

# Synthesis and characterization of new sulfide aggregates of the type $[\{\text{Pt}_2(\mu_3\text{-S})_2(\text{P-P})_2\}\text{M}(\text{C}_6\text{F}_5)_2]$ (M = Ni, Pd, Pt; P-P = 2PPh<sub>3</sub>, 2PMe<sub>2</sub>Ph, dppf)

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Received 11 March 2004; accepted 26 March 2004

## Abstract

The reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{P-P})_2]$  (P-P = 2PPh<sub>3</sub>, 2PMe<sub>2</sub>Ph, dppf) [dppf = 1,1'-bis(diphenylphosphino)ferrocene] with *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{PhCN})_2]$  (M = Ni, Pd) or *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  (THF = tetrahydrofuran) afforded sulfide aggregates of the type  $[\{\text{Pt}_2(\mu_3\text{-S})_2(\text{P-P})_2\}\text{M}(\text{C}_6\text{F}_5)_2]$  (M = Ni, Pd, Pt). X-ray crystal analysis revealed that  $[\{\text{Pt}_2(\mu_3\text{-S})_2(\text{dppf})_2\}\text{Pd}(\text{C}_6\text{F}_5)_2]$ ,  $[\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PPh}_3)_2\}\text{Ni}(\text{C}_6\text{F}_5)_2]$ ,  $[\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PPh}_3)_2\}\text{Pd}(\text{C}_6\text{F}_5)_2]$  and  $[\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PMe}_2\text{Ph})_2\}\text{Pt}(\text{C}_6\text{F}_5)_2]$  have triangular M<sub>3</sub>S<sub>2</sub> core structures capped on both sides by μ<sub>3</sub>-sulfido ligands. The structural features of these polymetallic complexes are described. Some of them display short metal–metal contacts.

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**Keywords:** Palladium; Platinum; Nickel; S ligands; Bridging ligands

## 1. Introduction

There has been considerable interest in the study of multinuclear d<sup>8</sup> metal complexes with bridging sulfide ligands [1]. This class of compounds displays diverse structural features and in some instances exhibits interesting reactivities and photoluminescence [2,3]. Complexes of the type  $[\text{L}_2\text{Pt}(\mu\text{-S})_2\text{PtL}_2]$  (L = phosphine) are one of the most effective metalloligands identified to date. This can mainly be attributed to the geometric features of the central Pt<sub>2</sub>S<sub>2</sub> ring with a flexible hinge angle between the two {Pt<sup>II</sup>S<sub>2</sub>} planes, and to the ability of the bridging sulfide ligands, which are highly nucleophilic, to co-ordinate additional metal ions to afford the preparation of aggregates and clusters [4–7].

In this communication, we report on the synthesis and characterization of homo- and hetero-trinuclear complexes with the {MPt<sub>2</sub>S<sub>2</sub>} core derived from  $[\text{L}_2\text{Pt}(\mu\text{-S})_2\text{PtL}_2]$ , (L<sub>2</sub> = 2PPh<sub>3</sub>, 2PMe<sub>2</sub>Ph or dppf) and the “M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>” fragments M = Ni, Pd, Pt. The crystalline

nature of de trinuclear complexes  $[\{\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})_2\}\text{M}(\text{C}_6\text{F}_5)_2]$  (M = Ni, Pd),  $[\{\text{Pt}_2(\text{PMe}_2\text{Ph})_4(\mu\text{-S})_2\}\text{Pt}(\text{C}_6\text{F}_5)_2]$  and  $[\{\text{Pt}_2(\text{dppf})_2(\mu\text{-S})_2\}\text{Pd}(\text{C}_6\text{F}_5)_2]$  has enabled us to determine their molecular structures. To the best of our knowledge, reported herein are the first organometallic sulfide-bridged aggregates of the type {MPt<sub>2</sub>S<sub>2</sub>}, M being nickel, palladium or platinum.

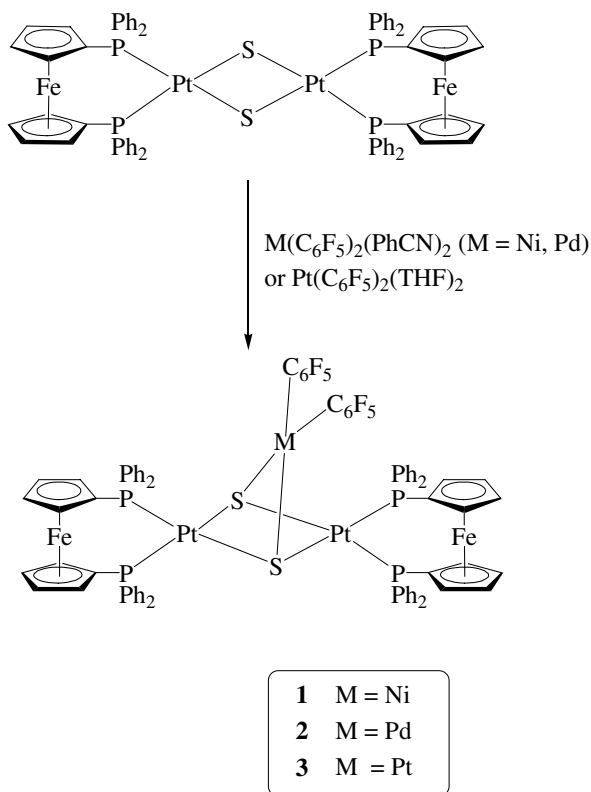
## 2. Results and discussion

### 2.1. Synthesis and spectroscopic characterization

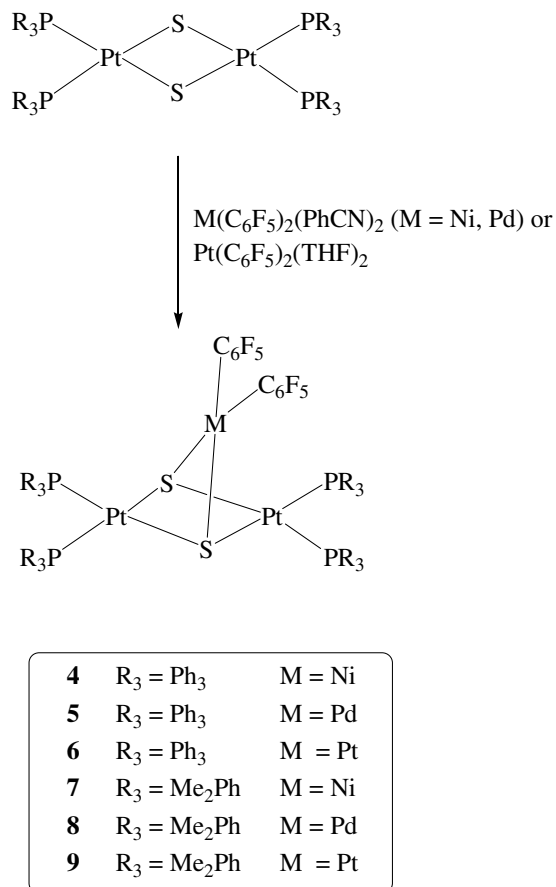
The reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{P-P})_2]$  (P-P = 2PPh<sub>3</sub>, 2PMe<sub>2</sub>Ph, dppf) [dppf = 1,1'-bis(diphenylphosphino)ferrocene] with *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{PhCN})_2]$  (M = Ni [8], Pd [9]) or *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  [10] (THF = tetrahydrofuran) in THF or CHCl<sub>3</sub> afforded sulfide aggregates of the type  $[\{\text{Pt}_2(\mu_3\text{-S})_2(\text{P-P})_2\}\text{M}(\text{C}_6\text{F}_5)_2]$  (M = Ni, Pd, Pt) (1)–(9) (Schemes 1 and 2) with the concomitant liberation of PhCN or THF. The ligand lability in *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{PhCN})_2]$  (M = Ni, Pd) or *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  enables them to function as a source of the “M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>” moiety.

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Scheme 1.



Scheme 2.

Complexes **1–9** have been characterized on the basis of partial elemental analyses and spectroscopic data (IR,  $^1H$ ,  $^{31}P$  and  $^{19}F$  NMR). The IR spectra of complexes **1–9** show the characteristic absorptions of the  $C_6F_5$  group [11] at 1630, 1490, 1450, 1050, 950 and a split band at ca.  $800\text{ cm}^{-1}$ , derived from the so-called X-sensitive mode in  $C_6F_5$ -halogen molecules, which is characteristic of the *cis*- $M(C_6F_5)_2$  fragment [12] and behaves like a  $\nu(M-C)$  band [13]. Mass spectra (FAB $^+$ ) of complexes **1–9** support the trinuclear nature of these complexes. The  $^{19}F$  NMR patterns are consistent with the presence of two equivalent  $C_6F_5$  groups, i.e., three sharp resonances with the intensity ratio  $2(F_o):1(F_p):2(F_m)$ , indicating freely rotating pentafluorophenyl rings around the C–M bond. As expected, the *ortho*-F signals of complexes **3**, **6** and **9** are flanked by the satellites due to coupling to  $^{195}Pt$ . The  $^{31}P$  NMR spectra of **1–9** show a singlet resonance for the phosphine ligands with expected  $\delta_P$  and  $J_{PtP}$  values for a diplatinum moiety of  $[L_2Pt(\mu-S)_2PtL_2]$ , ( $L_2 = 2PPh_3$ ,  $2PMe_2Ph$  or  $dppf$ ) and indicate that the phosphine ligands are chemically equivalent. No dynamic behaviour is observed.

## 2.2. Molecular structures

The molecular structure of **2** (Fig. 1) shows an isocel triangular  $PdPt_2$  core capped on both sides by  $\mu_3$ -sulfido ligands with a symmetric chelation of the dithio

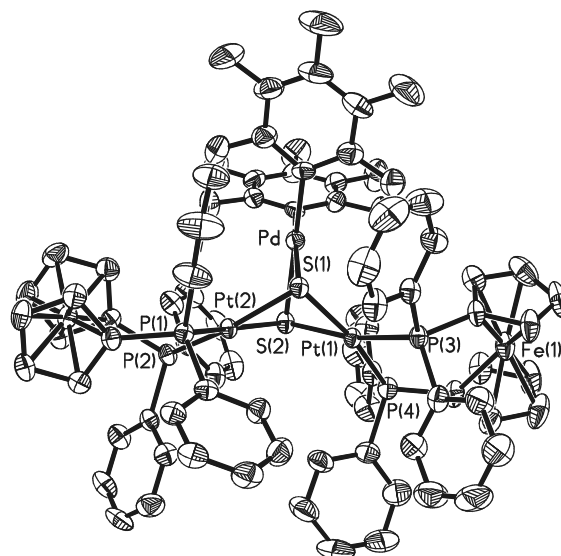


Fig. 1. ORTEP diagram of **2**. Thermal ellipsoids are at 50% probability.

ligand on the  $Pd^{II}$  with two similar Pd–S lengths [(Pd–S(2), 2.3648(16) vs. Pd–S(1), 2.3692(16) Å] (Table 1). These values are a bit higher than those observed

Table 1  
Selected bond lengths (Å) and angles (°) for complex 2

Bond lengths		Bond angles	
Pt(1)–P(3)	2.2790(15)	P(3)–Pt(1)–P(4)	98.92(6)
Pt(1)–P(4)	2.2842(16)	P(3)–Pt(1)–S(1)	91.48(5)
Pt(1)–S(1)	2.3394(14)	P(4)–Pt(1)–S(1)	168.97(5)
Pt(1)–S(2)	2.3498(14)	P(3)–Pt(1)–S(2)	168.31(6)
Pt(2)–P(2)	2.2685(15)	P(4)–Pt(1)–S(2)	91.05(5)
Pt(2)–P(1)	2.2816(15)	S(1)–Pt(1)–S(2)	79.03(5)
Pt(2)–S(2)	2.3432(14)	P(2)–Pt(2)–P(1)	99.94(5)
Pt(2)–S(1)	2.3578(14)	P(2)–Pt(2)–S(2)	91.86(5)
Pd–C(1)	2.023(6)	P(1)–Pt(2)–S(2)	167.86(5)
Pd–C(11)	2.028(6)	P(2)–Pt(2)–S(1)	167.64(6)
Pd–S(2)	2.3648(16)	P(1)–Pt(2)–S(1)	89.92(5)
Pd–S(1)	2.3692(16)	S(2)–Pt(2)–S(1)	78.80(5)
Fe(1)–C(21–25) (mean)	2.047	C(1)–Pd–C(11)	89.9(2)
Fe(1)–C(26–30) (mean)	2.037	C(1)–Pd–S(2)	96.33(16)
		C(11)–Pd–S(2)	173.79(17)
		C(1)–Pd–S(1)	173.92(16)
		C(11)–Pd–S(1)	95.69(17)
		S(2)–Pd–S(1)	78.14(5)

(2.287(2)–2.348(2) Å) in  $[\text{Pd}_3\text{Cl}(\text{dppf})_2(\text{PPh}_3)(\mu_3\text{-S})_2]\text{Cl}$  [14]. The metal–metal separations (3.087–3.284 Å) (Table 5) are outside the expected range for strong intermetal interactions, but are typical for related phosphine-bound  $[\text{M}_3\text{S}_2]$  derivatives [5] (3.00–3.18 Å for  $\text{M} = \text{Pd}$ , 3.11–3.18 Å for  $\text{M} = \text{Pt}$ ) and open up the possibility for weak metal–metal interactions in these *triangulo* complexes. The molecule shows a hinged  $\{\text{Pt}_2\text{S}_2\}$  central ring with a dihedral angle  $\theta = 129.8^\circ$ . The geometries at the individual Pt sites are approximately square planar, the main distortions being due to the reduction of the S–Pt–S angles from ideal  $90^\circ$  (average  $78.9^\circ$ ) [15], and by a twist of  $7.9^\circ$  between the Pt(1)S<sub>2</sub> and Pt(1)P<sub>2</sub> planes and of  $8.7^\circ$  between Pt(2)S<sub>2</sub> and Pt(2)P<sub>2</sub> [15]. The bite angle of the diphosphine ligand involving Pt(1) ( $98.9^\circ$ ) and Pt(2) ( $99.9^\circ$ ) compares well with those found in the related complexes  $[\text{Pt}_2\text{Ti}(\text{dppf})_2(\mu_3\text{-S})_2]\text{PF}_6$  ( $97.5^\circ$ ) [16] and  $[\text{Pt}_2\text{Ag}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2]$  ( $98.0^\circ$ ) [17]. The two C<sub>5</sub> rings of dppf, which are essentially coplanar (average dihedral angle  $\theta = 3.1^\circ$ ), adopt a common staggered (*gauche*) conformation [17]. The Fe–centroid distances are 1.64 Å. The palladium atom also exhibits an approximately square-planar geometry. The Pd–C<sub>6</sub>F<sub>5</sub> distances (2.023(6) and 2.028(6) Å) are in the range found in the literature [18]. The S–Pd–S “bite” angle of the  $\{\text{Pt}_2\text{S}_2\}$  metalloligand ( $78.14(5)^\circ$ ) is around the average for other adducts, e.g. those with square-planar metal centres such as  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{-Rh}(\text{CO})_2]^+$  ( $79.9(1)^\circ$ ) [19].

The molecular structure of 4 (Fig. 2) shows an isosceles triangular NiPt<sub>2</sub> core.

There is a symmetric chelation of the dithio ligand on the Ni<sup>II</sup> with two similar Ni–S lengths [Ni–S(2), 2.2239(10) vs. Ni–S(1), 2.2316(11) Å] (Table 2) which

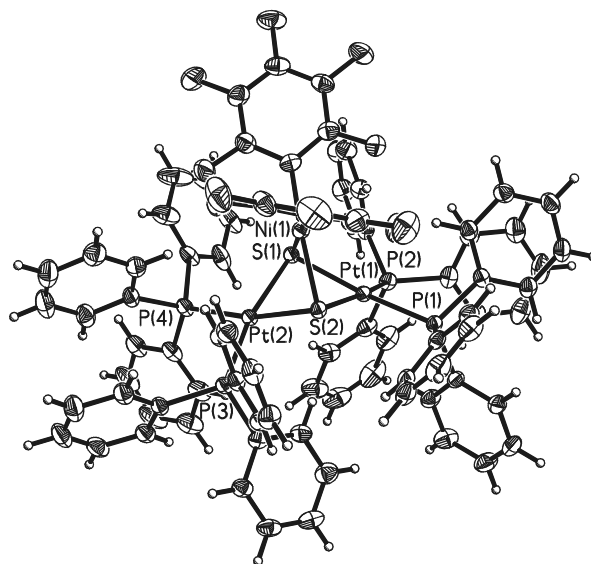


Fig. 2. ORTEP diagram of 4. Thermal ellipsoids are at 50% probability.

Table 2  
Selected bond lengths (Å) and angles (°) for complex 4

Bond lengths		Bond angles	
Pt(1)–P(1)	2.2836(9)	P(1)–Pt(1)–P(2)	98.51(4)
Pt(1)–P(2)	2.2941(10)	P(1)–Pt(1)–S(2)	93.53(3)
Pt(1)–S(2)	2.3406(9)	P(2)–Pt(1)–S(2)	166.42(3)
Pt(1)–S(1)	2.3501(9)	P(1)–Pt(1)–S(1)	167.06(4)
Pt(2)–P(4)	2.2747(10)	P(2)–Pt(1)–S(1)	91.51(3)
Pt(2)–P(3)	2.2808(10)	S(2)–Pt(1)–S(1)	77.56(3)
Pt(2)–S(2)	2.3470(9)	P(4)–Pt(2)–P(3)	99.00(4)
Pt(2)–S(1)	2.3380(9)	P(4)–Pt(2)–S(1)	93.84(3)
Ni(1)–C(301)	1.912(4)	P(3)–Pt(2)–S(1)	166.84(3)
Ni(1)–C(13)	1.914(4)	P(4)–Pt(2)–S(2)	167.53(4)
Ni(1)–S(2)	2.2239(10)	P(3)–Pt(2)–S(2)	90.09(3)
Ni(1)–S(1)	2.2316(11)	S(1)–Pt(2)–S(2)	77.68(3)
		C(301)–Ni(1)–C(13)	93.57(17)
		C(301)–Ni(1)–S(2)	90.95(12)
		C(13)–Ni(1)–S(2)	173.78(13)
		C(301)–Ni(1)–S(1)	172.17(12)
		C(13)–Ni(1)–S(1)	93.29(13)
		S(2)–Ni(1)–S(1)	82.51(4)

are similar values to those found in the trinuclear complex  $[\text{Ni}_3(\text{dippe})_2(\mu_3\text{-S})_2(2,2'\text{-biphenyl})]$  (dippe = 1,2-bis(diisopropylphosphino)ethane) [20]. The S···S intramolecular distance (2.938 Å) is similar to that found in  $[\text{Ni}_3(\text{dippe})_2(\mu_3\text{-S})_2(2,2'\text{-biphenyl})]$  (2.928 Å) but smaller than that found in complex 2. The S–Ni–S angle is rather acute ( $82.51^\circ$ ). The nickel–platinum separations are 2.957 and 2.979 Å (Table 5). The molecule shows a hinged  $\{\text{Pt}_2\text{S}_2\}$  central ring with a dihedral angle  $\theta = 128.27^\circ$ , a similar value to that found in complex 2. The nickel atom also exhibits an approximately square-planar geometry. The Ni–C<sub>6</sub>F<sub>5</sub> distances (1.912(4) and 1.914(4) Å) are in the range found in the literature [8].

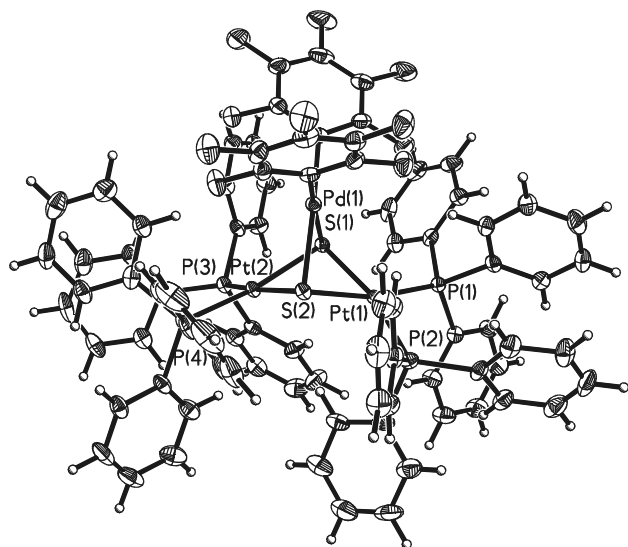


Fig. 3. ORTEP diagram of **5**. Thermal ellipsoids are at 50% probability.

Table 3  
Selected bond lengths (Å) and angles (°) for complex **5**

Bond lengths		Bond angles	
Pd(1)–C(11)	2.034(4)	C(11)–Pd(1)–C(1)	94.22(17)
Pd(1)–C(1)	2.039(4)	C(11)–Pd(1)–S(1)	172.73(12)
Pd(1)–S(1)	2.3548(11)	C(1)–Pd(1)–S(1)	92.20(13)
Pd(1)–S(2)	2.3651(11)	C(11)–Pd(1)–S(2)	95.34(12)
Pt(1)–P(1)	2.2796(11)	C(1)–Pd(1)–S(2)	169.96(12)
Pt(1)–P(2)	2.2901(11)	S(1)–Pd(1)–S(2)	78.45(4)
Pt(1)–S(1)	2.3443(10)	P(1)–Pt(1)–P(2)	98.66(4)
Pt(1)–S(2)	2.3546(11)	P(1)–Pt(1)–S(1)	93.29(4)
Pt(2)–P(4)	2.2716(11)	P(2)–Pt(1)–S(1)	166.35(4)
Pt(2)–P(3)	2.2789(11)	P(1)–Pt(1)–S(2)	167.58(4)
Pt(2)–S(2)	2.3412(10)	P(2)–Pt(1)–S(2)	90.37(4)
Pt(2)–S(1)	2.3535(10)	S(1)–Pt(1)–S(2)	78.87(4)
		P(4)–Pt(2)–P(3)	99.37(4)
		P(4)–Pt(2)–S(2)	93.41(4)
		P(3)–Pt(2)–S(2)	166.83(4)
		P(4)–Pt(2)–S(1)	167.39(4)
		P(3)–Pt(2)–S(1)	89.01(4)
		S(2)–Pt(2)–S(1)	78.95(4)

The molecular structure of **5** is shown in Fig. 3. The main geometrical results for **5** are essentially the same as those of **4**. The Pd–S lengths are 2.3651(11) and 2.3548(11) Å (Table 3). The palladium–platinum separations are 3.053 and 3.081 Å (Table 5). The molecule shows a hinged {Pt<sub>2</sub>S<sub>2</sub>} central ring with a very small dihedral angle ( $\theta = 103.48^\circ$ ). The palladium atom also exhibits an approximately square-planar geometry. The Pd–C<sub>6</sub>F<sub>5</sub> distances (2.034(4) and 2.039(4) Å) are in the range found in the literature [18].

Fig. 4 shows the X-ray structure of complex **9**, with selected bond lengths and angles listed in Table 4. The molecule is an aggregate with a {Pt<sub>3</sub>S<sub>2</sub>} trigonal bipyramidal molecular core. The dithio ligand is asymmetrically co-ordinated to the Pt(1) with a short Pt(1)–S(2)

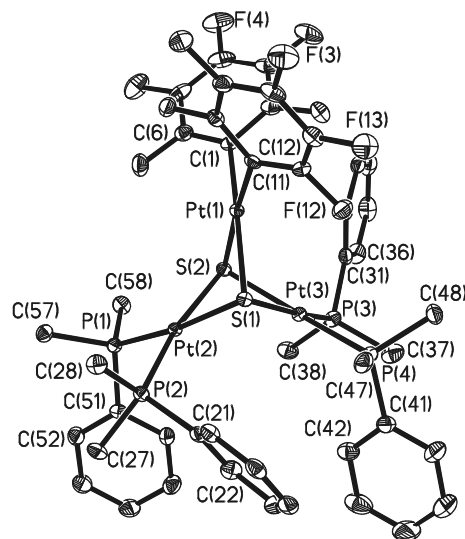


Fig. 4. ORTEP diagram of **9**. Thermal ellipsoids are at 50% probability.

Table 4  
Selected bond lengths (Å) and angles (°) for complex **9**

Bond lengths		Bond angles	
Pt(1)–C(1)	2.029(3)	C(1)–Pt(1)–C(11)	91.51(12)
Pt(1)–C(11)	2.031(3)	C(1)–Pt(1)–S(2)	93.49(9)
Pt(1)–S(2)	2.3526(8)	C(11)–Pt(1)–S(2)	174.60(9)
Pt(1)–S(1)	2.3676(8)	C(1)–Pt(1)–S(1)	172.69(9)
Pt(2)–P(1)	2.2555(8)	C(11)–Pt(1)–S(1)	95.76(9)
Pt(2)–P(2)	2.2672(8)	S(2)–Pt(1)–S(1)	79.22(3)
Pt(2)–S(2)	2.3559(7)	P(1)–Pt(2)–P(2)	96.86(3)
Pt(2)–S(1)	2.3642(8)	P(1)–Pt(2)–S(2)	93.44(3)
Pt(3)–P(4)	2.2521(9)	P(2)–Pt(2)–S(2)	168.65(3)
Pt(3)–P(3)	2.2585(8)	P(1)–Pt(2)–S(1)	171.82(3)
Pt(3)–S(1)	2.3673(7)	P(2)–Pt(2)–S(1)	90.77(3)
Pt(3)–S(2)	2.3731(8)	S(2)–Pt(2)–S(1)	79.22(3)
		P(4)–Pt(3)–P(3)	98.72(3)
		P(4)–Pt(3)–S(1)	93.47(3)
		P(3)–Pt(3)–S(1)	167.81(3)
		P(4)–Pt(3)–S(2)	171.94(3)
		P(3)–Pt(3)–S(2)	89.00(3)
		S(1)–Pt(3)–S(2)	78.81(3)

bond (2.3526(8) Å) accompanied by a longer Pt(1)–S(1) bond (2.3676(8) Å). These values are lower than the platinum–sulfur length found in [Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PPh<sub>3</sub>)–{S(AuPPh<sub>3</sub>)<sub>2</sub>}] (2.371(3) Å) [21]. The intermetallic bond distances lie in the range 3.078–3.282 Å (Table 5), the Pt(2)···Pt(3) distance (3.0941(2) Å) being a bit shorter than that observed in the parent compound [Pt<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>(μ-S)<sub>2</sub>] (3.17 Å) [22]. The molecule shows a hinged {Pt<sub>2</sub>S<sub>2</sub>} central ring with a dihedral angle  $\theta = 115.95^\circ$ , smaller than that found in the unbound metalloligand [Pt<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>(μ-S)<sub>2</sub>] (121°) [4]. Each platinum atom has square-planar coordination, distorted by a reduction of S–Pt–S and P–Pt–P angles from ideal 90°, and by twist of 6.2° between the Pt(2)S<sub>2</sub> and Pt(2)P<sub>2</sub> planes and of 2.4° between the Pt(3)S<sub>2</sub> and Pt(3)P<sub>2</sub> planes.

Table 5

Structural parameters (distances in Å, angles in °) describing the M{Pt<sub>2</sub>S<sub>2</sub>} core in complexes **2**, **4**, **5** and **9**

Complex	Pt···Pt	S···S	θ <sup>a</sup>	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> M···Pt
[{Pt <sub>2</sub> (dppf)(μ <sub>3</sub> -S) <sub>2</sub> }Pd(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ] ( <b>2</b> )	3.284	2.983	129.78	3.087; 3.073
[{Pt <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (μ <sub>3</sub> -S) <sub>2</sub> }Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ] ( <b>4</b> )	3.287	2.938	128.27	2.957; 2.979
[{Pt <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (μ <sub>3</sub> -S) <sub>2</sub> }Pd(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ] ( <b>5</b> )	3.293	2.985	103.48	3.053; 3.081
[{Pt <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> (μ <sub>3</sub> -S) <sub>2</sub> }Pt(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ] ( <b>9</b> )	3.094	3.009	115.95	3.078; 3.283

<sup>a</sup> Dihedral angle between two {Pt<sub>2</sub>S<sub>2</sub>} planes.

### 3. Experimental

#### 3.1. General information

C, H, and N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5°C min<sup>-1</sup> and the solid samples under nitrogen flow (100 ml min<sup>-1</sup>). Molar conductivities were measured in acetone solution ( $c \approx 5 \times 10^{-4}$  mol l<sup>-1</sup>) with a Crison 525 conductimeter. The <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using SiMe<sub>4</sub>, CFCl<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> as the standards, respectively. In the <sup>1</sup>H NMR spectra of the ionic compounds, the signals of the NBu<sub>4</sub><sup>+</sup> cation have been omitted. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Mass spectra were recorded on a Fisons V.G. Autospec spectrometer using the standard Cs<sup>+</sup> ion FAB (acceleration voltage 35 kV) and nitrobenzyl alcohol as matrix. The starting complexes [M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PhCN)<sub>2</sub>] (M = Ni [8], Pd [9]), [Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] [10], [(dppf)Pt(μ-S)<sub>2</sub>Pt(dppf)] [23] and [(PR<sub>3</sub>)<sub>2</sub>-Pt(μ-S)<sub>2</sub>Pt(PR<sub>3</sub>)<sub>2</sub>] (R<sub>3</sub> = Ph<sub>3</sub> [24], Me<sub>2</sub>Ph [25]) were prepared by procedures described elsewhere. Solvents were dried by the usual methods.

#### 3.2. Preparation of [Pt<sub>2</sub>(μ<sub>3</sub>-S)<sub>2</sub>(dppf)<sub>2</sub>]M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] [M = Ni (**1**), Pd (**2**) and Pt (**3**)]

To a suspension of [Pt<sub>2</sub>(dppf)(μ-S)<sub>2</sub>] (0.1 g, 0.064 mmol) in THF (20 cm<sup>3</sup>) was added M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(NCPH)<sub>2</sub> (M = Ni or Pd) or Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub> (0.064 mmol). The resulting solution was stirred for 5 h. Solvent was evaporated to dryness and the residue was treated with methanol to give a precipitate which was filtered off and air-dried. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-toluene-hexane to give orange crystals.

##### 3.2.1. [Pt<sub>2</sub>(μ<sub>3</sub>-S)<sub>2</sub>(dppf)<sub>2</sub>]Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (**1**)

Yield 65 mg, 52%. Anal. Found: C, 49.4; H, 2.9; S, 3.1. Calc. for C<sub>80</sub>H<sub>56</sub>F<sub>10</sub>Fe<sub>2</sub>NiP<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>: C, 49.1; H, 2.9; S, 3.3%; m.p.: 319 dec. IR (Nujol, cm<sup>-1</sup>): 768 (Ni-C<sub>6</sub>F<sub>5</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.90–6.80 (m, 40H, Ph), 4.76 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 4.44 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 4.17 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 3.87

(s, 4H, C<sub>5</sub>H<sub>4</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -112.9 (d, 4F<sub>o</sub>, J<sub>om</sub> = 30.1 Hz), -166.8 (t, 2F<sub>p</sub>, J<sub>mp</sub> = 20.7), -167.8 (m, 4F<sub>m</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 17.5 (s, J<sub>PtP</sub> = 3224 Hz). Positive-ion FAB mass spectrum: m/z 1622 (M-2C<sub>6</sub>F<sub>5</sub>+1)<sup>+</sup>.

##### 3.2.2. [Pt<sub>2</sub>(μ<sub>3</sub>-S)<sub>2</sub>(dppf)<sub>2</sub>]Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (**2**)

Yield 71 mg, 55%. Anal. Found: C, 48.2; H, 3.1; S, 3.1. Calc. for C<sub>80</sub>H<sub>56</sub>F<sub>10</sub>Fe<sub>2</sub>P<sub>4</sub>PdPt<sub>2</sub>S<sub>2</sub>: C, 48.0; H, 2.8; S, 3.2%; m.p.: 314 dec. IR (Nujol, cm<sup>-1</sup>): 774, 768 (Pd-C<sub>6</sub>F<sub>5</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.94–6.85 (m, 40H, Ph), 4.64 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 4.44 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 4.19 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 3.91 (s, 4H, C<sub>5</sub>H<sub>4</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -111.6 (d, 4F<sub>o</sub>, J<sub>om</sub> = 32.2 Hz), -166.1 (t, 2F<sub>p</sub>, J<sub>mp</sub> = 19.6), -166.9 (m, 4F<sub>m</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 17.4 (s, J<sub>PtP</sub> = 3157 Hz). Positive-ion FAB mass spectrum: m/z 1836 (M-C<sub>6</sub>F<sub>5</sub>)<sup>+</sup>, 1669 (M-2 C<sub>6</sub>F<sub>5</sub>)<sup>+</sup>.

##### 3.2.3. [Pt<sub>2</sub>(μ<sub>3</sub>-S)<sub>2</sub>(dppf)<sub>2</sub>]Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (**3**)

Yield 94 mg, 70%. Anal. Found: C, 45.9; H, 3.0; S, 2.9. Calc. for C<sub>80</sub>H<sub>56</sub>F<sub>10</sub>Fe<sub>2</sub>P<sub>4</sub>Pt<sub>3</sub>S<sub>2</sub>: C, 45.9; H, 2.7; S, 3.1%; m.p.: 309 dec. IR (Nujol, cm<sup>-1</sup>): 792, 780 (Pt-C<sub>6</sub>F<sub>5</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.92–6.86 (m, 40H, Ph), 4.62 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 4.42 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 4.20 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 3.92 (s, 4H, C<sub>5</sub>H<sub>4</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -115.5 (d, 4F<sub>o</sub>, J<sub>om</sub> = 31.0 Hz, J<sub>PtF<sub>o</sub></sub> = 479.8 Hz), -166.3 (t, 2F<sub>p</sub>, J<sub>mp</sub> = 20.6), -168.1 (m, 4F<sub>m</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 12.8 (s, J<sub>PtP</sub> = 3207 Hz). Positive-ion FAB mass spectrum: m/z 2092 (M)<sup>+</sup>.

#### 3.3. Preparation of complexes [Pt<sub>2</sub>(μ<sub>3</sub>-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>]M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] [M = Ni (**4**), Pd (**5**) and Pt (**6**)]

To a solution of [Pt<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>(μ-S)<sub>2</sub>] (0.1 g, 0.067 mmol) in CHCl<sub>3</sub> (20 cm<sup>3</sup>) was added M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(NCPH)<sub>2</sub> (M = Ni or Pd) or Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub> (0.067 mmol). The mixture was stirred for 30 min and then filtered through celite. Solvent was partially evaporated under reduced pressure and a solid was collected by filtration and air-dried. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-toluene-hexane to give yellow or orange crystals.

##### 3.3.1. [Pt<sub>2</sub>(μ<sub>3</sub>-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>]Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (**4**)

Yield 80 mg, 63%. Anal. Found: C, 52.9; H, 3.1; S, 3.2. Calc. for C<sub>84</sub>H<sub>60</sub>F<sub>10</sub>NiP<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>: C, 53.2; H, 3.2; S, 3.4%; m.p.: 317 dec. IR (Nujol, cm<sup>-1</sup>): 788 (Ni-C<sub>6</sub>F<sub>5</sub>).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.42 (m, 24H, Ph), 7.09 (t, 12H<sub>p</sub>, Ph,  $J_{pm} = 7.2$  Hz), 6.94 (m, 24H, Ph).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -112.6 (d, 4F<sub>o</sub>,  $J_{om} = 32.2$  Hz), -167.0 (t, 2F<sub>p</sub>,  $J_{mp} = 20.6$ ), -167.8 (m, 4F<sub>m</sub>).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  17.5 (s,  $J_{\text{PtP}} = 3145$  Hz). Positive-ion FAB mass spectrum:  $m/z$  1918 ((M + Na)<sup>+</sup>).

### 3.3.2. [ $\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PPh}_3)_4\}\text{Pd}(\text{C}_6\text{F}_5)_2$ ] (5)

Yield 91 mg, 70%. Anal. Found: C, 51.6; H, 3.2; S, 3.3. Calc. for C<sub>84</sub>H<sub>60</sub>F<sub>10</sub>PdP<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>: C, 51.9; H, 3.1; S, 3.3%; m.p.: 312 dec. IR (Nujol, cm<sup>-1</sup>): 788 (Pd–C<sub>6</sub>F<sub>5</sub>).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.40 (m, 24H, Ph), 7.09 (t, 12H<sub>p</sub>, Ph,  $J_{pm} = 7.2$  Hz), 6.94 (m, 24H, Ph).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -111.3 (d, 4F<sub>o</sub>,  $J_{om} = 33.8$  Hz), -166.1 (t, 2F<sub>p</sub>,  $J_{mp} = 21.2$ ), -166.8 (m, 4F<sub>m</sub>).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  18.4 (s,  $J_{\text{PtP}} = 3082$  Hz). Positive-ion FAB mass spectrum:  $m/z$  1776 (M – C<sub>6</sub>F<sub>5</sub>)<sup>+</sup>.

### 3.3.3. [ $\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PPh}_3)_4\}\text{Pd}(\text{C}_6\text{F}_5)_2$ ] (6)

Yield 101 mg, 74%. Anal. Found: C, 49.3; H, 3.1; S, 3.0. Calc. for C<sub>84</sub>H<sub>60</sub>F<sub>10</sub>P<sub>4</sub>Pt<sub>3</sub>S<sub>2</sub>: C, 49.6; H, 3.0; S, 3.2%; m.p.: 319 dec. IR (Nujol, cm<sup>-1</sup>): 792, 782 (Pt–C<sub>6</sub>F<sub>5</sub>).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.41 (m, 24H, Ph), 7.10 (t, 12H<sub>p</sub>, Ph,  $J_{pm} = 7.5$  Hz), 6.94 (m, 24H, Ph).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -115.2 (d, 4F<sub>o</sub>,  $J_{om} = 32.2$  Hz,  $J_{\text{PtFo}} = 460.0$  Hz), -168.1 (m, 2F<sub>p</sub> + 4F<sub>m</sub>).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  13.8 (s,  $J_{\text{PtP}} = 3134$  Hz). Positive-ion FAB mass spectrum:  $m/z$  2036 (M + 4)<sup>+</sup>.

## 3.4. Preparation of complexes [ $\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PMe}_2\text{Ph})_4\}\text{M}(\text{C}_6\text{F}_5)_2$ ] [M = Ni (7), Pd (8) and Pt (9)]

To a solution of [Pt<sub>2</sub>(PPhMe<sub>2</sub>)<sub>4</sub>(μ-S)<sub>2</sub>] (0.1 g, 0.099 mmol) in THF (20 cm<sup>3</sup>) was added M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(NCPH)<sub>2</sub> (M = Ni or Pd) or Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub> (0.099 mmol). The resulting solution was stirred for 1 h. Solvent was evaporated to dryness and the residue was treated with Et<sub>2</sub>O to give a precipitate which was filtered off and air-dried. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–toluene–hexane to give yellow or orange crystals.

### 3.4.1. [ $\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PMe}_2\text{Ph})_4\}\text{Ni}(\text{C}_6\text{F}_5)_2$ ] (7)

Yield 100 mg, 72%. Anal. Found: C, 37.7; H, 3.2; S, 4.5. Calc. for C<sub>44</sub>H<sub>44</sub>F<sub>10</sub>NiP<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>: C, 37.8; H, 3.2; S, 4.6%; m.p.: 316 dec. IR (Nujol, cm<sup>-1</sup>): 768 (Ni–C<sub>6</sub>F<sub>5</sub>).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.65 (m, 8H, Ph), 7.31 (m, 12H, Ph), 1.60 (m, 24H, Me).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -115.5 (d, 4F<sub>o</sub>,  $J_{om} = 33.9$  Hz), -166.1 (t, 2F<sub>p</sub>,  $J_{mp} = 18.8$ ), -166.9 (m, 4F<sub>m</sub>).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -15.7 (s,  $J_{\text{PtP}} = 3146$  Hz). Positive-ion FAB mass spectrum:  $m/z$  1230 (M – C<sub>6</sub>F<sub>5</sub> – 2)<sup>+</sup>, 1065 (M – 2C<sub>6</sub>F<sub>5</sub> + 1)<sup>+</sup>.

### 3.4.2. [ $\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PMe}_2\text{Ph})_4\}\text{Pd}(\text{C}_6\text{F}_5)_2$ ] (8)

Yield 106 mg, 74%. Anal. Found: C, 36.3; H, 3.3; S, 4.2. Calc. for C<sub>44</sub>H<sub>44</sub>F<sub>10</sub>PdP<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>: C, 36.5; H, 3.1; S, 4.4%; m.p.: 280 dec. IR (Nujol, cm<sup>-1</sup>): 778, 768 (Pd–

C<sub>6</sub>F<sub>5</sub>).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.62 (m, 8H, Ph), 7.32 (m, 12H, Ph), 1.61 (m, 24H, Me).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -113.4 (d, 4F<sub>o</sub>,  $J_{om} = 29.9$  Hz), -165.3 (t, 2F<sub>p</sub>,  $J_{mp} = 20.6$ ), -165.8 (m, 4F<sub>m</sub>).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -15.7 (s,  $J_{\text{PtP}} = 3070$  Hz). Positive-ion FAB mass spectrum:  $m/z$  1279 (M – C<sub>6</sub>F<sub>5</sub>)<sup>+</sup>.

### 3.4.3. [ $\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PMe}_2\text{Ph})_4\}\text{Pt}(\text{C}_6\text{F}_5)_2$ ] (9)

Yield 100 mg, 66%. Anal. Found: C, 34.2; H, 2.9; S, 3.9. Calc. for C<sub>44</sub>H<sub>44</sub>F<sub>10</sub>P<sub>4</sub>Pt<sub>3</sub>S<sub>2</sub>: C, 34.4; H, 2.9; S, 4.2%; m.p.: 285 dec. IR (Nujol, cm<sup>-1</sup>): 792, 782 (Pt–C<sub>6</sub>F<sub>5</sub>).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.69 (m, 8H, Ph), 7.34 (m, 12H, Ph), 1.60 (m, 24H, Me).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -117.3 (d, 4F<sub>o</sub>,  $J_{om} = 29.9$  Hz,  $J_{\text{PtFo}} = 483.7$  Hz), -167.2 (m, 2F<sub>p</sub> + 4F<sub>m</sub>).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -19.7 (s,  $J_{\text{PtP}} = 3132$  Hz). Positive-ion FAB mass spectrum:  $m/z$  1533 (M – 2)<sup>+</sup>.

## 3.5. X-ray structure determination

Single crystals of **2**, **4**, **5** and **9** suitable for diffraction studies were grown from dichloromethane–hexane–toluene, mounted on a glass fibre and transferred to the diffractometer. Data were collected using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). For compound **2** a Siemens P4 diffractometer was used ( $\omega$ -scans,  $2\theta_{\text{max}} 50^\circ$ , absorption correction by  $\psi$ -scans); for compounds **4**, **5** and **9**, a Bruker SMART APEX ( $\omega$ -scans,  $2\theta_{\text{max}} 56^\circ$ , absorption correction using multiple scans). Structures were refined anisotropically on  $F^2$  using the program SHELXL-97 [26]. Hydrogen atoms were included using a riding model. Disordered groups were refined using appropriate systems of similarity restraints. Other details of data collection and refinement are given in Table 6.

### 3.5.1. Special features of refinement

**Complex 2:** The poor crystal quality is reflected in the lack of precision; the solvent is disordered, one toluene is disordered over an inversion center and the other is resolved badly, corresponding methyl hydrogens were not located.

**Complex 4:** The structure contains three ill-defined solvent residues. One toluene and one dichloromethane disordered over two positions with occupations ca. 63:37%, and the other region were tentatively identified as a hexane associated with an inversion center. No hexane hydrogens were included in the refinement. The largest residual electron density was near the disordered dichloromethane.

**Complex 5:** The structure contains two ill-defined regions of residual electron density. One of them was identified as toluene disordered over two positions with occupations ca. 54:46%, whereas the other region was tentatively identified as hexane and resolved badly. No hexane hydrogens were included in the refinement.

Table 6

Crystal structure determination details

Compound	2 · CH <sub>2</sub> Cl <sub>2</sub> · 1.5PhMe	4 · CH <sub>2</sub> Cl <sub>2</sub> · PhMe · 0.5C <sub>6</sub> H <sub>14</sub>	5 · PhMe · C <sub>6</sub> H <sub>14</sub>	9
Formula	C <sub>91.50</sub> H <sub>70</sub> Cl <sub>2</sub> F <sub>10</sub> Fe <sub>2</sub> P <sub>4</sub> PdPt <sub>2</sub> S <sub>2</sub>	C <sub>95</sub> H <sub>77</sub> Cl <sub>2</sub> F <sub>10</sub> NiP <sub>4</sub> Pt <sub>2</sub> S <sub>2</sub>	C <sub>97</sub> H <sub>82</sub> F <sub>10</sub> P <sub>4</sub> PdPt <sub>2</sub> S <sub>2</sub>	C <sub>44</sub> H <sub>44</sub> F <sub>10</sub> P <sub>4</sub> Pt <sub>3</sub> S <sub>2</sub>
Formula weight	2226.66	2116.36	2122.21	1536.06
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
<i>a</i> (Å)	13.5100(13)	13.1924(7)	13.2466(8)	11.9397(8)
<i>b</i> (Å)	13.8301(13)	13.3509(7)	13.4324(8)	24.6595(16)
<i>c</i> (Å)	23.8122(15)	24.5327(12)	24.5745(15)	16.4110(11)
$\alpha$ (°)	102.482(7)	89.163(1)	89.882(1)	90
$\beta$ (°)	91.774(8)	78.404(1)	78.510(1)	91.588(1)
$\gamma$ (°)	103.989(8)	82.695(1)	83.465(1)	90
Unit cell volume (Å <sup>3</sup> )	4198.9(6)	4198.1(4)	4256.2(4)	4830.0(6)
<i>T</i> (K)	233(2)	100(2)	100(2)	100(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	2	2	2	4
$\mu$ (mm <sup>-1</sup> )	4.125	3.799	3.738	8.957
Reflections collected	17 524	45 946	45 957	28 555
Independent reflections	14 619	17 027	16 695	9863
<i>R</i> <sub>int</sub>	0.0323	0.0221	0.0260	0.0202
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0351	0.0315	0.0344	0.0191
<i>wR</i> <sub>2</sub> (all data)	0.0754	0.0805	0.0786	0.0429

#### 4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-221934 (2), CCDC-221935 (4), CCDC-221936 (5) and CCDC-221937 (9). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)].

#### Acknowledgements

This work was supported by the Dirección General de Investigación del Ministerio de Ciencia y Tecnología (Project No. BQU2001-0979-C02-01), Spain, and the Fundación Séneca de la Comunidad Autónoma de la Región de Murcia (Project No. PI-72-00773-FS-01).

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