $^{3}J_{10,9}$ 7.2, H-10), and 4.39 (*s*, 2H, C$\underline{H_2}$).

NMR numbering scheme, S-S = $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$:



Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(\eta^2\text{-}C_6H_4PPh_2\text{=}NPh\text{-}C,N)]PF_6$ 4·PF_6

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (100 mg, 0.066 mmol) and $[Pd(OAc)(\eta^2\text{-}C_6H_4PPh_2\text{=}NPh\text{-}C,N)]_2$ (68.3 mg, 0.066 mmol) were stirred in methanol (30 mL) at room temperature for 24 h. The resulting orange solution was filtered through Celite and washed until the washings were colourless, to give a clear orange solution. NH_4PF_6 (18 mg, 0.110 mmol) was added and the suspension stirred for a further 1 h resulting in the formation of a brown precipitate, which was filtered and washed successively with water (2 x 10 mL), methanol (2 x 5 mL), and diethyl ether (10 mL) and dried under vacuum giving **4**·PF_6 as yellow-brown plates (90 mg, 65%). Found: C, 54.2; H, 4.1; N, 1.2. $C_{96}H_{79}F_6NP_6PdPtS_2$ (M_r 2107) requires C, 54.7; H, 3.8; N, 0.7%. ESI MS, $[\mathbf{4}]^+$ *m/z* 1962. $^{31}P\{^1H\}$ NMR, δ 43.2 (*s*, N=PPh_2), 18.3 (*m*, $^1J_{PtP}$ 3073), 16.4 (*m*, $^1J_{PtP}$ 3152).

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(\eta^3\text{-}C_3H_5)]PF_6$ 5·PF_6

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (100 mg, 0.066 mmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (25 mg, 0.066 mmol) were stirred in methanol (30 mL) at room temperature for 3 h. NH_4PF_6 (17 mg, 0.104 mmol) was added and the suspension stirred for a further 1 h, after which time water (20

mL) was added, resulting in the formation of a pinkish precipitate, which was filtered through a fine glass frit, washed successively with water (2 x 10 mL), methanol (2 x 5 mL), and diethyl ether (10 mL) and dried under vacuum giving **5**·PF_6 as pale pink powder (56 mg, 47%). Found: C, 49.1; H, 3.7. $C_{75}H_{65}F_6P_5PdPt_2S_2$ (M_r 1796) requires C, 50.2; H, 3.7%. ESI MS, [**5**]$^+$ *m/z* 1650. $^{31}P\{^1H\}$ NMR, δ 19.6 (*s*, $^1J_{PtP}$ 3121). ^1H NMR (selected signals only), δ 5.17 (*qn*, 1H, $^3J_{B,A/C}$ 4, CH), 3.54 (*d*, 2H, $^3J_{A,B}$ 7, *syn*-CH_2), 2.70 (d, 2H, $^3J_{C,B}$ 12, *anti*-CH_2).

Synthesis of [Pt_2(μ-S)$_2$(PPh_3)$_4$Pd(C_5H_4N)($PMePh_2$)]PF_6 6·PF_6

[Pt_2(μ-S)$_2$(PPh_3)$_4$] (100 mg, 0.066 mmol) and *trans*-[PdBr(C_5H_4N)($PMePh_2$)$_2$] (44 mg, 0.066 mmol) were stirred in methanol (30 mL) at room temperature for 12 h. The resulting yellow solution was filtered through Celite and the filter washed with methanol until the washings were colourless, resulting in a clear yellow solution. ESI MS analysis of the solution showed the [**6** + H]$^{2+}$ ion of the product at *m/z* 944.5. NH_4PF_6 (20 mg, 0.123 mmol) was added and the suspension stirred for a further 1 h, after which time water (20 mL) was added, resulting in the formation of a light yellow precipitate, which was filtered and washed successively with water (2 x 10 mL), methanol (2 x 5 mL), and diethyl ether (10 mL) and dried under vacuum giving **6**·PF_6 as an off-white powder (109 mg, 80%). Found: C, 52.9; H, 3.7; N, 0.8. $C_{90}H_{77}F_6NP_6PdPt_2S_2$ (M_r 2033) requires C, 53.2; H, 3.8; N, 0.7%. ESI MS, [**6** + H]$^{2+}$ *m/z* 944.5. $^{31}P\{^1H\}$ NMR, δ 21.4 (s, $PMePh_2$), 18.4 (*m*, $^1J_{PtP}$ 3204), 16.5 (*m*, $^1J_{PtP}$ 3140).

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]PF_6$ 7·PF_6

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (259 mg, 0.172 mmol) and *trans*-$[PdBrPh(PPh_3)_2]$ (144 mg, 0.183 mmol) were stirred in methanol (40 mL) at room temperature for 24 h. The mixture was filtered giving a clear yellow solution. NH_4PF_6 (300 mg, 1.84 mmol) was added to the filtrate giving a cream precipitate. After 10 min. water (20 mL) was added to assist precipitation. The product was filtered, and washed successively with water (20 mL), and diethyl ether (2 x 10 mL) and dried under vacuum giving **7**·PF_6 as a cream powder (250 mg, 69%). Found: C, 54.8; H, 3.8. $C_{96}H_{80}F_6P_6PdPt_2S_2$ (M_r 2094) requires C, 55.1; H, 3.9%. ESI MS, $[\mathbf{7}]^+$ *m/z* 1948. $^{31}P\{^1H\}$ NMR, δ 21.4 (*m*, Pd-PPh_3), 18.4 (*m*, $^1J_{PtP}$ 3081), and 16.4 (*m*, $^1J_{PtP}$ 3121).

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]PF_6$ 8·PF_6

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (423 mg, 0.281 mmol) and *trans*-$[PtHCl(PPh_3)_2]$ (120 mg, 0.159 mmol) were stirred and refluxed in methanol (30 mL) for 3 h, giving a yellow suspension. The mixture was filtered and excess NH_4PF_6 (300 mg, 1.84 mmol) was added to the filtrate giving a cream precipitate. This was filtered, washed with water (2 x 10 mL) and petroleum spirits (2 x 10 mL) and dried under vacuum to give **8**·PF_6 as a cream powder (204 mg, 34%). Found: C, 50.6; H, 3.6. $C_{90}H_{76}F_6P_6Pt_3S_2$ (M_r 2107) requires C, 51.3; H, 3.6%. ESI MS, $[\mathbf{8}]^+$ *m/z* 1961. $^{31}P\{^1H\}$ NMR, δ 16.6 (*m*, $PtHPPh_3$, $^1J_{PtP}$ 4094), 15.2 (*m*, $^1J_{PtP}$ 3130) and 14.1 (*m*, $^1J_{PtP}$ 3209). ^1H NMR, δ 7.21-6.83 (*m*, Ph) and -12.50 (*dt*, $^1J_{PtH}$ 1295).

X-ray structure determinations

X-ray data were collected on a Bruker Apex II CCD diffractometer, and corrected for absorption by a multi-scan procedure (SADABS).[37] Structures were solved and refined using the SHELX programs.[38] Crystal and refinement data are summarised in Table 3.

*$[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]PF_6$ (**7**·PF_6·0.75CH_2Cl_2)*

The CH_2Cl_2 molecules in the lattice are disordered over two partially occupied sites.

*$[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]PF_6$ (**8**·PF_6)*

Only thin plate crystals were obtained, giving a weak data set and a difficult absorption correction. Agreement indices are therefore higher than usual, and some appreciable, though chemically insignificant, residual peaks remained. The hydride on Pt(3) could not be located in the analysis, but its position *trans* to S(2) could be readily inferred.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 769419 (**7**) and 769420 (**8**). 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 (Å) and angles (°) for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]PF_6$ **7**·PF_6

Pt(1)-P(2)	2.2804(8)	Pt(1)-P(1)	2.3003(9)
Pt(1)-S(2)	2.3472(8)	Pt(1)-S(1)	2.3560(8)
Pt(2)-P(3)	2.2760(9)	Pt(2)-P(4)	2.2871(9)
Pt(2)-S(1)	2.3482(8)	Pt(2)-S(2)	2.3620(8)
Pd(1)-C(1)	2.034(3)	Pd(1)-P(5)	2.2713(9)
Pd(1)-S(1)	2.3531(9)	Pd(1)-S(2)	2.4157(8)

P(2)-Pt(1)-P(1)	99.54(3)	S(2)-Pt(1)-S(1)	80.01(3)
P(3)-Pt(2)-P(4)	97.70(3)	S(1)-Pt(2)-S(2)	79.86(3)
C(1)-Pd(1)-P(5)	87.17(10)	C(1)-Pd(1)-S(1)	89.78(10)
P(5)-Pd(1)-S(2)	105.30(3)	S(1)-Pd(1)-S(2)	78.68(3)

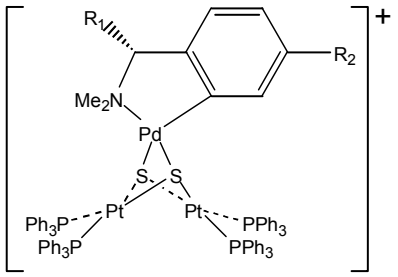
Table 2 Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]PF_6$ **8**·PF_6

Pt(1)-P(4)	2.270(4)	Pt(1)-P(3)	2.284(4)
Pt(1)-S(2)	2.344(4)	Pt(1)-S(1)	2.368(3)
Pt(2)-P(2)	2.275(3)	Pt(2)-P(1)	2.278(4)
Pt(2)-S(1)	2.351(4)	Pt(2)-S(2)	2.380(3)
Pt(3)-P(5)	2.219(4)	Pt(3)-S(1)	2.350(4)
Pt(3)-S(2)	2.427(4)		

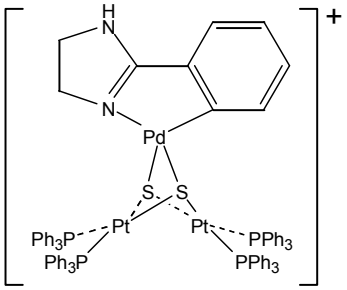
P(4)-Pt(1)-P(3)	99.68(14)	S(2)-Pt(1)-S(1)	79.29(12)
P(2)-Pt(2)-P(1)	99.60(13)	S(1)-Pt(2)-S(2)	78.92(12)
P(5)-Pt(3)-S(1)	174.35(13)	P(5)-Pt(3)-S(2)	106.07(12)
S(1)-Pt(3)-S(2)	78.00(12)		

Table 3 Crystal data and refinement details for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]PF_6$ **7**·PF_6 and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]PF_6$ **8**·PF_6

	7·PF_6·0.75CH_2Cl_2	**8**·PF_6
Molecular formula	$C_{96.75}H_{81.5}Cl_{1.5}F_6P_6PdPt_2S_2$	$C_{90}H_{76}F_6P_6Pt_3S_2$
Formula weight	2157.81	2106.72
Temperature (K)	93(2)	93(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	Pbca
Unit cell dimensions		
a (Å)	49.9819(19)	23.978(4)
b (Å)	15.1532(6)	25.180(2)
c (Å)	26.5295(10)	27.590(4)
β (°)	119.597(2)	90
V (Å^3)	17471.3(12)	16658(4)
Z	8	8
$D_{(calc)}$ (g cm^{-3})	1.641	1.680
μ(Mo-Kα) (mm^{-1})	3.662	5.250
F(000)	8524	8208
Crystal size (mm)	0.26 x 0.20 x 0.13	0.50 x 0.40 x 0.04
θ range for data collection (°)	2.70 to 31.95	2.02 to 26.00
Reflections collected	118062	67979
Independent reflections	27546	15760
$R_{(int)}$	0.0503	0.0802
Max and min. transmission	0.6475 and 0.4494	0.8175 and 0.1788
Data/restraints/parameters	27546 / 0 / 1069	15760 / 0 / 928
GOF on F^2	1.020	1.050
Final *R* indices		
R_1 [$I > 2\sigma(I)$]	0.0330	0.0641
R_1 (all data)	0.0605	0.1353
wR_2 [$I > 2\sigma(I)$]	0.0743	0.1559
wR_2 (all data)	0.0857	0.2095
Largest peak and	2.119	3.510
hole (e Å^{-3})	-1.539	-2.465



1a; $R_1 = R_2 = H$
1b; $R_1 = H$, $R_2 = OMe$
1c; $R_1 = Me$, $R_2 = H$



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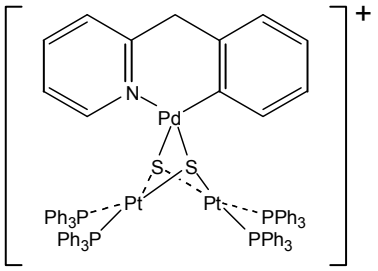

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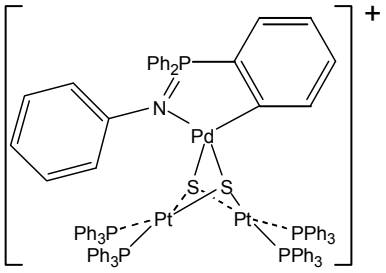

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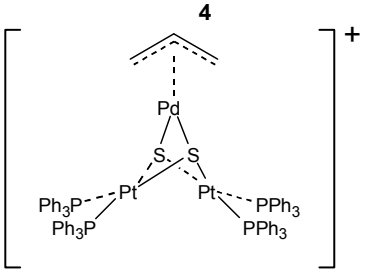

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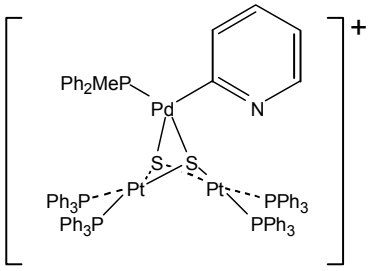

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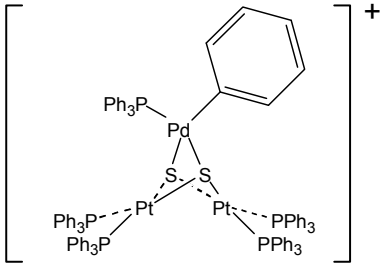

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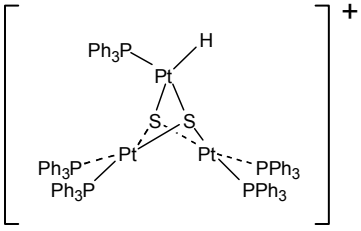

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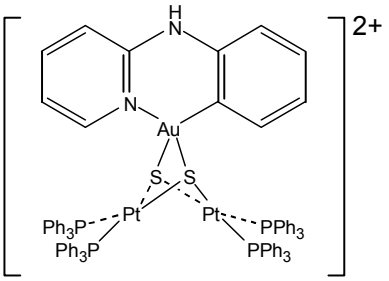

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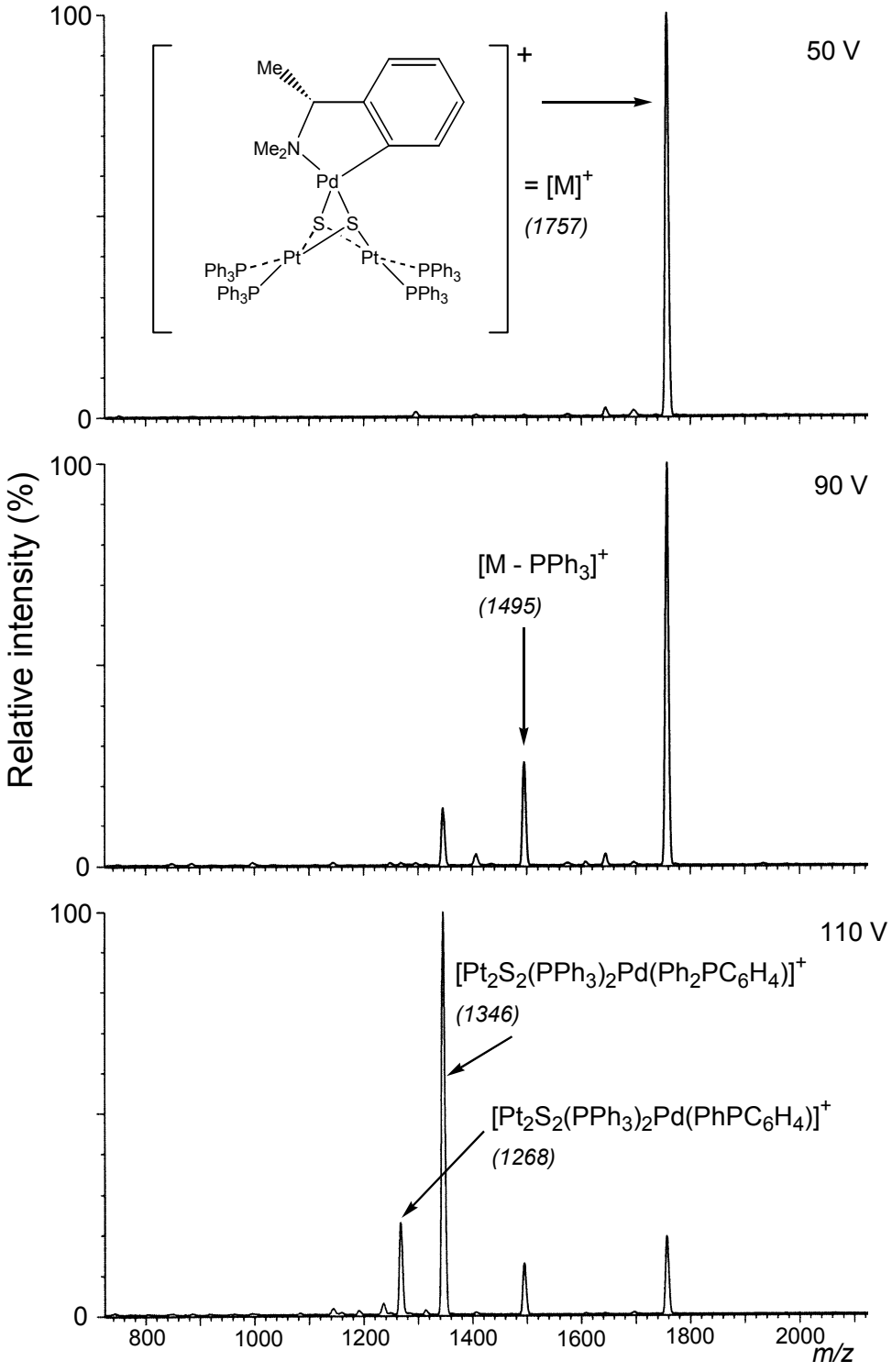

Figure 1 Positive ion ESI mass spectra of complex **1c**·PF_6 at cone voltages of 50, 90 and 100 V; *m/z* values of major ions are given in italics.

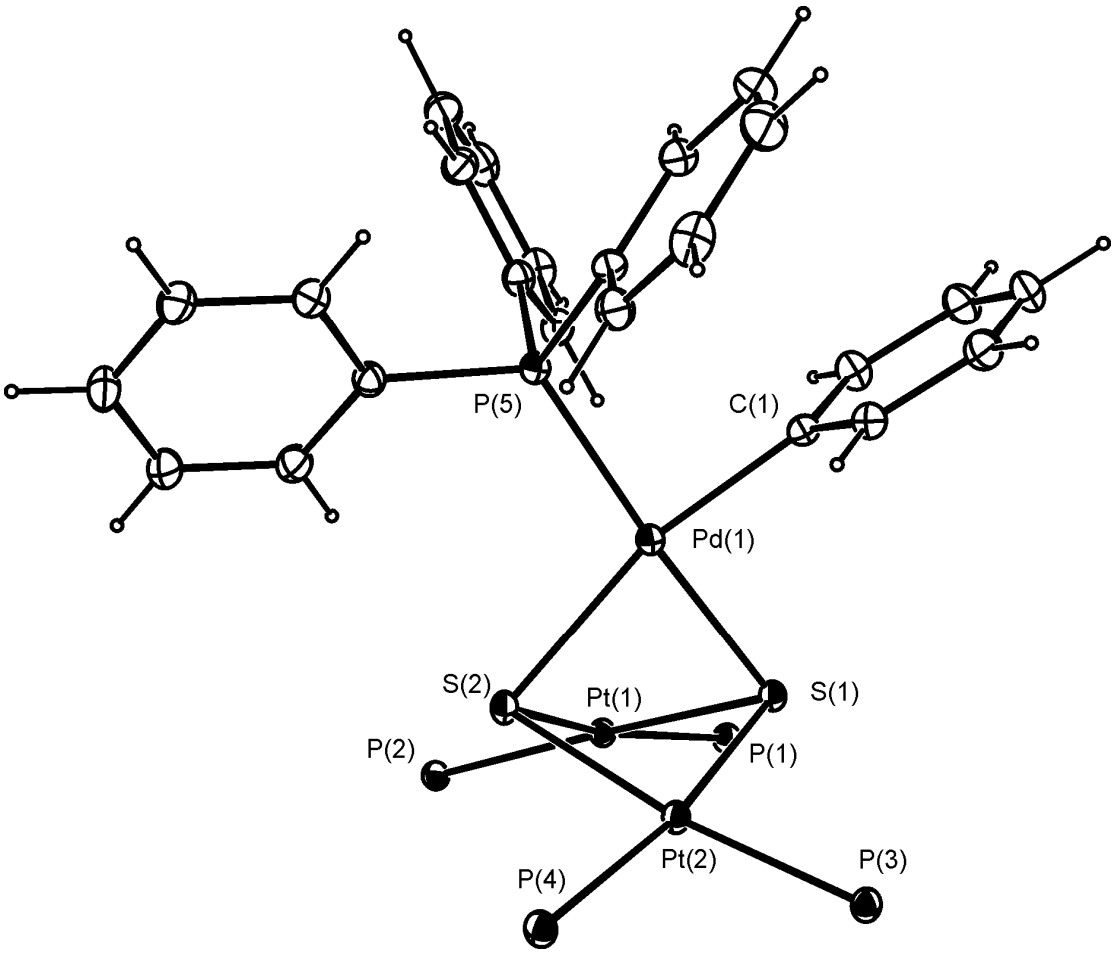

Figure 2 Molecular structure of the cation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]PF_6$ (**7**·PF_6); phenyl rings of the platinum-bonded PPh_3 ligands have been omitted for clarity.

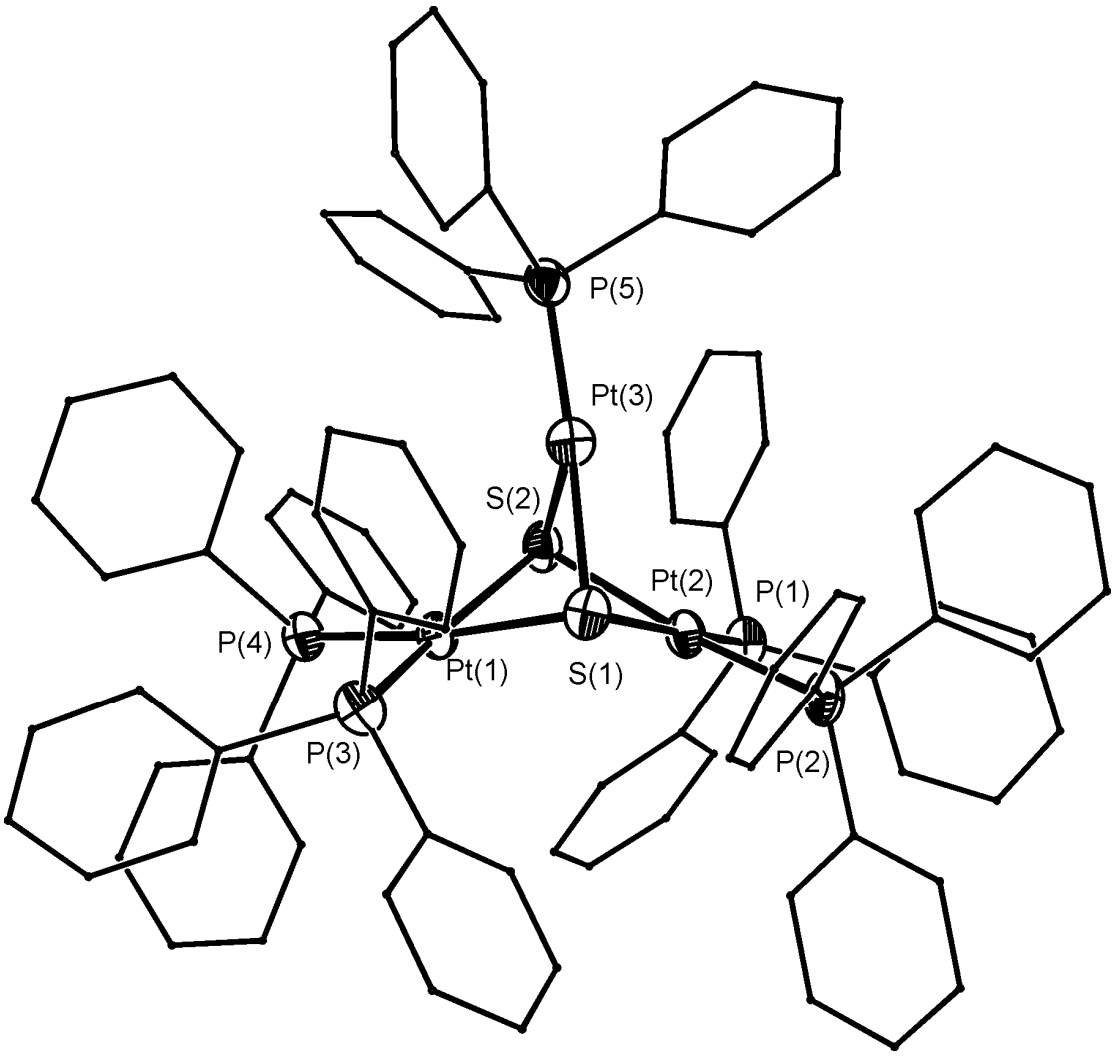

Figure 3 Molecular structure of the cation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]PF_6$ (**8**·PF_6)

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