Synthesis and Characterisation of Homo- and Hetero-trinuclear Complexes containing the Triply-bridging Diphenylthiophosphinito $[\mu_3\text{-SPPh}_2]^-$ Ligand: Molecular Structure of $[Pd_3(\mu_3\text{-SPPh}_2)_2(C_6F_5)_2(C_6H_4CH_2NMe_2\text{-}2)(PPh_3)_2]ClO_4\cdot0.8CH_2Cl_2$†

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The dinuclear complex $[\{Pd(\mu\text{-SPPh}_2)(C_6F_5)(PPh_3)\}_2]$ reacted with the cationic precursors $[PdL(Me_2CO)_2]^+$ [L = 2-(dimethylaminomethyl)phenyl-*C*¹,*N*, quinolin-8-ylmethyl-*C*,*N* or phenylazophenyl-*C*¹,*N*] and with the neutral precursors $[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt, thf = tetrahydrofuran) to give the corresponding cationic homotrinuclear complexes $[Pd_3(\mu_3\text{-SPPh}_2)_2(C_6F_5)_2L(PPh_3)_2]ClO_4$ (L = $C_6H_4CH_2NMe_2$-2 **1**, $NC_9H_6CH_2$-8 **2** or $PhN{=}NC_6H_4$ **3**) and the neutral homo- and hetero-trinuclear complexes $[Pd_2M(\mu_3\text{-SPPh}_2)_2(C_6F_5)_4(PPh_3)_2]$ (M = Pd **4** or Pt **5**) in which the $[SPPh_2]^-$ group acts as a triply-bridging ligand. Complexes **1**–**5** have been characterized by spectroscopic methods (IR; ^{1}H, ^{19}F and ^{31}P-{^{1}H} NMR) and the molecular structure of $[Pd_3(\mu_3\text{-SPPh}_2)_2(C_6F_5)_2(C_6H_4CH_2NMe_2\text{-}2)(PPh_3)_2]ClO_4$ **1** has been determined crystallographically. Complex **1**·$0.8CH_2Cl_2$ crystallizes in the monoclinic system, space group $P2_1/c$, a = 14.185(3), b = 21.589(4), c = 27.440(5) Å, β = 104.95(3)° and Z = 4. The model refined to final values of R = 0.0702 and R' = 0.0849 for 5989 observed reflections [$F > 4.0\sigma(F)$] and 860 parameters. The structure shows that the $[Pd(\mu\text{-SPPh}_2)(C_6F_5)(PPh_3)]_2$ unit behaves as a cyclic bidentate sulfur ligand, co-ordinated to the $[Pd(C_6H_4CH_2NMe_2\text{-}2)]^+$ group through the two S atoms. The central $Pd_3(SPPh_2)_2$ cage contains two μ_3-$SPPh_2$ ligands linking the three palladium atoms.

Several co-ordination modes are known for the anionic ligand diphenylthiophosphinito $[SPPh_2]^-$ as is represented in Fig. 1: (*a*) P-monodentate,[1] (*b*) S-monodentate,[1a,2] (*c*) P,S-chelate[1a,3c,4] and (*d*) di-μ-P,S-bridging,[1a,3] the last representing the most numerous group, probably due to the stability of the six-membered ring thereby generated.[1a]

Recently we have reported the synthesis and structural characterization of M^{II} complexes (M = Pd or Pt) containing the anionic group $[SPPh_2]^-$ (diphenylthiophosphinito) acting as a di-μ-P,S-bridging ligand[5] with the $M_2(\mu\text{-SPPh}_2)_2$ core adopting a boat conformation. In these complexes, which contain two μ-$SPPh_2$ bridges, the sulfur atoms still have free electron pairs and can behave as donor atoms towards electrophilic metal substrates. We report in this paper the synthesis and characterization of the cationic homotrinuclear complexes $[Pd_3(\mu\text{-SPPh}_2)_2(C_6F_5)_2L(PPh_3)_2]ClO_4$ [L = 2-(dimethylaminomethyl)phenyl-*C*¹,*N*, quinolin-8-ylmethyl-*C*,*N* or phenylazophenyl-*C*¹,*N*] and the neutral homo- and hetero-trinuclear complexes $[Pd_2M(\mu\text{-SPPh}_2)_2(C_6F_5)_4(PPh_3)_2]$ (M = Pd or Pt), obtained by reaction of $[\{Pd(\mu\text{-SPPh}_2)(C_6F_5)(PPh_3)\}_2]$ with the cationic $[PdL(Me_2CO)_2]^+$ or the neutral $[M(C_6F_5)_2(thf)_2]$ (thf = tetrahydrofuran) substrates. These trinuclear derivatives are, as far as we know, the only reported complexes which contain the $[SPPh_2]^-$ ligand bridging three metal centres (μ_3-co-ordination).

Results and Discussion

$[Pd_3(\mu_3\text{-SPPh}_2)_2(C_6F_5)_2L(PPh_3)_2]ClO_4$.—The dinuclear complex $[\{Pd(\mu\text{-SPPh}_2)(C_6F_5)(PPh_3)\}_2]$ reacts, in refluxing acetone, with the solvated precursors $[PdL(Me_2CO)_2]ClO_4$ (1 : 1 molar ratio) giving the corresponding cationic trinuclear derivatives $[Pd_3(\mu_3\text{-SPPh}_2)_2(C_6F_5)_2L(PPh_3)_2]ClO_4$ in good yield. The solvated complexes $[PdL(Me_2CO)_2]ClO_4$ were obtained by treatment of the chloride bridged complexes $[\{Pd(\mu\text{-Cl})L\}_2]$ with $AgClO_4$ (molar ratio 1 : 2) in acetone and were used as acetone solutions without isolation of the solid product. The general process is shown in equation (1).

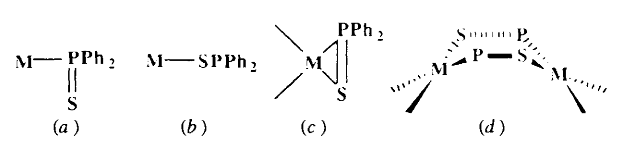
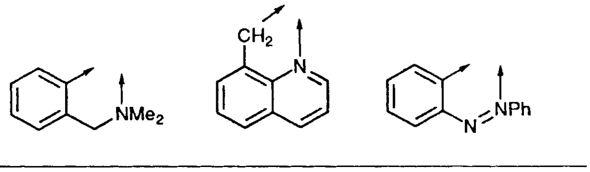


Fig. 1 Different co-ordination modes of the ligand $[SPPh_2]^-$

$$[\{Pd(\mu\text{-SPPh}_2)(C_6F_5)(PPh_3)\}_2] + [PdL(Me_2CO)_2]ClO_4 \longrightarrow [Pd_3(\mu_3\text{-SPPh}_2)_2(C_6F_5)_2L(PPh_3)_2]ClO_4 \quad (1)$$

L
1 $C_6H_4CH_2NMe_2$-2
2 $NC_9H_6CH_2$-8
3 $PhN{=}NC_6H_4$



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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Complexes **1**–**3** gave satisfactory elemental analysis and behave as 1 : 1 electrolytes in acetone solutions[6] (see Experimental section). Their mass spectra (positive FAB) indicate their trinuclear nature by the observation of a weak peak (10–15%) corresponding to the molecular peak of the cation: $[Pd_3(\mu_3\text{-}SPPh_2)_2(C_6F_5)_2L(PPh_3)_2]^+$ [*m/z* 1746 (**1**), 1754 (**2**) or 1793 (**3**)]. Their IR spectra (see Experimental section) show absorptions corresponding to the presence of co-ordinated C_6F_5 (ref. 7) and cyclometallated L groups,[8] and of the ClO_4^- anion.[9] It must be noted that the absorption due to $\nu_{P=S}$ (which in the starting material appears at 570 cm^{-1}) cannot be unambiguously assigned in these complexes since it appears at lower energies and in the same region (< 550 cm^{-1}) as internal absorptions of the phosphines. This fact is related with the S-co-ordination of the cationic $[PdL]^+$ fragment, which results in a decrease in the strength of the P–S bond. Finally, other absorptions due to the $[SPPh_2]^-$ and PPh_3 groups are overlapped, precluding an unambiguous assignment.

The $^{31}P\text{-}\{^1H\}$ NMR spectra of complexes **1**–**3** show a similar pattern of four doublet resonances (two AX systems) corresponding to the expected four chemically inequivalent phosphorus atoms of the molecule, as a result of the presence of the asymmetric $[PdL]^+$ group. For complex **1** each phosphorus atom of the $\mu_3\text{-}SPPh_2$ bridge is coupled to the phosphorus of the PPh_3 ligand of the other system; this coupling is not observed in **2** or **3**. The lowest field doublet [$\delta_{P^{A1}}$ 69.63 (**1**), 68.58 (**2**), 65.42 (**3**)] can be assigned to the P atom of the $[SPPh_2]^-$ bridge having the S atom *trans* to the carbon atom of the cyclometallated group (see Fig. 2), by comparison of these values with that found in complex **4** (δ 65.59), in which both S atoms of the $[SPPh_2]^-$ bridging ligand are *trans* to a carbon atom (C_6F_5) (see below and Experimental section). Due to the similar values of the coupling constant $^2J_{P^A\text{-}P^X}$, the accurate attribution of the different resonances was made by means of the two-dimensional ^{31}P–^{31}P correlation (COSY) spectra of these complexes (see Fig. 3).

The ^{19}F NMR spectrum of complexes **1**–**3** show four doublets (partially overlapped) in the *ortho*-F region, four complex resonances in the region of *meta*-F atoms and two triplets for the *para*-F atoms. This pattern of signals indicates that both pentafluorophenyl groups are chemically inequivalent and that both halves of each C_6F_5 ligand are inequivalent, as a consequence of the restricted rotation of the C_6F_5 group around the Pd–C_{ipso} bond (Fig. 2).

The ^1H NMR spectrum of complex **1** shows an AB system for the diastereotopic CH_2N protons and two singlets for the methyl groups of the NMe_2 group. In the low-field region, four resonances for the aromatic H atoms of $C_6H_4CH_2NMe_2\text{-}2$ are observed (two doublets and two triplets) together with complex multiplet resonances of the Ph groups. For complex **2**, an AB system is observed for the diastereotopic CH_2–Pd protons. For compound **3**, a complex set of resonances was observed in the low-field region, attributed to the aromatic protons of the C_6H_4N=NPh and Ph groups. Finally, upfield shifts of the signals due to H_o in **1** and **3** [$\delta(H_o)$ 5.85 **1**, 6.15 **3**], or to one of the methyl groups of the NMe_2 unit in **1** [δ(Me) 1.29] can be explained as a consequence of the anisotropic shielding[10] of adjacent Ph rings, probably those of the bridging $[SPPh_2]^-$ group. Fig. 4 illustrates the disposition of these Ph groups relative to the $C_6H_4CH_2NMe_2\text{-}2$ ligand.

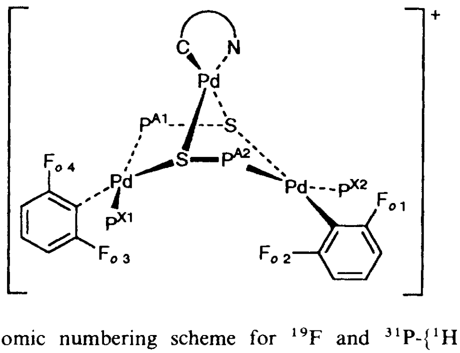

Fig. 2 Atomic numbering scheme for ^{19}F and $^{31}P\text{-}\{^1H\}$ NMR spectral assignment of the cationic complexes **1**, **2** and **3**

Crystal Structure of $[Pd_3(\mu_3\text{-}SPPh_2)_2(C_6F_5)_2(C_6H_4CH_2NMe_2\text{-}2\text{-}C^1,N)(PPh_3)_2]ClO_4\cdot 0.8CH_2Cl_2$.—Part of the cationic complex $[Pd_3(\mu\text{-}SPPh_2)_2(C_6F_5)_2(C_6H_4CH_2NMe_2\text{-}2)(PPh_3)_2]^+$ is disordered in the crystal structure. The following description of the disorder is best understood with reference to Fig. 5(*a*) and (*b*). The majority of the atoms of the cation, comprising the bulky fragment $Pd_2(PPh_2)_2(C_6F_5)_2(PPh_3)_2$, the lower part of the molecule in the figures, is not disordered. This fragment has local, non-rigorous two-fold symmetry. The upper portion of the cation, consisting of the less voluminous S atom of the $SPPh_2$ and $[Pd(C_6H_4CH_2NMe_2\text{-}2)]^+$ fragments, and which does not have two-fold symmetry, is disordered about the axis that serves as the local two-fold symmetry element of the bulkier bottom part of the cation. The two disordered congeners have occupancies of 0.65 [molecule A, Fig. 5(*a*)] and 0.35 [molecule B, Fig. 5(*b*)]. The connectivity of the cation is the same for the two cases; and it is easy to see that the two orientations of the cation in the crystal are equally favourable energetically, since it is the more expansive bottom

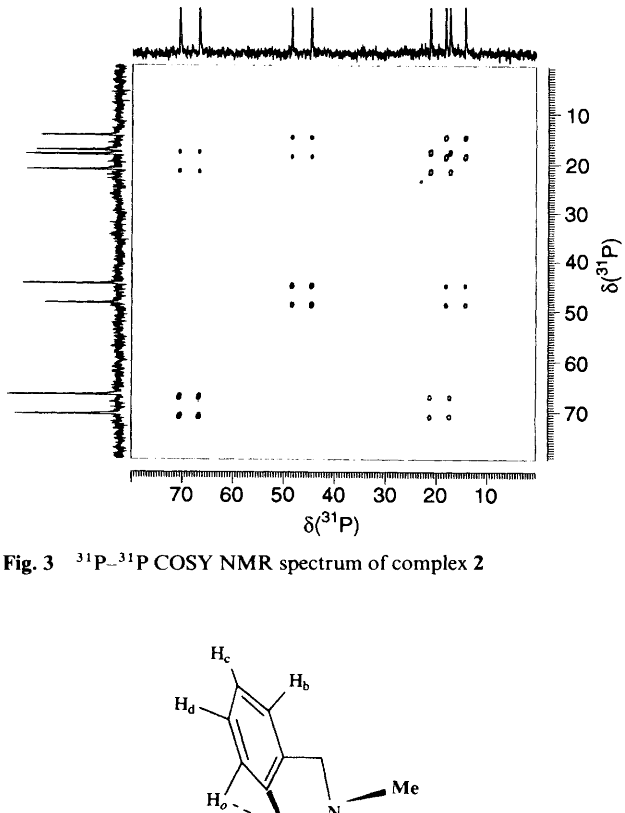

Fig. 3 ^{31}P–^{31}P COSY NMR spectrum of complex **2**

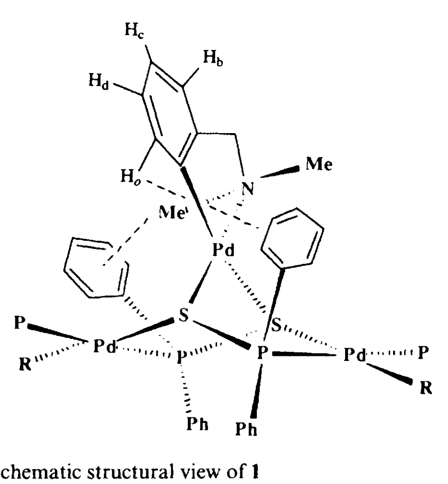

Fig. 4 Schematic structural view of **1**

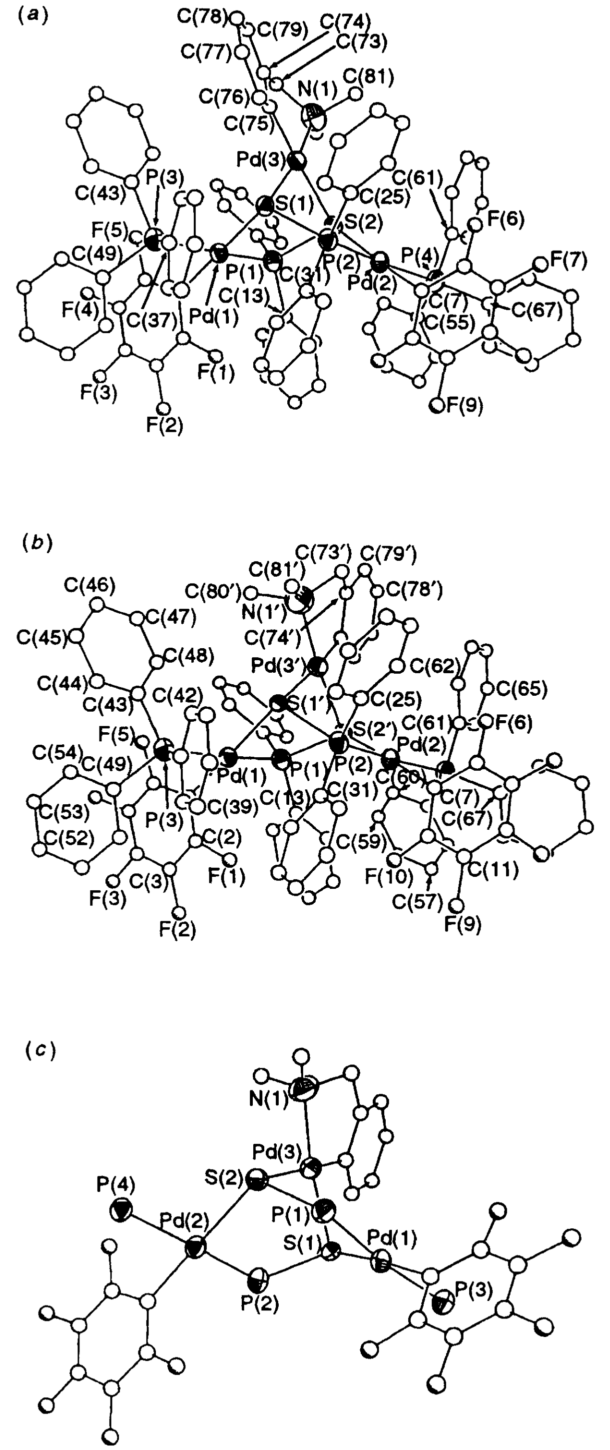

Fig. 5 Molecular structure of the complex **1**; molecule A (*a*), molecule B (*b*) and skeletal view (*c*)

half of this moiety that largely determines the crystal packing. Selected bond distances and angles are summarized in Table 1 and atomic coordinates are collected in Table 2.

The trinuclear cation contains three palladium atoms linked by two $[SPPh_2]^-$ bridging ligands. These $[SPPh_2]^-$ ligands are co-ordinated through the P and S atoms to two of the Pd centres [Pd(1) and Pd(2)], in a mutually *cis* head-to-tail arrangement, and through the S atoms to the third Pd centre [Pd(3)].

Each palladium atom is located in a slightly distorted square-planar environment: both Pd(1) and Pd(2) centres are surrounded by a PPh_3 and a C_6F_5 ligand (mutually *cis*), a phosphorus atom of one bridging $[SPPh_2]^-$ ligand and a sulfur atom of the other $[SPPh_2]^-$ group; the environment of the Pd(3) centre is formed by the two sulfur atoms of the two bridging $[SPPh_2]^-$ ligands and by the C,N-cyclometallated $C_6H_4CH_2NMe_2$-2 ligand. The skeleton Pd(1)S(1)P(2)Pd(2)-S(2)P(1), which in the starting material $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ displayed a boat conformation,[5] is now very distorted having lost this form [see Fig. 5(*c*)]. Moreover, the significant loss of planarity of the skeleton Pd(3)-C(75)C(74)C(73)N(1) of the $C_6H_4CH_2NMe_2$-2 ligand is remarkable.

The Pd(1, 2)–C(C_6F_5), Pd(1, 2)–P[PPh_3 or P(S)Ph_2] and Pd(1, 2)–S($SPPh_2$) bond distances (see Table 1) are similar to related values found in the literature,[11] as are the distances Pd(3)–C and Pd(3)–N to the cyclometallated ligand. Considering first molecule A, the Pd(3)–S($SPPh_2$) distances [2.305(10) and 2.500(12) Å] are rather different as a result of the different *trans*-influence of the nitrogen and carbon atoms of $C_6H_4CH_2NMe_2$-2, but are similar to those found in the related compound $[Pd_3(C_6H_4CH_2NMe_2)_3(pyt)_2]BF_4$[10] (pyt = pyridine-2-thione). A similar situation obtains in molecule B, for which the respective distances Pd(3')–S'($SPPh_2$) are 2.313(23) and 2.445(22) Å. The Pd(3)–C(75) and Pd(3)–N(1) (molecule A) distances are also slightly different from those found in molecule B [Pd(3')–C(75') and Pd(3')–N(1')] and so also the chelating angle N–Pd–C [C(75)–Pd(3)–N(1) 83.7(8), C(75')–Pd(3')–N(1') 77.3(15)°] although all these values are in the usual range found in other cyclometallated complexes.[8a,10b] We consider the differences found between molecules A and B to be insignificant from a chemical point of view. These distances are affected by correlation in the refinement, which is also reflected in the relatively high estimated standard deviations of parameters involved in the distorted groups.

The distances between the palladium centres [ranging from 3.578(3) to 4.671(2) Å] indicate that there are no metal–metal bonds. The mean of the value of the P–S distances in the bridging $[SPPh_2]^-$ group [2.115(28) Å] is slightly longer than that found in $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ [2.048(4) Å].[5]

The dihedral angle between the best least-square planes[12] defined by Pd(1)C(1)P(3)P(1)S(1) and Pd(2)C(7)P(4)P(2)S(2) is 62.1(3)° and the dihedral angles between each one of these planes and the best least-squares plane defined by Pd(3)S(1)S(2)N(1)C(75) [and Pd(3')S(1')S(2')N(1')C(75')] are 115.5(3) [118.3(4)] and 53.2(3) [56.3(5)°], respectively. On the other hand, the torsion angles[12] defined by Pd(1)–S(1)–P(2)–Pd(2) and Pd(1)–P(1)–S(2)–Pd(2) are 63.24 and 73.67° respectively, showing the high degree of distortion undergone by the central core of the molecule after co-ordination of the $[Pd(C_6H_4CH_2NMe_2\text{-}2)]^+$ fragment. The corresponding values for molecule B are Pd(1)–P(1)–S(2')–Pd(2) 56.75° and Pd(1)–S(1')–P(2)–Pd(2) 80.82°.

Finally, in the NMR discussion of complex **1**, we have remarked on the upfield shielding of both the *ortho*-H and one of the methyl groups of the NMe_2 unit of $C_6H_4CH_2NMe_2$-2, probably induced by the phenyl groups of the $[SPPh_2]^-$ bridging ligands. The calculated distance[12] between the H atom bonded to C(76) (*ortho*-H, in calculated position) and the centre of the phenyl ring C(25)–C(30) is 3.089 Å and the angle between the line C(76)–H(76) and the perpendicular to this ring is 57.47°. Moreover, the shortest distance between the H atoms bonded to C(80) (methyl group, in calculated positions) and the centre of the phenyl ring C(19)–C(24) is 2.770 Å. In this case, the angle between the line C(80)–H(80) and the perpendicular to this ring is 35.22°. The values of this set of parameters are in the appropriate range to propose anisotropic shielding, consistent with observations of Deeming *et al.*[10]

$[Pd_2M(\mu_3\text{-}SPPh_2)_2(C_6F_5)_4(PPh_3)_2]$ (M = Pd *or* Pt).— As expected, the dinuclear precursor $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)$-

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

Pd(1)–P(1)	2.306(4)	Pd(3′)–N(1′)	2.096(39)	Pd(1)–P(3)	2.362(4)	Pd(3′)–C(75′)	1.941(34)
Pd(1)–S(1)	2.349(9)	P(1)–S(2)	2.153(14)	Pd(1)–S(1′)	2.378(20)	P(1)–S(2′)	2.020(28)
Pd(1)–C(1)	2.030(14)	P(1)–C(13)	1.825(9)	Pd(2)–P(2)	2.296(4)	P(1)–C(19)	1.816(9)
Pd(2)–P(4)	2.383(4)	P(2)–S(1)	2.074(11)	Pd(2)–S(2)	2.375(13)	P(2)–S(1′)	2.213(19)
Pd(2)–S(2′)	2.371(30)	P(2)–C(25)	1.825(9)	Pd(2)–C(7)	2.012(16)	P(2)–C(31)	1.843(11)
Pd(3)–S(1)	2.305(10)	P(3)–C(37)	1.830(10)	Pd(3)–S(2)	2.500(12)	P(3)–C(43)	1.786(10)
Pd(3)–N(1)	2.131(24)	P(3)–C(49)	1.839(10)	Pd(3)–C(75)	1.986(17)	P(4)–C(55)	1.821(8)
Pd(3′)–S(1′)	2.445(22)	P(4)–C(61)	1.797(12)	Pd(3′)–S(2′)	2.313(23)	P(4)–C(67)	1.827(10)
P(1)–Pd(1)–P(3)	173.9(2)	Pd(2)–P(2)–C(25)	115.3(4)	P(1)–Pd(1)–S(1)	95.4(3)	S(1)–P(2)–C(25)	95.9(4)
P(3)–Pd(1)–S(1)	87.1(3)	S(1′)–P(2)–C(25)	96.7(6)	P(1)–Pd(1)–S(1′)	87.1(5)	Pd(2)–P(2)–C(31)	112.7(3)
P(3)–Pd(1)–S(1′)	94.5(5)	S(1)–P(2)–C(31)	102.7(5)	S(1)–Pd(1)–S(1′)	11.0(5)	S(1′)–P(2)–C(31)	113.3(7)
P(1)–Pd(1)–C(1)	88.5(4)	C(25)–P(2)–C(31)	106.9(5)	P(3)–Pd(1)–C(1)	89.4(4)	Pd(1)–P(3)–C(37)	114.0(4)
S(1)–Pd(1)–C(1)	175.5(5)	Pd(1)–P(3)–C(43)	111.1(4)	S(1′)–Pd(1)–C(1)	173.4(6)	C(37)–P(3)–C(43)	104.6(5)
P(2)–Pd(2)–P(4)	174.7(1)	Pd(1)–P(3)–C(49)	114.3(4)	P(2)–Pd(2)–S(2)	89.7(3)	C(37)–P(3)–C(49)	107.9(6)
P(4)–Pd(2)–S(2)	93.3(3)	C(43)–P(3)–C(49)	103.9(5)	P(2)–Pd(2)–S(2′)	96.1(6)	Pd(2)–P(4)–C(55)	116.6(4)
P(4)–Pd(2)–S(2′)	87.5(6)	Pd(2)–P(4)–C(61)	111.0(4)	P(2)–Pd(2)–C(7)	86.5(4)	C(55)–P(4)–C(61)	104.1(5)
P(4)–Pd(2)–C(7)	90.2(4)	Pd(2)–P(4)–C(67)	113.4(3)	S(2)–Pd(2)–C(7)	174.6(5)	C(55)–P(4)–C(67)	106.7(5)
S(2′)–Pd(2)–C(7)	175.8(6)	C(61)–P(4)–C(67)	103.8(6)	S(1)–Pd(3)–S(2)	90.6(4)	Pd(1)–S(1)–Pd(3)	100.5(4)
S(1)–Pd(3)–N(1)	171.1(7)	Pd(1)–S(1)–P(2)	111.6(4)	S(2)–Pd(3)–N(1)	96.2(6)	Pd(3)–S(1)–P(2)	98.1(4)
S(1)–Pd(3)–C(75)	89.9(6)	Pd(2)–S(2)–Pd(3)	106.3(5)	S(2)–Pd(3)–C(75)	176.2(7)	Pd(2)–S(2)–P(1)	109.4(5)
N(1)–Pd(3)–C(75)	83.7(8)	Pd(3)–S(2)–P(1)	94.3(5)	S(1′)–Pd(3′)–S(2′)	90.0(8)	Pd(1)–S(1′)–P(2)	105.8(7)
S(1′)–Pd(3′)–N(1′)	100.0(13)	Pd(3′)–S(1′)–P(2)	99.7(8)	S(2′)–Pd(3′)–N(1′)	170.0(15)	Pd(2)–S(2′)–Pd(3′)	102.2(9)
S(1′)–Pd(3′)–C(75′)	174.2(11)	Pd(2)–S(2′)–P(1)	114.5(13)	S(2′)–Pd(3′)–C(75′)	92.7(11)	Pd(3′)–S(2′)–P(1)	94.1(11)
Pd(1)–P(1)–S(2)	113.9(4)	Pd(3)–N(1)–C(73)	103.7(17)	Pd(1)–P(1)–S(2′)	122.5(7)	Pd(3)–N(1)–C(80)	118.9(18)
Pd(1)–P(1)–C(13)	114.2(4)	C(73)–N(1)–C(80)	106.8(21)	S(2)–P(1)–C(13)	110.0(5)	Pd(3)–N(1)–C(81)	111.0(16)
S(2′)–P(1)–C(13)	100.2(8)	C(73)–N(1)–C(81)	107.2(19)	Pd(1)–P(1)–C(19)	113.2(4)	C(80)–N(1)–C(81)	108.5(24)
S(2)–P(1)–C(19)	98.1(5)	Pd(3′)–N(1′)–C(73′)	106.6(26)	S(2′)–P(1)–C(19)	98.4(9)	Pd(3′)–N(1′)–C(80′)	106.4(27)
C(13)–P(1)–C(19)	106.0(5)	C(73′)–N(1′)–C(80′)	122.0(39)	Pd(2)–P(2)–S(1)	121.2(3)	Pd(3′)–N(1′)–C(81′)	112.7(29)
Pd(2)–P(2)–S(1′)	111.0(5)	C(73′)–N(1′)–C(81′)	101.6(33)	S(1)–P(2)–S(1′)	11.6(6)		

$(PPh_3)\}_2]$ also reacts with the neutral substrates *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt) (1 : 1 molar ratio, CH_2Cl_2) to give the corresponding neutral homo- and hetero-trinuclear complexes $[Pd_2M(\mu_3\text{-}SPPh_2)(C_6F_5)_4(PPh_3)_2]$ (M = Pd **4** or Pt **5**) respectively [equation (2)].

$$[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2] + [M(C_6F_5)_2(thf)_2] \longrightarrow [Pd_2M(\mu_3\text{-}SPPh_2)(C_6F_5)_4(PPh_3)_2] \quad (2)$$
$$M = Pd\ \mathbf{4}\ \text{or}\ Pt\ \mathbf{5}$$

Complexes **4** and **5** show satisfactory elemental analyses and behave as non-electrolytes in acetone solutions.[6] Their mass spectra do not provide valuable information in this case, showing only peaks due to fragmentation and redistribution of ligands, but not the molecular peak. The IR spectra show similar features to those described for complexes **1**–**3**: absorptions corresponding to the presence of co-ordinated C_6F_5, $[SPPh_2]^-$ and PPh_3 groups are present.

The $^{31}P\text{-}\{^1H\}$ NMR spectra of complexes **4** and **5** show the presence of a single AX system, with ^{195}Pt satellites in the case of **5**. This pattern of signals is in agreement with the proposed structure (Fig. 6).

The ^{19}F NMR spectrum of **4** shows four resonances (two partially overlapped) due to *ortho*-F atoms, two triplets corresponding to the *para*-F atoms and three complex resonances of relative intensity 1 : 1 : 2, corresponding to the *meta*-F atoms. A similar pattern of signals can be observed in the ^{19}F NMR spectrum of **5**, the *ortho*-F region showing four well separated signals, two of them with ^{195}Pt satellites. This pattern is in good agreement with the proposed structure (Fig. 6) and implies: (*a*) the equivalence of the C_6F_5 groups of the $[Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)]_2$ fragment and the equivalence of the rings of the $M(C_6F_5)_2$ fragment; (*b*) the rigidity of the molecule on the NMR time-scale and (*c*) the restricted rotation of the pentafluorophenyl ligands around the $M\text{–}C_{ipso}$ bonds. Full assignment of the resonances in **5** was made through selective irradiation experiments.

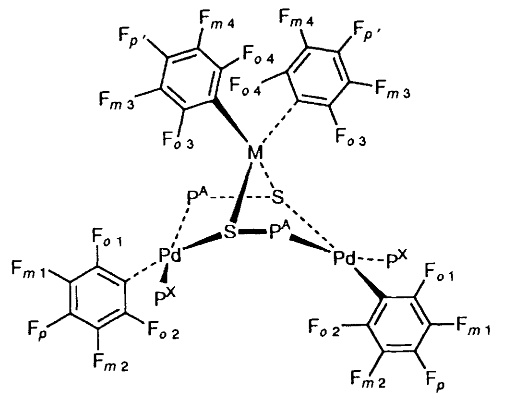

Fig. 6 Atomic numbering scheme for ^{19}F and $^{31}P\text{-}\{^1H\}$ NMR spectral assignment of the neutral complexes **4** and **5**

Experimental

Solvents were dried and distilled under nitrogen by standard methods prior to use. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer in Nujol mulls between polyethylene sheets. NMR spectra were recorded on a Bruker ARX-300 spectrometer; ^1H NMR spectra were recorded at 300.13 MHz in $CDCl_3$ using the solvent signal as internal standard; ^{19}F NMR spectra were recorded at 282.30 MHz and externally referenced to $CFCl_3$; $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded at 121.49 MHz and externally referenced to H_3PO_4 (85%). Mass spectra were recorded on a V.G. Autospec. Conductivity measurements were carried out in acetone solutions ($\approx 5 \times 10^{-4}$ mol dm^{-3}) on a Philips PW-9509 digital conductivity meter. The starting compounds $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$,[5]

Table 2 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Pd(1)	6 303(1)	7 561(1)	2 191(1)
Pd(2)	8 227(1)	8 720(1)	1 378(1)
Pd(3)	6 484(2)	7 318(1)	928(1)
Pd(3′)	7 056(3)	7 242(2)	959(2)
P(1)	7 880(3)	7 374(2)	2 147(2)
P(2)	6 581(3)	8 777(2)	1 308(1)
P(3)	4 668(3)	7 637(2)	2 238(2)
P(4)	9 907(3)	8 713(2)	1 380(2)
S(1)	5 780(7)	7 994(4)	1 381(3)
S(2)	8 148(9)	7 624(6)	1 435(5)
S(1′)	5 949(14)	7 843(8)	1 325(8)
S(2′)	8 377(18)	7 644(14)	1 553(9)
C(1)	6 681(9)	7 231(7)	2 908(5)
C(2)	7 131(10)	7 617(8)	3 299(6)
C(3)	7 362(11)	7 436(8)	3 794(6)
C(4)	7 146(11)	6 876(8)	3 919(6)
C(5)	6 694(12)	6 478(7)	3 548(6)
C(6)	6 476(11)	6 650(7)	3 057(6)
F(1)	7 319(6)	8 217(4)	3 192(3)
F(2)	7 800(7)	7 859(5)	4 148(3)
F(3)	7 376(7)	6 705(5)	4 412(3)
F(4)	6 462(7)	5 901(5)	3 685(3)
F(5)	5 987(7)	6 249(4)	2 713(3)
C(7)	8 180(10)	9 644(7)	1 275(7)
C(8)	8 138(12)	9 932(9)	789(8)
C(9)	8 175(13)	10 557(10)	728(9)
C(10)	8 205(14)	10 948(10)	1 111(12)
C(11)	8 234(12)	10 709(9)	1 593(11)
C(12)	8 268(11)	10 046(8)	1 704(10)
F(6)	8 150(7)	9 576(5)	407(4)
F(7)	8 205(8)	10 800(6)	286(5)
F(8)	8 262(9)	11 550(5)	1 066(6)
F(9)	8 348(9)	11 066(5)	2 014(6)
F(10)	8 371(8)	9 832(5)	2 147(4)
C(13)	8 815(6)	7 710(4)	2 664(3)
C(14)	9 035	8 340	2 658
C(15)	9 651	8 615	3 082
C(16)	10 049	8 262	3 511
C(17)	9 830	7 632	3 517
C(18)	9 213	7 357	3 093
C(19)	8 167(7)	6 555(4)	2 139(4)
C(20)	7 422	6 115	2 033
C(21)	7 642	5 493	1 979
C(22)	8 606	5 311	2 030
C(23)	9 351	5 752	2 135
C(24)	9 131	6 373	2 190
C(25)	5 831(7)	8 999(5)	687(3)
C(26)	6 171	8 904	259
C(27)	5 550	9 000	−220
C(28)	4 590	9 191	−270
C(29)	4 250	9 286	158
C(30)	4 871	9 190	637
C(31)	6 281(7)	9 317(4)	1 767(3)
C(32)	5 896	9 907	1 638
C(33)	5 777	10 312	2 014
C(34)	6 044	10 127	2 518
C(35)	6 429	9 537	2 646
C(36)	6 547	9 132	2 271
C(37)	4 077(7)	8 369(4)	2 000(4)
C(38)	4 144	8 896	2 302
C(39)	3 677	9 442	2 100
C(40)	3 143	9 462	1 596
C(41)	3 076	8 936	1 294
C(42)	3 543	8 389	1 496
C(43)	3 925(7)	7 056(5)	1 860(4)
C(44)	2 930	7 044	1 833
C(45)	2 326	6 612	1 525
C(46)	2 717	6 192	1 243
C(47)	3 713	6 204	1 270
C(48)	4 317	6 636	1 579
C(49)	4 496(8)	7 509(5)	2 872(3)
C(50)	4 873	7 934	3 256
C(51)	4 775	7 827	3 741
C(52)	4 302	7 295	3 844
C(53)	3 926	6 870	3 460
C(54)	4 023	6 977	2 974
C(55)	10 764(6)	8 444(5)	1 955(3)
C(56)	11 464	8 830	2 258
C(57)	12 071	8 605	2 706
C(58)	11 977	7 993	2 852
C(59)	11 277	7 607	2 549
C(60)	10 670	7 833	2 101
C(61)	10 118(8)	8 209(5)	897(4)
C(62)	9 368	8 115	461
C(63)	9 536	7 759	68
C(64)	10 453	7 498	110
C(65)	11 203	7 593	546
C(66)	11 035	7 948	939
C(67)	10 351(7)	9 465(4)	1 230(4)
C(68)	10 577	9 565	770
C(69)	10 878	10 150	655
C(70)	10 953	10 635	999
C(71)	10 727	10 535	1 458
C(72)	10 426	9 950	1 574
N(1)	6 955(16)	6 596(10)	516(8)
C(73)	6 098(21)	6 147(11)	397(10)
C(74)	5 156(13)	6 533(8)	266(7)
C(75)	5 172	7 114	491
C(76)	4 344	7 489	370
C(77)	3 500	7 284	24
C(78)	3 484	6 704	−202
C(79)	4 312	6 328	−80
C(80)	7 795(24)	6 247(13)	755(12)
C(81)	7 076(19)	6 828(13)	30(9)
N(1′)	6 040(30)	6 787(20)	378(16)
C(73′)	6 473(24)	6 783(21)	−83(17)
C(74′)	7 426(19)	6 482(16)	199(12)
C(75′)	7 871	6 690	685
C(76′)	8 839	6 535	912
C(77′)	9 363	6 172	653
C(78′)	8 919	5 964	166
C(79′)	7 950	6 119	−61
C(80′)	5 741(42)	6 140(27)	624(22)
C(81′)	5 093(33)	7 167(21)	176(17)
Cl(1)	5 167(6)	4 653(4)	1 224(3)
O(1)	6 037(18)	4 292(12)	1 349(9)
O(2)	5 355(17)	5 175(12)	1 562(9)
O(3)	4 321(18)	4 348(11)	1 240(9)
O(4)	4 939(17)	4 865(11)	741(10)
C(82)	8 380(21)	5 512(36)	−924(19)
Cl(2)	9 036(24)	5 089(15)	−1 244(11)
Cl(3)	9 133(24)	5 759(15)	−371(11)
C(82′)	2 193(80)	5 931(25)	−242(14)
Cl(2′)	1 852(30)	5 472(16)	−761(17)
Cl(3′)	2 524(30)	6 638(17)	−415(16)

$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt),[13,14] $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2\text{-}2)\}_2]$,[15] $[\{Pd(\mu\text{-}Cl)(NC_9H_6CH_2\text{-}8)\}_2]$[16] and $[\{Pd(\mu\text{-}Cl)(PhN{=}NC_6H_4)\}_2]$[17] were prepared according to published procedures.

Synthesis of Cationic Complexes $[Pd_3(\mu_3\text{-}SPPh_2)_2(C_6F_5)_2L(PPh_3)_2]ClO_4$ (L = $C_6H_4CH_2NMe_2$-2 **1**, $NC_9H_6CH_2$-8 **2** *or* $PhN{=}NC_6H_4$ **3**).—As a general method, we describe here the synthesis of $[Pd_3(\mu_3\text{-}SPPh_2)_2(C_6F_5)_2(C_6H_4CH_2NMe_2\text{-}2)(PPh_3)_2]ClO_4$ **1**: to a suspension of $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2\text{-}2)\}_2]$ (0.137 g, 0.249 mmol) in acetone (20 cm^3) was added $AgClO_4$ (0.103 g, 0.498 mmol). The resulting mixture was stirred for 45 min at room temperature with exclusion of the light and then filtered. To the freshly prepared solution of $[Pd(C_6H_4CH_2NMe_2\text{-}2)(Me_2CO)_2]ClO_4$ was added $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ (0.750 g, 0.498 mmol) suspended in acetone (30 cm^3) and then heated at the reflux temperature. The initially yellow suspension gradually dissolved and its colour changed, giving an orange solution after 45 min refluxing. The resulting solution was cooled and the solvent removed to small volume ($\approx$4 cm^3). Addition of Et_2O (30 cm^3) and stirring gave **1** as an orange solid, 0.690 g (75% yield) (Found: C, 52.45; H, 3.50; N, 0.70. $C_{81}H_{62}ClF_{10}NO_4P_4Pd_3S_2$ requires C, 52.70; H, 3.40; N, 0.75%). IR (cm^{-1}): 1580m (L), 1505vs (C_6F_5), 1100vs (ClO_4^-), 956vs (C_6F_5), 845s (L), 782s (C_6F_5, X-sensitive), 623vs (ClO_4^-), 523vs, 520vs, 510vs and 490vs [$(SPPh_2)^-$ + PPh_3]. Λ_M = 106 Ω^{-1} cm^2 mol^{-1}. NMR (room temp.): ^{1}H, δ 8.21–6.93 (m, 50 H, Ph), 6.87 (d, 1 H, H^b of L, $^3J_{H^b\text{-}H^c}$ = 7.22), 6.81 (t, 1 H, H^c of L), 6.25 (t, 1 H, H^d of L, $^3J_{H^c\text{–}H^d}$ = 7.10), 5.85 (d, 1 H, H$_o$ of L, $^3J_{H^d\text{–}H_o}$ = 7.80), 3.74, 3.18 (AB system, 2 H, CH_2N, $^2J_{H^a\text{–}H^b}$ = 14), 2.12 (s, 3 H, NMe_2) and 1.29 (s, 3 H, NMe_2); ^{19}F, δ −114.87 (d, 1 F, F$_o$), −115.00 (d, 1 F, F$_o$), −115.23 (d, 1 F, F$_o$), −115.36 (d, 1 F, F$_o$), −159.07 (t, 1 F, F$_p$), −159.14 (t, 1 F, F$_p$), −160.92 (m, 1 F, F$_m$), −161.16 (m, 1 F, F$_m$), −161.36 (m, 1 F, F$_m$) and −161.58 (m, 1 F, F$_m$); ^{31}P-{^{1}H}, δ 69.63 (dd, 1 P, P^{A1}–S *trans* C, $^2J_{P^{A1}\text{–}P^{X1}}$ = 468, $^3J_{P^{A1}\text{–}P^{X2}}$ = 10.5), 56.24 (dd, 1 P, P^{A2}–S *trans* N, $^2J_{P^{A2}\text{–}P^{X2}}$ = 472, $^3J_{P^{A2}\text{–}P^{X1}}$ = 10.5 Hz), 16.57 (dd, 1 P, P^{X1}Ph$_3$) and 15.87 (dd, 1 P, P^{X2}Ph$_3$).

Complexes **2** and **3** were prepared similarly. Complex **2**. The complex [{Pd(μ-Cl)($NC_9H_6CH_2$-8)}$_2$] (0.142 g, 0.249 mmol) was treated with $AgClO_4$ (0.103 g, 0.498 mmol) and [{Pd(μ-SPPh$_2$)(C_6F_5)(PPh$_3$)}$_2$] (0.750 g, 0.498 mmol) to give **2** (0.646 g, 70% yield) as a pale-orange solid (Found: C, 52.90; H, 3.55; N, 0.85. $C_{82}H_{58}ClF_{10}NO_4P_4Pd_3S_2$ requires C, 53.10; H, 3.15; N, 0.75%). IR (cm^{-1}): 1635m, 1615m, 1590m (L), 1500vs (C_6F_5), 1100vs (ClO_4^-), 955vs (C_6F_5), 830s (8-mq), 775s (C_6F_5, X-sensitive), 623vs (ClO_4^-), 525vs, 510vs, 505vs and 485vs [$(SPPh_2)^-$ + PPh_3]. Λ_M = 94 Ω^{-1} cm^2 mol^{-1}. NMR (room temp.): ^{1}H, δ 8.50–6.76 (m, aromatics) and 3.12, 2.97 (AB system, 2 H, CH_2Pd, $^2J_{H^a\text{–}H^b}$ = 13.8 Hz); ^{19}F, δ −114.53 (m, 2 F, F$_o$), −115.15 (d, 1 F, F$_o$), −116.26 (d, 1 F, F$_o$), −159.25 (t, 1 F, F$_p$), −159.29 (t, 1 F, F$_p$), −160.87 (m, 1 F, F$_m$), −161.27 (m, 1 F, F$_m$), −161.63 (m, 1 F, F$_m$) and −162.17 (m, 1 F, F$_m$); ^{31}P-{^{1}H}, δ 68.58 (d, 1 P, P^{A1}–S *trans* C, $^2J_{P^{A1}\text{–}P^{X1}}$ = 468 Hz), 46.56 (d, 1 P, P^{A2}–S *trans* N, $^2J_{P^{A2}\text{–}P^{X2}}$ = 468 Hz), 19.33 (d, 1 P, P^{X1}Ph$_3$), 16.34 (d, 1 P, P^{X2}Ph$_3$). Complex **3**. The complex [{Pd(μ-Cl)(PhN=NC$_6$H$_4$)}$_2$] (0.149 g, 0.229 mmol) was treated with $AgClO_4$ (0.096 g, 0.459 mmol) and [{Pd(μ-SPPh$_2$)(C_6F_5)-PPh$_3$)}$_2$] (0.692 g, 0.459 mmol) to give **3** (0.531 g, 61% yield) as a pale-orange solid (Found: C, 53.20; H, 3.25; N, 1.45. $C_{84}H_{59}ClF_{10}N_2O_4P_4Pd_3S_2$ requires C, 53.30; H, 3.15; N, 1.50%). IR (cm^{-1}): 1570m (L), 1500vs (C_6F_5), 1090vs (ClO_4^-), 955vs (C_6F_5), 780s (C_6F_5, X-sensitive), 765s (L), 623vs (ClO_4), 520vs, 505vs, 480vs [$(SPPh_2)^-$ + PPh_3]. Λ_M = 105 Ω^{-1} cm^2 mol^{-1}. NMR (room temp.): ^{1}H, δ 8.02–6.59 (m, aromatics) and 6.15 (d, 1 H, H$_o$, $^3J_{H\text{–}H}$ = 7.27 Hz); ^{19}F, δ −114.14 (d, 1 F, F$_o$), −114.25 (d, 1 F, F$_o$), −115.25 (d, 1 F, F$_o$), −115.35 (d, 1 F, F$_o$), −158.53 (t, 2 F, 2 F$_p$), −160.68 (m, 1 F, F$_m$), −160.76 (m, 1 F, F$_m$), −161.10 (m, 1 F, F$_m$) and −161.49 (m, 1 F, F$_m$); ^{31}P-{^{1}H}, δ 65.42 (d, 1 P, P^{A1}–S *trans* C, $^2J_{P^{A1}\text{–}P^{X1}}$ = 468), 54.45 (d, 1 P, P^{A2}–S *trans* N, $^2J_{P^{A2}\text{–}P^{X2}}$ = 464 Hz), 17.43 (d, 1 P, P^{X1}Ph$_3$) and 16.79 (d, 1 P, P^{X2}Ph$_3$).

Synthesis of [Pd$_2$M(μ$_3$-SPPh$_2$)$_2$(C_6F_5)$_4$(PPh$_3$)$_2$] (M = Pd **4** *or* Pt **5**).—Complex **4**. To a solution of [{Pd(μ-SPPh$_2$)(C_6F_5)-PPh$_3$)}$_2$] (0.413 g, 0.274 mmol) in CH_2Cl_2 (25 cm^3) was added [Pd(C_6F_5)$_2$(thf)$_2$] (0.160 g, 0.274 mmol). The resulting pale yellow solution was stirred at room temperature for 45 min and then evaporated to dryness. Addition of *n*-hexane (20 cm^3) and stirring gave [Pd$_3$(μ$_3$-SPPh$_2$)$_2$(C_6F_5)$_4$(PPh$_3$)$_2$] **4** (0.422 g, 79% yield) as a pale yellow solid (Found: C, 51.45; H, 2.55. $C_{84}H_{50}F_{20}P_4Pd_3S_2$ requires C, 51.85; H, 2.60%). IR (cm^{-1}): 1500vs (C_6F_5), 960vs (C_6F_5), 800s, 790s, 780s (C_6F_5, X-sensitive), 510vs, 505vs and 490vs [$(SPPh_2)^-$ + PPh_3]. NMR (room temp.): ^{19}F, δ −110.71 (d, 4 F, F$_o$), −114.92 (d, 2 F, F$_o$), −115.60 (d, 2 F, F$_o$), −160.34 (t, 2 F, F$_p$), −161.30 (m, 2 F, F$_m$), −162.44 (m, 2 F, F$_m$), −163.26 (t, 2 F, F$_p$) and −165.01 (m, 4 F, F$_m$); ^{31}P-{^{1}H}, δ 65.59 (d, 2 P, μ$_3$-P^{A}S) and 16.30 (d, 2 P, P^{X}Ph$_3$) (AX system, $^2J_{P^A\text{–}P^X}$ = 464 Hz).

Complex **5** was prepared similarly: [{Pd(μ-SPPh$_2$)(C_6F_5)-(PPh$_3$)}$_2$] (0.424 g, 0.281 mmol), [Pt(C_6F_5)$_2$(thf)$_2$] (0.189 g, 0.281 mmol), [Pd$_2$Pt(μ$_3$-SPPh$_2$)$_2$(C_6F_5)$_4$(PPh$_3$)$_2$] **5** (0.480 g, 84% yield), yellow solid (Found: C, 48.95; H, 2.50. $C_{84}H_{50}F_{20}P_4Pd_2PtS_2$ requires C, 49.55; H, 2.45%). IR (cm^{-1}): 1500vs(C_6F_5), 957vs(C_6F_5), 798s, 789s, 777s(C_6F_5, X-sensitive), 532vs, 520vs, 491vs [$(SPPh_2)^-$ + PPh_3]. NMR (room temp.): ^{19}F, δ −110.78 (d, 2 F, F$_o$), −113.84 (d, 2 F, F$_o$, $^3J_{Pt\text{–}F_o}$ = 435), −115.07 (d, 2 F, F$_o$), −118.97 (d, 2 F, F$_o$, $^3J_{Pt\text{–}F_o}$ = 373 Hz), −160.17 (t, 2 F, F$_p$), −161.59 (m, 2 F, F$_m$), −162.47 (m, 2 F, F$_m$), −164.66 (t, 2 F, F$_p$) and −165.94 (m, 4 F, F$_m$); ^{31}P-{^{1}H}, δ 73.74 (d, 2 P, μ$_3$-P^{A}S, $^2J_{Pt\text{–}P^A}$ = 114) and 16.70 (d, 2 P, P^{X}Ph$_3$, $^3J_{Pt\text{–}P^X}$ = 90) (AX system, $^2J_{P^A\text{–}P^X}$ = 459 Hz).

^{31}P–^{31}P *COSY Experiments.*—The experiments were performed at a measuring frequency of 121.5014 MHz in $CDCl_3$. The data were acquired into a 256 × 1024 matrix and then transformed into 1024 × 1024 points using a sine window in each dimension.

Crystal Structure Determination.—Suitable crystals of complex **1** (crystal size 0.25 × 0.45 × 0.35 mm) were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of the crude product at room temperature. Intensity data were recorded at room temperature using graphite-monochromated Mo-Kα X-radiation on a Enraf-Nonius CAD4 diffractometer (θ_{max} = 22°). Accurate lattice parameters were determined from the position of 25 reflections ($20 \leqslant 2\theta \leqslant 21°$). The cell dimensions and Laue group were verified by axial photographs of [1 0 0], [0 1 0], [0 0 1] and [1 0 2]. The latter was photographed because it is an axis of a possible transformation to a metrically orthorhombic, *C*-centred cell. The photo of [0 1 0] clearly showed the presence of mirror symmetry, while all of the other photographs clearly showed the absence of mirrors. We did not detect any signs of superlattice scattering in any of the photographs. Intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied.

Crystal data. $C_{81}H_{62}ClF_{10}NO_4Pd_3P_4S_2 \cdot 0.8CH_2Cl_2$, **1**·0.8$CH_2Cl_2$, *M* = 1913.99, monoclinic, space group $P2_1/c$, a = 14.185(3), b = 21.589(4), c = 27.440(5) Å, β = 104.95(3)°, U = 8118.79 Å^3, Z = 4, D_c = 1.56 g cm^{-3}, $F(000)$ = 3864, μ = 9.6 cm^{-1}, 10751 unique data, 5989 observed data [$F > 4.0\sigma(F)$] for the refinement of 860 parameters, scan method ω–2θ, $w = 1/[\sigma^2(F) + 0.00077F^2]$, R = 0.0702, R' = 0.0849, Δ/σ = 0.002, largest, smallest difference peaks 0.78, −1.01 e Å^{-3}.

Structure solution and refinement. The structure was solved by the use of Patterson and Fourier methods. In the final refinement all non-hydrogen atoms, except the light atoms of the disordered S(1′,2′)Pd(3′)($C_6H_4CH_2NMe_2$-2) group, the perchlorate anion and the CH_2Cl_2 moiety, were refined with anisotropic thermal parameters. The phenyl groups, *i.e.* C_6H_5 but not C_6F_5, were refined as rigid groups with idealized geometry, as was the six-membered ring of the dimethylbenzylamine ligand. Loose observational restraints were used for the interatomic distances of the CH_2Cl_2 solvent molecule. Blocked full-matrix least-squares calculations were done on a VAX 4000–300 computer using the SHELXTL-PLUS software package.[18] Hydrogen atoms were not included in the structural model. Other than the inability to use anisotropic thermal parameters for the C, S and N atoms of the disordered group, we did not observe any specially deleterious effects resulting from the disorder. We conducted one further test for 'missing symmetry' as follows. If the structure pertained to a higher-symmetry crystal system, such as orthorhombic, then our data set, consisting of a quadrant, would have at least two equivalents of each unique reflection. Symmetry equivalent data must have the same value of 2θ. Therefore, we listed F_o and F_c values at the end of the refinement, sorted by 2θ. A visual inspection of this list did not show any pairing of reflections with similar F_o and F_c at equal or nearly equal 2θ values.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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