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Dinuclear platinum(II) sulfide-thiolate complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ containing fluorinated substituents and the identification of a $S\cdots C_6F_5$ π interaction in the crystal structure of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]BPh_4\cdot 2C_6H_6$

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ABSTRACT

Reactions of the platinum(II) sulfido complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the alkyl iodides $ICH_2CH_2(CF_2)_nCF_3$ (n = 3, 7) gives good yields of the monoalkylated products $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2(CF_2)_nCF_3\}(PPh_3)_4]^+$, which were isolated as PF_6^- or BPh_4^- salts, and characterised by ESI mass spectrometry, NMR spectroscopy and elemental analysis. The complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2(CF_2)_nCF_3\}(PPh_3)_4]^+$ appears to have normal reactivity for this type of complex, namely reaction with Ph_3PAuCl to give $[Pt_2(\mu\text{-}SAuPPh_3)\{\mu\text{-}SCH_2CH_2(CF_2)_nCF_3\}(PPh_3)_4]^{2+}$, and reaction with Me_2SO_4 to give $[Pt_2(\mu\text{-}SMe)\{\mu\text{-}SCH_2CH_2(CF_2)_nCF_3\}(PPh_3)_4]^{2+}$. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $C_6F_5CH_2Br$ gave $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]^+$, isolated as its BPh_4^- salt, and characterised by NMR spectroscopy and a single-crystal X-ray structure determination. The C_6F_5 group lies above the $\{Pt_2S_2\}$ core of the complex as a result of a $S\cdots C_6F_5$ π interaction, in contrast to the published structure of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]PF_6$, where the C_6H_5 group projects away from the $\{Pt_2S_2\}$ core.

Keywords: Platinum complexes; Sulfide complexes; Thiolate complexes; Alkylation reactions; π interactions; Crystal structure

1. Introduction

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1**[1] is known to undergo alkylation reactions with a wide range of alkylating agents, resulting in the conversion of μ-sulfide to μ-thiolate ligands. Such chemistry allows the designer synthesis of a wide range of functionalised thiolate complexes,[2,3,4] while the stepwise use of two different alkylating agents gives a practical syntheses of the mixed thiolate complexes $[Pt_2(\mu\text{-}SR^1)(\mu\text{-}SR^2)(PPh_3)_4]^{2+}$, that have not to date been easily accessible by other methodologies.[5,6] Further interest in the reactivity of complexes with $\{Pt_2S_2\}$ cores with organo-fluorine compounds comes from the successful use of aryl-fluorides as arylation reagents through aromatic C-F bond activation, leading to aromatic thiolate complexes of platinum[7,8] and from the interesting activation of an sp^3 C-F bond in $FCH_2CH(OH)CH_2F$ by $[Pt_2(\mu\text{-}S)_2\{Ph_2P(CH_2)_3PPh_2\}_2]$ where nucleophilic attack by sulfide is assisted by an O-H···F hydrogen bond which assists in the departure of the fluoride ion leaving group.[9]

In this paper we describe the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards alkylating agents that contain a fluorinated alkyl or aryl group, giving fluorinated alkylthiolate complexes. The alkylating agents chosen are the iodides $ICH_2CH_2(CF_2)_nCF_3$ (n = 3 or 7) containing fluorous 'pony tails', and $C_6F_5CH_2Br$, containing the pentafluorophenyl ring. Complexes of fluorinated thiolates, in particular pentafluorobenzene thiolate ($C_6F_5S^-$) and closely related analogues, have been extensively studied, because of the ability of these ligands to stabilise unusual oxidation states, coordination geometries, and inter- or intra-molecular interactions.[10,11,12,13,14] Pentafluorobenzylbromide has been employed in the alkylation derivatisation of thiols for analysis by GC-chemical ionisation MS,[15] but the $C_6F_5CH_2S^-$ ligand has, to date, been little studied, and we are unaware of any metal

complexes of this ligand. Metal complexes of the type M-$SCH_2CH_2(CF_2)_nCF_3$ are also rare [with only one known example, $Sn\{SCH_2CH_2(CF_2)_5CF_3\}_4$[16]] despite commercial availability of some thiols $HSCH_2CH_2(CF_2)_nCF_3$ (n = 5, 7).[17]

2. Results and discussion

2.1 Synthesis and spectroscopic studies

The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** with excess $ICH_2CH_2(CF_2)_7CF_3$ proceeds slowly at room temperature in methanol suspension, eventually (after several days) giving a clear bright yellow solution containing exclusively the cation $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2(CF_2)_7CF_3\}(PPh_3)_4]^+$. Reactions were monitored using positive-ion ESI mass spectrometry, which we have previously shown to be a powerful technique for investigating the reaction chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$[2,18] and related systems.[19] The fluoroalkylthiolate complex was isolated in reasonable yields as its BPh_4^- and PF_6^- salts, **2a** and **2b** respectively. The shorter chain analogue $ICH_2CH_2(CF_2)_3CF_3$ reacts in the same way, giving the analogous complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2(CF_2)_3CF_3\}(PPh_3)_4]^+$ which was isolated as its PF_6^- salt **2c**. Pentafluorobenzyl bromide reacts rapidly with **1** to give the yellow pentafluorobenzyl derivative $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]^+$, isolated as the BPh_4^- salt **3**. This complex is related to the benzyl derivative itself, $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]^+$, which was one of the first alkylated derivatives of a $\{Pt_2S_2\}$ complex reported in very early studies in the field.[20]

All complexes show a dominant $[M]^+$ ion for the parent cation in their positive-ion ESI mass spectra, and the behaviour of complex **2a** was investigated at elevated cone voltages (Figure 1). At a relatively high cone voltage of 70V, the parent $[M]^+$ cation remains the sole peak in the spectrum while at 110V fragmentation primarily occurs by loss of up to two PPh_3 ligands, with formation of some $[Pt_2\{\mu\text{-}SCH_2CH_2(CF_2)_3CF_3\}(PPh_3)_2]^+$ also observed. This behaviour parallels that of analogous complexes, such as $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$.[8]

Although benzyl bromide does not easily dialkylate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$,[4] we considered that pentafluorobenzyl bromide may be more reactive, as a result of the electron-withdrawing C_6F_5 group. However, on prolonged heating of **1** with excess $C_6F_5CH_2Br$ to near reflux in methanol, no dialkylated product $[Pt_2(\mu\text{-}SCH_2C_6F_5)_2(PPh_3)_4]^{2+}$ was observed in the ESI mass spectrum. Refluxing **1** with an excess of $ICH_2CH_2(CF_2)_7CF_3$ also does not form any dialkylated product. While short chain alkyl iodides readily dialkylate **1**, longer chain iodides such as 1-iodopentane are far less reactive, giving predominantly monoalkylation,[2] so the behaviour observed by $ICH_2CH_2(CF_2)_7CF_3$ is in accordance with these previous studies.

All complexes are soluble in chlorinated hydrocarbon solvents (CH_2Cl_2 and $CHCl_3$) and slightly soluble in methanol and toluene. Complexes **2a** and **2b** are soluble in hexafluoroisopropanol but effectively insoluble in octafluorotoluene, which is as expected given the significant dilution of the fluorous characteristics by the four PPh_3 ligands. Their solubilities therefore more closely resemble non-fluorinated complexes such as $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]PF_6$.

The $^{31}P\{^{1}H\}$ NMR spectra of the complexes **2** and **3** are similar to those of related monoalkylated derivatives.[4] For **2** a single central ^{31}P resonance is seen (due to coincident chemical shifts for the two types of nominally inequivalent phosphines, *trans* to sulfide or thiolate ligands), with two sets of satellites due to coupling to ^{195}Pt. However, in **3**, there is a small separation of the resonances, which appear at δ 23.8 and 24.3, a similar difference to that observed in $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$[20] and $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$.[8] The $^{1}J(PtP)$ coupling constants [for example 3304 and 2580 Hz for the phosphines *trans* to thiolate and sulfide respectively in **2a**] are similar to other monofunctionalised complexes such as $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]PF_6$ (3291 and 2613 Hz).[8]

Complexes **2** show a broad multiplet in their ^{1}H NMR spectra at around 2.4 ppm, assigned to the SCH_2 protons because of satellites due to ^{195}Pt coupling (the satellites were not well resolved and appeared as broad shoulders, but the value of $^{3}J(PtH)$ is estimated to be around 30 Hz). This chemical shift is similar to that observed for the SCH_2 protons in the butylthiolate analogue $[Pt_2(\mu\text{-}S)(\mu\text{-}S^nBu)(PPh_3)_4]^+$ (2.29 ppm), but somewhat more shielded than the SCH_2 protons in the (longer chain) free thiol $HSCH_2CH_2(CF_2)_{10}CF_3$ (2.70-2.90 ppm)[21] and the related sulfide $S(CH_2CH_2(CF_2)_7CF_3)_2$ (2.79 ppm).[22] The CH_2CF_2 protons of **2** appear as a complex multiplet around δ 1.3 ppm, somewhat shielded from 2.30-2.55 ppm observed in $HSCH_2CH_2(CF_2)_{10}CF_3$, and 2.34-2.47 ppm in $S(CH_2CH_2(CF_2)_7CF_3)_2$. The origin of the shielding of the SCH_2CH_2 protons in **2** might be due to aromatic ring effects arising from the PPh_3 ligands. The ^{1}H NMR spectrum of the pentafluorobenzyl complex **3** showed (in addition to a complex set of phenyl resonances) a broad multiplet at δ 3.52 ppm due to the CH_2 protons, with $^{3}J(PtH)$

coupling of around 24 Hz. The ^{19}F NMR spectra of complexes **2a** and **2c** show the expected number of resonances due to the CF_2 and CF_3 protons (the latter appearing as the expected triplet with J(FF) around 10 Hz), while the pentafluorobenzyl complex **3** shows the expected three resonances due to the *ortho*, *meta* and *para* C-F groups.

The presence of fluorinated substituents does not seem to impede reactions of these complexes at the free sulfide centre. Thus, reaction of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2(CF_2)_7CF_3\}(PPh_3)_4]^+$ (generated *in situ* from **1** and $ICH_2CH_2(CF_2)_7CF_3$) with Ph_3PAuCl and NH_4PF_6 results in the formation of $[Pt_2(\mu\text{-}SAuPPh_3)\{\mu\text{-}SCH_2CH_2(CF_2)_7CF_3\}(PPh_3)_4](PF_6)_2$ **4** as a white solid, in analogous fashion to the previously reported syntheses of $[Pt_2(\mu\text{-}SAuPPh_3)(\mu\text{-}SR)(PPh_3)_4](PF_6)_2$ (R = n-Bu or Ph).[23] The complex was characterised by its distinctive dication (*m/z* 1204.5, 100%) as the base peak in the positive-ion ESI mass spectrum, and by excellent microanalytical data. Alkylation of the sulfide ligand of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2(CF_2)_7CF_3\}(PPh_3)_4]^+$ with excess Me_2SO_4 followed by precipitation with $NaBPh_4$ gave a white solid that showed the dication $[Pt_2(\mu\text{-}SMe)\{\mu\text{-}SCH_2CH_2(CF_2)_7CF_3\}(PPh_3)_4]^{2+}$ (*m/z* 982.3) as the base peak in the positive-ion ESI mass spectrum.

2.2 X-ray structure determination on $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]BPh_4$ **3**

Crystals of complex **3** suitable for an X-ray structural study were obtained from a saturated benzene solution. As the structure of the benzyl complex is known,[4] the structure of the fluoro analogue was determined in order to identify any effects of fluorine substitution. The molecular structure of the cation is shown in Figure 2, together

with the atom numbering scheme, while selected bond lengths and angles are summarised in Table 1.

The structure confirms the identity of the cation as the expected monoalkylated complex containing bridging thiolate and sulfide ligands, and is generally comparable to other monoalkylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. In **3**, the platinum-sulfide bond distances Pt(1)-S(1) 2.3230(15) and Pt(2)-S(1) 2.3394(16) Å are significantly shorter than the platinum-thiolate bond distances Pt(1)-S(2) 2.3508(15) and Pt(2)-S(2) 2.3514(15) Å. The corresponding benzyl complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]PF_6$[4] has very comparable Pt-sulfide bond distances to **3** [2.3209(13) and 2.3363(13) Å], while the Pt-thiolate distances are slightly longer in the benzyl derivative [2.3667(13) and 2.3594(13) Å], due to the electron-withdrawing nature of the C_6F_5 group in **3**. In **3** the Pt-P bond distances *trans* to the sulfide S(1) [Pt(1)-P(2) 2.3031(15), Pt(2)-P(4) 2.3038(17) Å] are longer than those *trans* to thiolate [Pt(1)-P(1) 2.2797(16), Pt(2)-P(3) 2.2975(15) Å] as a result of the higher *trans* influence[24] of the sulfide ligand, this effect being a typical feature of such monoalkylated $\{Pt_2S_2\}$ derivatives. The dihedral angle between the two PtS_2 planes of **3** (141.4°) is very similar to that in $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]^+$ (140°).

The key difference between **3** and the benzyl analogue $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]PF_6$ can be seen by comparing the cores of the two structures, shown in Figure 3. It is noteworthy that in **3** the C_6F_5 ring lies over the $\{Pt_2S_2\}$ core, while the benzyl analogue has the phenyl ring twisted away from the core. Despite its greater steric bulk, there is clearly an interaction holding the C_6F_5 group in the observed position, which is illustrated by a side view of the complex looking down the Pt···Pt vector, Figure

4. The distance between the centroid of the pentafluorophenyl ring and the sulfide S(1) is 3.613 Å, while the closest contact between S(1) and an individual carbon atom of this ring is 3.409 Å to the *ipso* carbon, C(2). The interaction is not symmetrical, with the sulfur lying slightly to one side of the ring, such that S···C(3) is 3.491 Å, while S···C(7) is 3.814 Å.

Sulfur-π interactions have been relatively little studied compared to other types of π interactions, but the observation that these might play a significant role in the structures of sulfur-containing proteins[25] has led to theoretical studies of S-π interacting systems such as the H_2S-benzene dimer (though in this system the interaction is between the δ+ hydrogens and the δ- benzene ring).[26] Such an interaction in **3** is promoted by the positive charge at the centre of the fluoroaryl ring,[27] which interacts (as an electron acceptor) with the electron-rich sulfide donor of the $\{Pt_2S_2\}$ core. In theoretical studies on adducts formed between C_6F_6 and either PMe_3 or P^tBu_3, a significant (up to 12 kcal mol^{-1}) phosphorus···C_6F_6 π interaction is obtained, which in the case of the PMe_3 adduct had a maximum interaction with an approximately 30° tilting of the principal axis of the PMe_3 towards the C_6F_6 plane, and a 0.2 Å displacement from the ring centre.[28] This geometry is reminiscent of the relationship between the free sulfide and the C_6F_5 ring in **3**, suggesting that this compound may contain a significant S···C_6F_5 π interaction.

The S···π interaction in complex **3** is supported by additional C-H···F interactions. The shortest distances are between the methylene protons and the *ortho* fluorines of the C_6F_5 ring, such that F(5)···H(1A) is 2.477 Å and F(1)···H(1B) is 2.495 Å. These distances are considerably less than the sum of the van der Waals radii of H and F (about 2.67 Å), and F···H distances of up to 2.9 Å have been considered as F···H

interactions.[23] Additional F···H interactions in **3** include those between the *ortho* fluorine F(1) with two of the *ortho* hydrogens of one of the triphenylphosphine ligands; F(1)···H(2E) 2.710 Å, F(1)···H(2C) 2.310 Å. H···F distances involving the other *ortho* fluorine F(5) and *ortho* triphenylphosphine hydrogens are > 2.9 Å.

In contrast, an S···fluoroaryl π interaction is not possible in the previously reported tetrafluoropyridyl system $[Pt_2(\mu\text{-}S)\{\mu\text{-}(p\text{-}SC_5F_4N)\}\{Ph_2P(CH_2)_3PPh_2\}]^+$ because of the lack of a flexible CH_2 spacer; in this complex the tetrafluoropyridyl ring adopts a rare *endo* configuration, which permits π-π interactions with phenyl rings of the phosphine ligands.[7] Such interactions between electron donor phenyl and acceptor fluorophenyl rings are well-known.[23,29,30]

Conclusions

In this work we have extended the range of monoalkylated sulfide-thiolate dinuclear complexes formed by alkylation of the platinum-sulfido complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** to include compounds with fluorinated substituents. While these complexes show a great deal of similarity to non-fluorinated analogues in many respects, the crystal structure of the pentafluorobenzyl complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]BPh_4$ **3** has revealed an interesting sulfide···pentafluorophenyl π interaction, suggesting that further study of related systems might reveal further instances of the electron-donor participation of the free sulfide ligands of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and monoalkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$.

3. Experimental

3.1 Materials and 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 20V unless otherwise stated. High resolution ESI mass spectra were recorded on a Bruker MicrOTOF instrument, calibrated using a solution of sodium formate. Samples of isolated products were prepared by dissolving a small quantity of the solid in a few drops of CH_2Cl_2, followed by dilution with methanol. Assignment of ions utilised the ISOTOPE simulation program[31] or a Bruker instrument-based program. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 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). ^{19}F NMR spectra were recorded in $CDCl_3$ solution at 376.46 MHz. Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago, Dunedin.

Reactions were carried out in LR grade methanol, without exclusion of moisture or air. Petroleum spirits refers to the fraction of boiling point 40-60 ºC. Sodium tetraphenylborate (BDH), ammonium hexafluorophosphate (Aldrich), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane (Aldrich), 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodohexane (Fluka), octafluorotoluene (Aldrich) and pentafluorobenzyl bromide (Aldrich) were used as supplied. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** was

synthesised from *cis*-[$PtCl_2(PPh_3)_2$] and $Na_2S{\cdot}9H_2O$ in benzene suspension.[20] Ph_3PAuCl was prepared by the literature procedure.[32]

3.2 Syntheses

3.2.1 Synthesis of [$Pt_2(\mu$-S){μ-$SCH_2CH_2(CF_2)_7CF_3$}$(PPh_3)_4$]BPh_4 ***2a***

A suspension of [$Pt_2(\mu$-$S)_2(PPh_3)_4$] **1** (366 mg, 0.244 mmol) and $ICH_2CH_2(CF_2)_7CF_3$ (255 mg, 0.444 mmol) in methanol (30 mL) was stirred at room temperature for 5 days, giving a bright yellow solution. $NaBPh_4$ (200 mg, 0.585 mmol) was added, giving a yellow precipitate in a yellow solution. Water (10 mL) was added to assist precipitation. The solid was isolated by filtration, washed successively with water (2 x 20 mL), methanol-water (1:1, 10 mL) and diethyl ether (2 x 10 mL) and dried under vacuum to give **2a** as a yellow solid (305 mg, 55%). Found: C, 55.00; H, 3.69. $C_{106}H_{84}BF_{17}P_4Pt_2S_2$ (M_r 2269.77) requires C, 56.09; H, 3.73%. Recrystallisation from dichloromethane-diethyl ether gave bright yellow needles. ESI MS, *m/z* 1950 (100%), [**2a**-BPh_4]$^+$. $^{31}P\{^1H\}$ NMR, δ 25.0 [s, ^1J(PtP) 3304 and 2580 Hz]. ^1H NMR, δ 7.48-6.87 (m, Ph), 2.41 (m, 2H, CH_2S) and 1.38 (m, 2H, CH_2CF_2). ^{19}F NMR, δ -80.64 [t, 3F, CF_3, J(FF) 10.0], -114.15 (m, 2F, CF_2), -121.49 (m, 2F, CF_2), -121.78 (m, 4F, CF_2), -122.56 (m, 2F, CF_2), -123.30 (m, 2F, CF_2), -125.95 (m, 2F, CF_2). The complex is soluble in dichloromethane and benzene, and slightly soluble in methanol.

3.2.2 Synthesis of [$Pt_2(\mu$-S){μ-$SCH_2CH_2(CF_2)_7CF_3$}$(PPh_3)_4$]PF_6 ***2b***

Following the procedure for **2a**, [$Pt_2(\mu$-$S)_2(PPh_3)_4$] **1** (200 mg, 0.133 mmol) and $ICH_2CH_2(CF_2)_7CF_3$ (140 mg, 0.244 mmol) in methanol (25 mL) gave a yellow solution, to which was added NH_4PF_6 (200 mg, 1.23 mmol). Water (30 mL) was added dropwise to effect precipitation. The solid was isolated by filtration, washed successively with water (3 x 20 mL) and diethyl ether (3 x 10 mL) and dried *in vacuo* to give **2b** as a yellow solid (209 mg, 75%) that had an identical $^{31}P\{^1H\}$ NMR spectrum of the platinum-containing cation as the BPh_4 salt **2a**. Found: C, 46.33; H, 3.22. $C_{82}H_{64}F_{23}P_5Pt_2S_2$ (M_r 2095.51) requires C, 47.00; H, 3.08%.

3.2.3 Synthesis of [$Pt_2(\mu$-S){μ-$SCH_2CH_2(CF_2)_3CF_3$}$(PPh_3)_4$]PF_6 ***2c***

A suspension of [$Pt_2(\mu$-$S)_2(PPh_3)_4$] **1** (300 mg, 0.200 mmol) and $ICH_2CH_2(CF_2)_3CF_3$ (10 drops, excess) in methanol (30 mL) was stirred at room temperature for 2 days to give a yellow solution. After filtration to remove a trace of insoluble matter, NH_4PF_6 (200 mg, 1.23 mmol) was added to the stirred filtrate, giving a yellow precipitate. Water (20 mL) was added dropwise to assist precipitation. The product was filtered, washed with water (3 x 10 mL) and hexane (10 mL), and then dried under vacuum to give **2c** as a yellow solid (300 mg, 79%). Found: C, 49.28; H, 3.28. $C_{78}H_{64}F_{15}P_5Pt_2S_2$ (M_r 1894.45) requires C, 49.41; H, 3.40%. ESI MS (high resolution), obs. *m/z* 1750.3186 (100%); $C_{78}H_{64}F_9P_4Pt_2S_2$ calc. *m/z* 1750.2561, [**2c**-PF_6]$^+$. $^{31}P\{^1H\}$ NMR, δ 24.9 [s, ^1J(PtP) 3307 and 2582 Hz]. ^1H NMR, δ 7.41-7.06 (m, Ph), 2.36 (m, 2H, CH_2S) and 1.33 (m, 2H, CH_2CF_2). ^{19}F NMR, δ -73.90 [d, PF_6^-, ^1J(PF) 708.9], -80.94 [t, 3F, CF_3, J(FF) 9.8], -114.40 (m, 2F, CF_2), -124.34 (m, 2F, CF_2), -125.85 (m, 2F, CF_2).

*3.2.4 Synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]BPh_4$ **3***

A mixture of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (318 mg, 0.212 mmol) and $C_6F_5CH_2Br$ (0.1 mL, excess) in methanol (25 mL) was stirred for 40 min. to produce a clear yellow solution. After filtration to remove a trace of insoluble matter, $NaBPh_4$ (200 mg, 0.585 mmol) was added to the filtrate, to give a yellow precipitate. The product was filtered, washed successively with methanol (10 mL), water (10 mL), and methanol (10 mL) and dried under vacuum to give **3** (269 mg, 63%). Found: C, 61.41; H, 4.11. $C_{103}H_{82}BF_5P_4Pt_2S_2$ (M_r 2002.63) requires C, 61.72; H, 4.13%. ESI MS, *m/z* 1684 (100%), [**3**-BPh_4]$^+$. $^{31}P\{^1H\}$ NMR, δ 24.3 [m, ^1J(PtP) 3341] and 23.8 [m, ^1J(PtP) 2595]. ^1H NMR, δ 7.51-6.91 (m, Ph), 3.52 [m, br, CH_2, ^3J(PtH) *ca* 24]. ^{19}F NMR, δ -137.29 (m, 2F, *ortho*), -155.78 [t, 1F, *para*, ^3J(FF) 20.6] and -162.00 (m, 2F, *meta*).

*3.2.5 Attempted dialkylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** using $C_6F_5CH_2Br$ or $ICH_2CH_2(CF_2)_7CF_3$*

A mixture of **1** (*ca.* 100 mg) and 10 drops (a large excess) of $C_6F_5CH_2Br$ in methanol (20 mL) was stirred for 16 hours, to give a clear yellow solution that was then heated to near reflux for 16 hours. ESI MS of the resulting yellow solution showed only $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]^+$ at *m/z* 1684, with no dialkylated (or other) product.

In a separate experiment, **1** (100 mg, 0.065 mmol) and $ICH_2CH_2(CF_2)_7CF_3$ (155 mg, 0.270 mmol), after refluxing for 5 hours and stirring at room temperature for 3 days gave a yellow solution shown by positive-ion ESI MS to contain only $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2(CF_2)_7CF_3\}(PPh_3)_4]^+$.

*3.2.6 Synthesis of [$Pt_2(\mu$-$SAuPPh_3)\{\mu$-$SCH_2CH_2(CF_2)_7CF_3\}(PPh_3)_4](PF_6)_2$ **4***

Following the procedure for **2a**, a mixture of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (297 mg, 0.198 mmol) and $ICH_2CH_2(CF_2)_7CF_3$ (190 mg, 0.331 mmol) in methanol (30 mL) for 5 days gave a yellow solution, which was filtered to remove a trace of insoluble matter. Solid Ph_3PAuCl (100 mg, 0.202 mmol) was added, and the yellow solution stirred at room temperature for 10 min. Solid NH_4PF_6 (200 mg, 1.23 mmol) was added to the stirred mixture, resulting in the deposition of a white solid after several minutes. After stirring for 1 hour, the white product was filtered, washed with methanol (2 x 5 mL) and dried under vacuum to give **4** (390 mg, 73%). Found: C, 44.40; H, 2.89. $C_{100}H_{79}AuF_{29}P_7Pt_2S_2$ (M_r 2698.46) requires C, 44.47; H, 2.95%. ESI MS, *m/z* 1204.5 (100%), $[\mathbf{4}\text{-}2PF_6]^{2+}$.

*3.3 X-ray crystal structure determination on $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]BPh_4\cdot 2C_6H_6$ **3**$\cdot 2C_6H_6$*

Crystals of complex **3** (as a di-benzene solvate) were obtained by slow evaporation of a benzene solution at room temperature. A crystal was mounted on a glass fibre. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo-K_α radiation at 223K, with the SMART suite of programs.[33] Data were processed and corrected for Lorentz and polarisation effects with SAINT,[34] and for absorption effects with SADABS.[35] Structural solution and refinement were carried out with the SHELXTL suite of programs.[36] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All

H-atoms were included in calculated positions. Crystal and refinement details are given in Table 2.

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Supplementary information

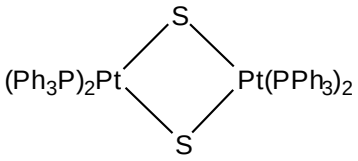
Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 795494. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 1 Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]BPh_4 \cdot 2C_6H_6$ (**3**$\cdot 2C_6H_6$)

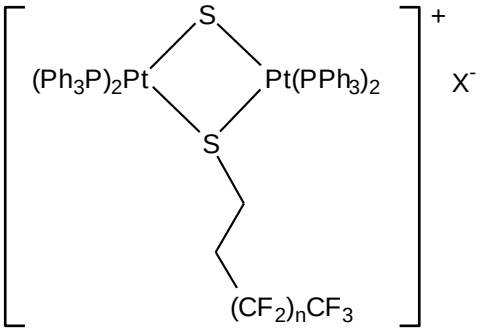
Pt(1)-P(1)	2.2797(16)	Pt(1)-P(2)	2.3031(15)
Pt(2)-P(3)	2.2975(15)	Pt(2)-P(4)	2.3038(17)
Pt(1)-S(1)	2.3230(15)	Pt(1)-S(2)	2.3508(15)
Pt(2)-S(1)	2.3394(16)	Pt(2)-S(2)	2.3514(15)
S(2)-C(1)	1.863(7)	F(1)-C(3)	1.368(8)
F(2)-C(4)	1.345(9)	F(3)-C(5)	1.356(10)
F(4)-C(6)	1.362(8)	F(5)-C(7)	1.345(8)
C(1)-C(2)	1.500(9)	C(2)-C(3)	1.349(10)
C(2)-C(7)	1.387(9)	C(3)-C(4)	1.359(11)
C(4)-C(5)	1.358(12)	C(5)-C(6)	1.371(11)
C(6)-C(7)	1.364(10)		
P(1)-Pt(1)-P(2)	98.28(6)	P(1)-Pt(1)-S(1)	92.19(6)
P(2)-Pt(1)-S(2)	87.73(5)	S(1)-Pt(1)-S(2)	81.88(5)
P(3)-Pt(2)-P(4)	101.42(6)	P(3)-Pt(2)-S(1)	86.21(6)
P(4)-Pt(2)-S(2)	90.63(5)	S(1)-Pt(2)-S(2)	81.52(5)
Pt(1)-S(1)-Pt(2)	91.61(5)	Pt(1)-S(2)-Pt(2)	90.62(5)
C(1)-S(2)-Pt(1)	109.5(2)	C(1)-S(2)-Pt(2)	109.3(2)
C(2)-C(1)-S(2)	116.8(5)	C(3)-C(2)-C(7)	115.8(7)
C(3)-C(2)-C(1)	123.2(7)	C(7)-C(2)-C(1)	121.0(7)
C(2)-C(3)-C(4)	124.2(7)	C(2)-C(3)-F(1)	119.2(7)
C(4)-C(3)-F(1)	116.6(7)	F(2)-C(4)-C(5)	119.6(9)
F(2)-C(4)-C(3)	121.6(8)	C(5)-C(4)-C(3)	118.7(8)
F(3)-C(5)-C(4)	121.6(8)	F(3)-C(5)-C(6)	118.6(9)
C(4)-C(5)-C(6)	119.7(8)	F(4)-C(6)-C(7)	120.0(8)
F(4)-C(6)-C(5)	120.3(8)	C(7)-C(6)-C(5)	119.7(8)
F(5)-C(7)-C(6)	118.5(7)	F(5)-C(7)-C(2)	119.8(7)
C(6)-C(7)-C(2)	121.7(7)		

Table 2 Crystal data and refinement details for $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]BPh_4 \cdot 2C_6H_6$ (**3**$\cdot 2C_6H_6$)

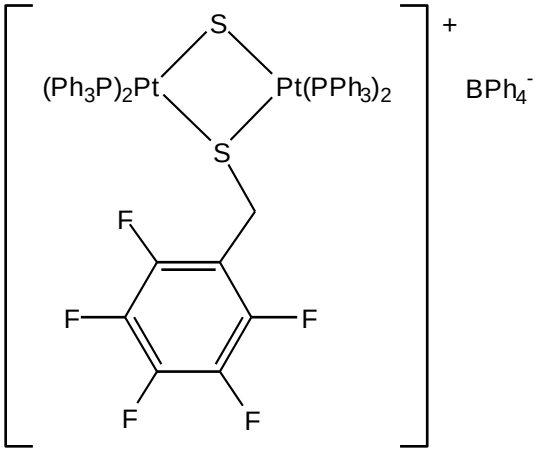
Empirical formula	$C_{115}H_{94}BF_5P_4Pt_2S_2$
Formula weight	2159.89
Temperature (K)	223(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions (Å, °)	
a	18.6503(7)
b	13.9385(5)
c	37.6107(14)
β	100.9530(10)
Volume ($Å^3$)	9599.1(6)
Z 4	
Density (calculated, g cm^{-3})	1.495
Absorption coefficient (mm^{-1})	3.082
F(000)	4328
Crystal size	0.58 x 0.30 x 0.16 mm^3
Reflections collected	66792
Independent reflections	21953 [R_{int} = 0.0780]
Max. and min. transmission	0.6384 and 0.2680
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21953 / 0 / 1138
Goodness-of-fit on F^2	1.053
Final R indices [$I>2\sigma(I)$]	R_1 0.0603, wR_2 0.1177
R indices (all data)	R_1 0.0837, wR_2 0.1267
Largest diff. peak and hole (e $Å^{-3}$)	2.274 and -1.388



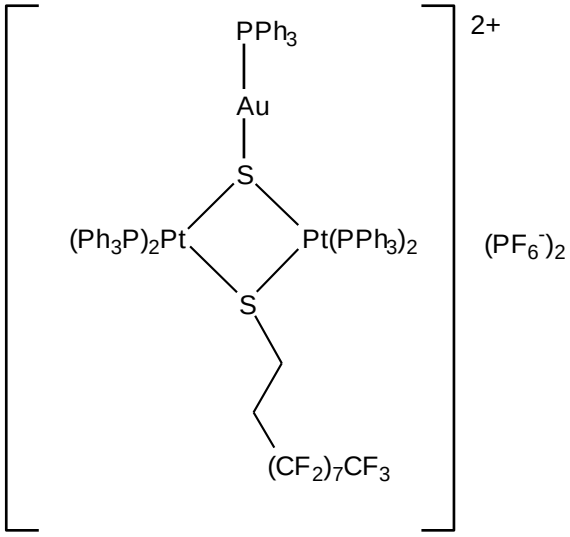
1



2a, n = 7, X = BPh_4
2b, n = 7, X = PF_6
2c, n = 3, X = PF_6



3



4

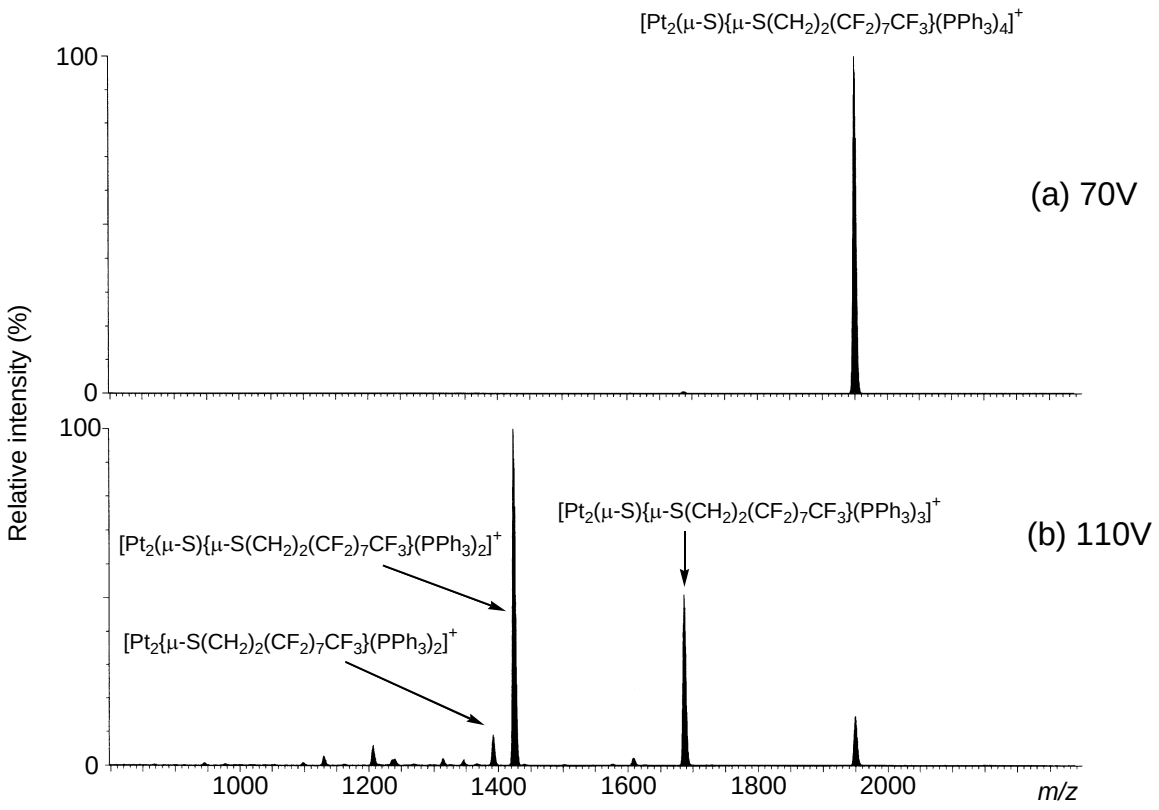


Figure 1 Positive-ion ESI mass spectra of $[Pt_2(\mu\text{-}S)\{\mu\text{-}S(CH_2)_2(CF_2)_7CF_3\}(PPh_3)_4]BPh_4$ **2a** at cone voltages of (a) 70V, showing the intact parent ion and (b) 110V, showing fragmentation primarily through loss of PPh_3 ligands

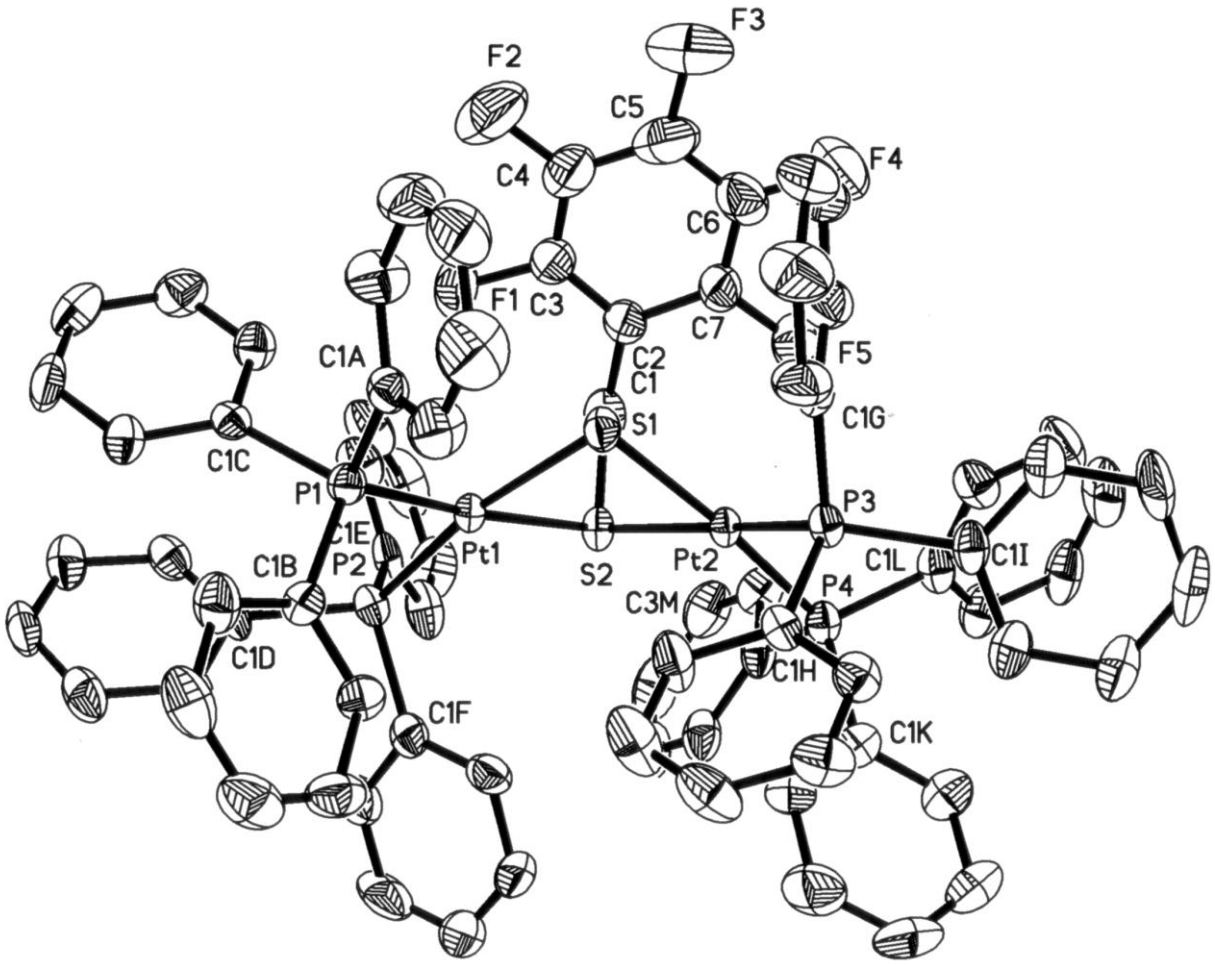


Figure 2 ORTEP diagram of the cation of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]BPh_4 \cdot 2C_6H_6$ (**3**$\cdot 2C_6H_6$) showing the atom numbering scheme (core atoms only). Thermal ellipsoids are shown at the 50% probability level

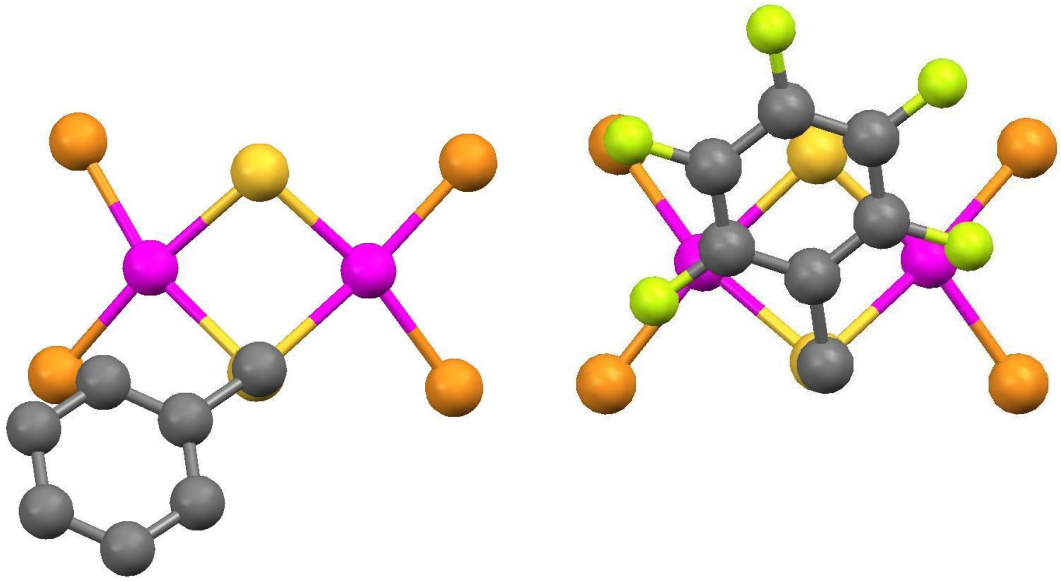


Figure 3 A comparison of the cores of the structures of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]PF_6$ (left) and $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]BPh_4 \cdot 2C_6H_6$ (**3**$\cdot 2C_6H_6$, right), showing the arrangement of the benzyl and pentafluorobenzyl substituents relative to the $\{Pt_2S_2\}$ cores

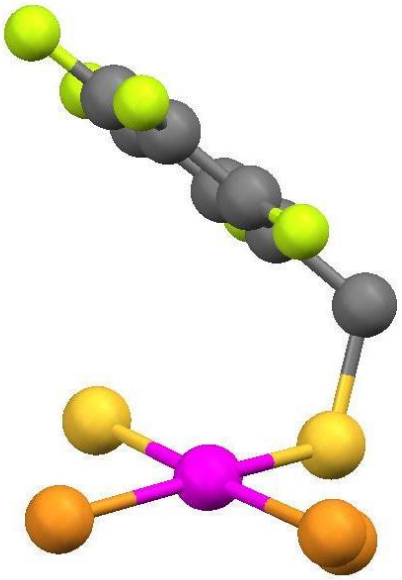


Figure 4 Side view (looking down the Pt-Pt vector) of the core of the cation $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6F_5)(PPh_3)_4]^+$, with PPh_3 carbons omitted for clarity

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