Different Co-ordination Modes of the Ligand [SPPh₂]⁻ in Complexes of Pdᴵᴵ and Ptᴵᴵ. Crystal Structures of [{Pd(µ-SPPh₂)(C₆F₅)(PPh₃)}₂] and [Pd(SPPh₂)(PPh₃)₂]ClO₄·CH₂Cl₂†

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The neutral complexes [{M(µ-SPPh₂)(C₆F₅)(PR₃)}₂] (M = Pd or Pt; PR₃ = PPh₃ or PPh₂Et) containing the P,S-bridging [SPPh₂]⁻ have been synthesised by reaction of the corresponding acetylacetonate (acac) derivatives [M(C₆F₅)(acac-O,O')(PR₃)] with HP(S)Ph₂. However, the reaction of the cationic complexes [M(acac-O,O')(PPh₃)₂]ClO₄ (M = Pd or Pt) with HP(S)Ph₂ affords mononuclear [M(SPPh₂)(PPh₃)₂]ClO₄ in which the [SPPh₂]⁻ ligand is co-ordinated as a P,S-chelate. The anionic complex [NBu₄]₂[{Pd(µ-SPPh₂)(C₆F₅)₂}₂] has also been synthesised. The crystal structures of [{Pd(µ-SPPh₂)(C₆F₅)(PPh₃)}₂] and [Pd(SPPh₂)(PPh₃)₂]ClO₄·CH₂Cl₂ have been determined by X-ray diffraction methods; the former adopts a boat conformation.
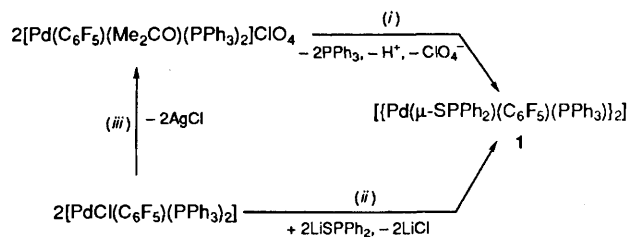
The anionic ligand [SPPh₂]⁻ (diphenylthiophosphinite) can be co-ordinated to metal centres as: (*a*) P-monodentate,[1] (*b*) S-monodentate,[1a,2] (*c*) P,S-chelate[1a,3c,4] or (*d*) di-µ-P,S-bridge,[1,3] the last representing the most numerous group, probably due to the stability of the six-membered ring generated.[1a]

M—PPh₂   M—S—PPh₂

(structures with Ph₂ groups labelled (a), (b), (c), (d))

(a)   (b)   (c)   (d)
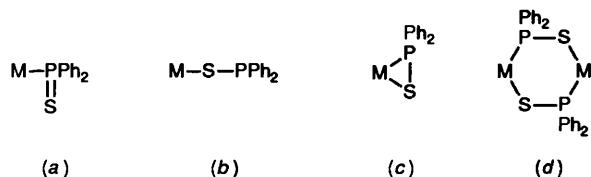
In the course of our current research on the reactivity of perhalogenophenyl derivatives of Pdᴵᴵ and Ptᴵᴵ with polyfunctional anionic ligands such as [Ph₂PCHPPh₂]⁻ or [C(PPh₂)₃]⁻ we have shown the utility of acetylacetonato (acac) derivatives as starting materials[5] for the preparation of these type of complexes. This paper deals with the reactions of HP(S)Ph₂ with neutral or cationic acac-O,O' derivatives of Pdᴵᴵ or Ptᴵᴵ which render di- or mono-nuclear SPPh₂ complexes depending on the starting materials.

Results and Discussion

Neutral Complexes [{M(µ-SPPh₂)(C₆F₅)(PR₃)}₂].—The reaction of the neutral derivatives [M(C₆F₅)(acac-O,O')(PR₃)] (M = Pd or Pt; PR₃ = PPh₃ or PPh₂Et) with H(S)PPh₂ in CH₂Cl₂ solution, at room temperature, results in displacement of the acac⁻ group as Hacac and co-ordination of the [SPPh₂]⁻ anion as a bridging ligand, yielding the corresponding neutral dinuclear derivatives [{M(µ-SPPh₂)-(C₆F₅)(PR₃)}₂] (M = Pd, PR₃ = PPh₃ 1 or PPh₂Et 2; M = Pt, PR₃ = PPh₃ 3 or PPh₂Et 4) [equation (1)]. Complex 1 can also be obtained, although in lower yields, through two other synthetic procedures (Scheme 1): (*a*) [Pd(C₆F₅)-(Me₂CO)(PPh₃)₂]ClO₄ reacts with H(S)PPh₂ in acetone; (*b*)

2[Pd(C₆F₅)(Me₂CO)(PPh₃)₂]ClO₄

(scheme diagram)

(i) — 2PPh₃, − H⁺, − ClO₄⁻

(iii) − 2AgCl

[{Pd(µ-SPPh₂)(C₆F₅)(PPh₃)}₂]
1

2[PdCl(C₆F₅)(PPh₃)₂]

(ii)

+ 2LiSPPh₂, − 2LiCl

Scheme 1 (*i*) 2Ph₂P(S)H, Me₂CO; (*ii*) thf–toluene, N₂; (*iii*) 2AgClO₄, Me₂CO

the reaction between [PdCl(C₆F₅)(PPh₃)₂] and LiSPPh₂ in tetrahydrofuran (thf)–toluene.

$$2[M(C_6F_5)(acac\text{-}O,O')(PR_3)] + 2Ph_2P(S)H \longrightarrow$$
$$[\{M(\mu\text{-}SPPh_2)(C_6F_5)(PR_3)\}_2] + 2Hacac \quad (1)$$
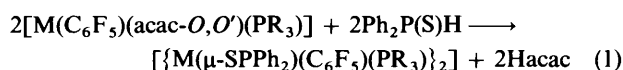
These complexes gave satisfactory elemental analyses and show a strong IR band in the range 565–570 cm⁻¹ (see Experimental section) which can be assigned to ν(P=S) of the co-ordinated [SPPh₂]⁻; it appears at lower wavenumbers than for unco-ordinated diphenylphosphine sulfide (640 cm⁻¹).[6] Characteristic absorptions assignable to the presence of C₆F₅ groups[5,7] are observed. The analytical and IR data are not sufficiently informative to infer the structural configuration of these compounds, but the ³¹P-{¹H} and ¹⁹F NMR data do (Table 1).

The ³¹P-{¹H} NMR spectra of complexes 1–4 show a pattern which can be analysed as an AA'BB' spin system (Fig. 1). This indicates the dinuclear nature of the complexes, since for a mononuclear compound (P,S-chelate co-ordination) a spectrum corresponding to an AB system should be obtained. In principle, two different geometries are possible (Scheme 2), but the large value of ²J(Pₐ–Pᵦ) (488–460 Hz) precludes configuration A, in which the two P donor atoms are mutually *cis*, and is in agreement with configuration B, with two P donor atoms mutually *trans*. The X-ray diffraction study of ([{Pd(µ-SPPh₂)(C₆F₅)(PPh₃)}₂] 1 confirms geometry B, and shows that the central portion of the molecule adopts a boat conformation.

Table 1 Fluorine-19 and ^{31}P-$\{^1H\}$ NMR ^{a} data for complexes 1–7

	δ(F_o)	δ(F_m)	δ(F_p)	³J(Pt–F_o)	δ(P_a)	δ(P_{b,x})	δ(P_m)	²J(P_a–P_{b,x})	³J(P_a–P_{b'})	³J(P_a–P_{a'})	¹J(Pt–P_a)	¹J(Pt–P_{b,x})
1^b	−116.15	−164.13			51.54	24.69		488	1.0	67.8		
1^c	−113.51	−161.65	−162.09									
	−113.96	−162.39										
2^d	−115.13	−162.96			50.54	19.20		489	0.6	71.1		
3^b	−117.81	−165.94		363.5	36.22	21.15		473	4.0	53.4	2821	2496
3^c	−115.62	−160.89	−161.24	246.5								
	−118.78	−161.65		281.1								
4^d	−116.43	−164.10		376.8	37.35	9.70		460	3.5	48.3	2695	2459
5	−113.44	−166.8	−165.42		46.08							
	−114.13		−167.73									
6^e					67.41	24.07	26.55	283				
7^f					53.33	19.05	16.70	288			1823	3123

^{a} J in Hz. ^{b} ^{19}F NMR spectrum measured at room temperature in CDCl₃. ^{c} ^{19}F NMR spectrum measured at −80 °C in CD₂Cl₂. ^{d} Signals due to F_o and F_m do not split at −80 °C (see text). ^{e} ²J(P_m–P_x) 36 Hz. ^{f} ²J(P_a–P_m) = ²J(P_m–P_x) = 17, ¹J(Pt–P_m) 4098 Hz.
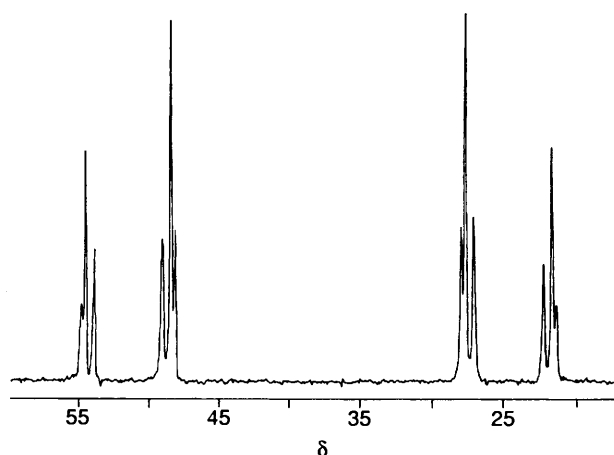
Fig. 1 ^{31}P-$\{^1H\}$ NMR spectrum of complex 1
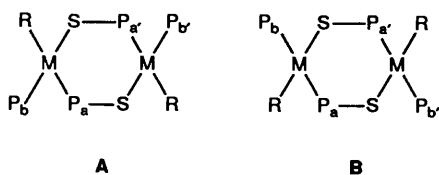
Scheme 2

(signals due to *m*- and *p*-F overlap), revealing: (*a*) that both C₆F₅ groups are equivalent (from the geometry of the molecule, point group C_2), and (*b*) that both halves of each C₆F₅ group are equivalent. The last fact seems to indicate a dynamic process in solution. At low temperature (−80 °C) the spectra of **1** and **3** show that F_o (and F_m as well) are inequivalent, although the spectra of **2** and **4** at this temperature do not show split signals for F_o and F_m. A mechanism which could explain this equivalence is a rapid interconversion between the boat and chair conformations.

Structure of [{Pd(μ-SPPh₂)(C₆F₅)(PPh₃)}₂] **1**.—The structure of complex **1** is depicted in Fig. 2. Selected bond distances and angles are presented in Table 2, atomic coordinates in Table 3. The complex consists of two Pd(C₆F₅)(PPh₃) moieties connected by two bridging [SPPh₂]⁻ ligands. The palladium(II) centres, related by a two-fold axis, display a slightly distorted square-planar environment with the two P donor atoms on each centre mutually *trans*. The six-membered ring Pd(1)–S–P(1')–Pd(1')–S'–P(1) displays a boat conformation. A similar conformation has been observed in [Pt₂H₂(PBuᵗ₃)₂(μ-SPPh₂)₂],^{1b} but in [{Pt(S₂CNPrⁱ₂)(μ-

Table 2 Selected bond lengths (Å) and angles (°) for [{Pd-(μ-SPPh₂)(C₆F₅)(PPh₃)}₂]

P(1)–Pd(1)	2.312(2)	P(2)–Pd(1)	2.361(2)
S–Pd(1)	2.359(2)	C(31)–Pd(1)	2.027(7)
P(1)–S'	2.048(4)		
P(2)–Pd(1)–P(1)	175.3(1)	S–Pd(1)–P(1)	93.2(1)
S–Pd(1)–P(2)	86.9(1)	C(31)–Pd(1)–P(1)	90.2(2)
Pd(1)–S–P(1')	115.3(1)	Pd(1)–P(1)–S'	118.7(1)
C(31)–Pd(1)–P(2)	89.5(2)	C(31)–Pd(1)–S	175.9(2)

SPPh₂)}₂]^{10a} and [Pd₂(μ-SPBuᵗ₂)₂(SPBuᵗ₂)₂]^{3c} the M₂(μ-SPR₂)₂ fragment adopts a chair conformation. This suggests that if monodentate ligands are present the boat conformation is preferred, whereas if a bidentate chelate ligand is linked to each metal(II) centre the chair conformation appears.^{1a}

The Pd–C(C₆F₅), Pd–P(PPh₃), Pd–P(SPPh₂), Pd–S(SPPh₂) and P–S(SPPh₂) distances are similar to related values found in the literature.^{3,8} The P–S distance [2.048(4) Å] is longer than that corresponding to a P=S double bond (1.926–1.966 Å)$^{9-11}$ but shorter than that of a P–S single bond (2.122 Å).^{9} The dihedral angle formed by the best least-squares planes through Pd(1), C(31), P(1), P(2), S and through Pd(1'), C(31'), P(1'), P(2'), S' is 85.9°, *i.e.* both co-ordination planes are almost mutually perpendicular. The torsion angle Pd(1)–P(1)–S'–Pd(1') is 16.9°. The two P atoms and the two S atoms of the (μ-SPPh₂)₂ groups are not coplanar with the S atoms lying 0.17 Å to one side of the best least-squares plane through P(1)–S–P(1')–S' and the P atoms lying 0.04 Å to the other side of the same plane.

[NBu₄]₂[{Pd(μ-SPPh₂)(C₆F₅)₂}₂] **5**.—The reactions of [NBu₄]₂[{Pd(μ-X)(C₆F₅)₂}₂] with HP(S)Ph₂ [X = C₆F₅, Cl (in the presence of NEt₃)] or with LiSPPh₂ (X = Cl) (Scheme 3) allow the synthesis of the anionic dinuclear derivative [NBu₄]₂[{Pd(μ-SPPh₂)(C₆F₅)₂}₂] **5**. However, when similar reactions are carried out with the analogous platinum derivatives [NBu₄]₂[{Pt(μ-X)(C₆F₅)₂}₂] (X = C₆F₅ or Cl) a mixture of complexes that we have not been able to separate is obtained. Complex **5** gave satisfactory elemental analyses and shows in the IR spectrum a strong absorption at 566 cm⁻¹ assignable to ν(P=S). Two bands with similar intensity (778s and 765s cm⁻¹) indicate the presence of two C₆F₅ groups disposed mutually *cis*.^{12}

The ^{31}P-$\{^1H\}$ NMR spectrum (Table 1) shows only a broad singlet at δ 46.08. The ^{19}F NMR spectrum, at room temperature, shows two signals in the *o*- and *p*-F region (*m*-F signals are partially overlapped), again indicating the presence of two types of inequivalent C₆F₅ groups. Both halves of each

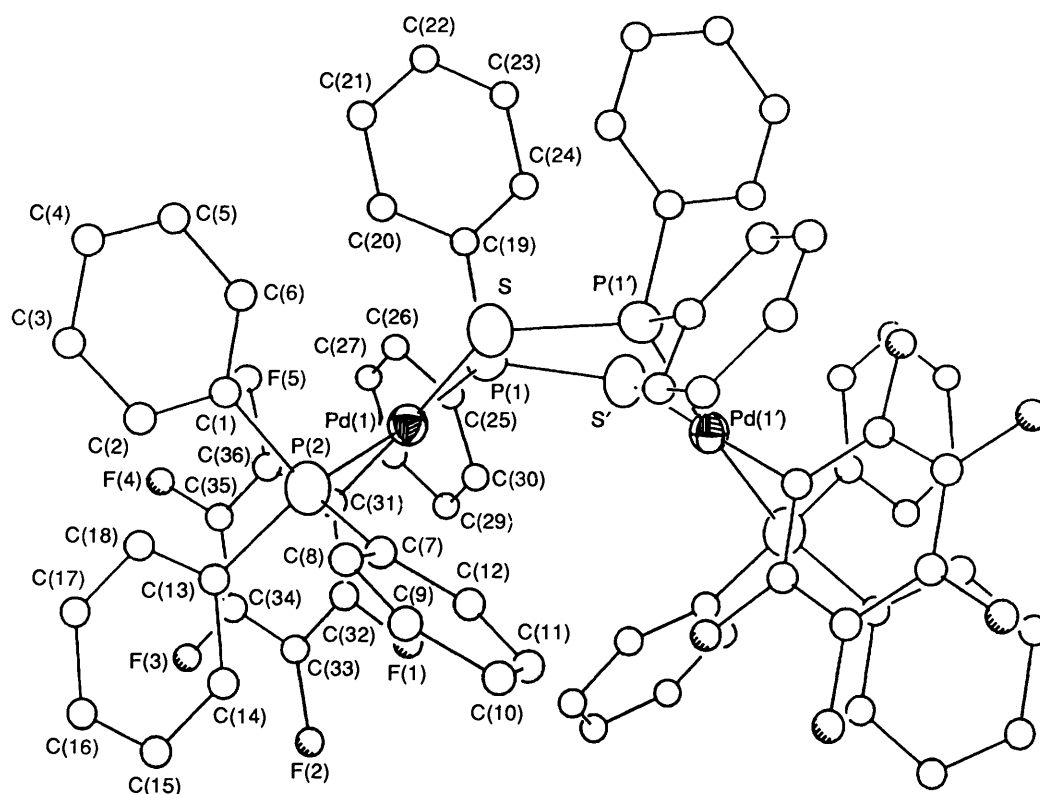**Fig. 2** Molecular structure of the complex $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ **1**

Table 3 Fractional atomic coordinates ($\times 10^4$) for $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pd(1)	5283(1)	5617(1)	1704(1)	C(20)	5056	2896	1444
P(1)	4424(1)	4583(2)	1925(1)	C(21)	5190	1811	1341
P(2)	6179(1)	6564(2)	1425(1)	C(22)	4878	993	1611
S	5943(1)	4758(2)	2336(1)	C(23)	4431	1261	1985
C(1)	6763(2)	5671(5)	1142(2)	C(24)	4296	2346	2088
C(2)	7269	6097	868	C(25)	3714(2)	4772(5)	1517(2)
C(3)	7694	5403	629	C(26)	3540	4053	1113
C(4)	7615	4283	664	C(27)	3018	4273	791
C(5)	7110	3857	937	C(28)	2669	5213	872
C(6)	6684	4551	1176	C(29)	2842	5931	1276
C(7)	6550(2)	7360(5)	1949(2)	C(30)	3364	5711	1598
C(8)	7192	7573	1961	C(31)	4770(3)	6366(6)	1127(3)
C(9)	7447	8258	2348	C(32)	4605(3)	7429(6)	1171(3)
C(10)	7061	8730	2723	C(33)	4278(4)	7986(7)	786(3)
C(11)	6420	8516	2711	C(34)	4098(4)	7466(7)	331(3)
C(12)	6164	7831	2324	C(35)	4243(4)	6388(7)	268(3)
C(13)	6049(2)	7524(4)	882(2)	C(36)	4580(3)	5872(7)	662(3)
C(14)	6059	8642	964	F(1)	4783(2)	8004(3)	1610(2)
C(15)	5907	9344	547	F(2)	4136(3)	9043(4)	8529(2)
C(16)	5744	8927	49	F(3)	3783(3)	8008(5)	−56(2)
C(17)	5734	7809	−32	F(4)	4068(3)	5883(5)	−180(2)
C(18)	5887	7107	384	F(5)	4724(2)	4823(4)	566(2)
C(19)	4608(3)	3164(3)	1818(2)				

C_6F_5 group behave as equivalent which can be explained by assuming the existence of a dynamic process similar to that displayed by the neutral complexes.

Cationic Complexes $[M(SPPh_2)(PPh_3)_2]ClO_4$.—The reaction between $[M(acac-O,O')(PPh_3)_2]ClO_4$ (M = Pd or Pt) and $HP(S)Ph_2$ renders complexes with the stoichiometry $[M(SPPh_2)(PPh_3)_2]ClO_4$ (M = Pd **6** or Pt **7**). Complexes **6** and **7** give satisfactory elemental analyses and show the IR absorption due to $v(P=S)$ at higher frequencies than those for

the dinuclear complexes 1–5 (see Experimental section). The $^{31}P\text{-}\{^1H\}$ NMR spectra (Table 1) of complexes **6** and **7** show a pattern which can be analysed as an AMX spin system (with ^{195}Pt satellites for **7**), pointing to a mononuclear structure C (Scheme 4). A dinuclear system should present, in the $^{31}P\text{-}\{^1H\}$ NMR spectrum, an AA'MM'XX' spin system, as can be seen from D.

The equivalent conductivities (Λ_e) in nitromethane solutions of these cationic complexes at different concentrations give values of A in Onsager's equation $\Lambda_e = \Lambda_o - Ac^{\frac{1}{2}}$ of 153 (**6**)

$2[NBu_4]_2[\{Pd(\mu-C_6F_5)(C_6F_5)_2\}_2]$ $\xrightarrow{(i) \quad -2C_6F_5H}$

$(ii) \quad -2[NEt_3H]Cl$

$2[NBu_4]_2[\{Pd(\mu-Cl)(C_6F_5)_2\}_2]$ $\qquad$ $[NBu_4]_2[\{Pd(\mu-SPPh_2)(C_6F_5)_2\}_2]$

5

$(iii) \quad -2LiCl$
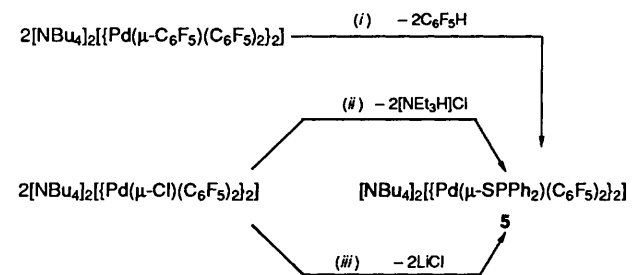
Scheme 3 (i) $2Ph_2P(S)H$, CH_2Cl_2; (ii) $2Ph_2P(S)H$, NEt_3; (iii) thf, N_2, $2LiSPPh_2$

C **D**

Scheme 4
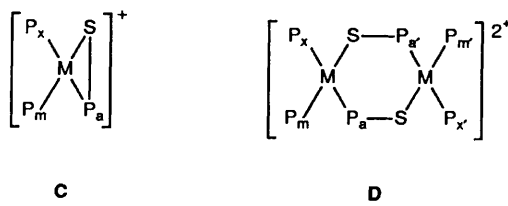
Table 4 Selected bond lengths (Å) and angles (°) for [Pd-$(SPPh_2)(PPh_3)_2]ClO_4\cdot CH_2Cl_2$

| P(1)–Pd	2.377(2)	P(2)–Pd	2.292(2)
P(3)–Pd	2.245(2)	S–Pd	2.387(2)
S–P(3)	2.004(3)		
P(2)–Pd–P(1)	104.2(1)	P(3)–Pd–P(1)	150.1(1)
P(3)–Pd–P(2)	104.5(1)	S–Pd–P(1)	99.4(1)
S–Pd–P(2)	155.1(1)	S–Pd–P(3)	51.2(1)
S–P(3)–Pd	68.1(1)	P(3)–S–Pd	60.8(1)

and 138 ohm^{-1} cm^2 mol^{-1} (**7**), that is in agreement with a mononuclear nature (1 : 1 electrolytes).[13] The X-ray diffraction study of complex **6** confirms the proposed structure.

Structure of [Pd(SPPh$_2$)(PPh$_3$)$_2$]ClO$_4$·CH$_2$Cl$_2$.—The structure of the cation [Pd(SPPh$_2$)(PPh$_3$)$_2$]$^+$ is presented in Fig. 3. Selected bond distances and angles are in Table 4, atomic coordinates in Table 5. The palladium atom has a distorted square-planar environment formed by two P atoms (PPh$_3$ ligands) and the P and S atoms of the SPPh$_2$ chelating group. The very small P(3)–Pd–S angle [51.2(1)°] is a consequence of the chelating nature of the diphenylthiophosphinite, which results in the formation of a three-membered ring. The large P(1)–Pd–P(2) angle [104.2(1)°] is obviously related to that. The four atoms linked to the Pd are coplanar and the Pd atom lies 0.132 Å out of this plane.

The Pd–P and Pd–S distances are in the usual ranges for palladium(ii) complexes with P or S donor ligands.[8b] The rather different Pd–P(PPh$_3$) distances [2.245(2) and 2.377(2) Å] point to the different *trans* influences of the P and S atoms of the SPPh$_2$ group. Finally, the P–S distance [2.004(3) Å] is shorter than that in complex **1** [2.048(4) Å] with a μ-SPPh$_2$ co-ordination mode. This feature is similar to that observed in [Pd$_2$(μ-SPBu$^t_2$)$_2$(SPBu$^t_2$)$_2$].[3c]

Experimental

Materials.—Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Perkin Elmer 883 spectrophotometer and NMR spectra (CDCl$_3$ solvent) with a Varian XL-200 spectrometer. Elemental analyses were carried out with a Perkin Elmer 240-B microanalyser. The starting compounds [M(C$_6$F$_5$)(acac-
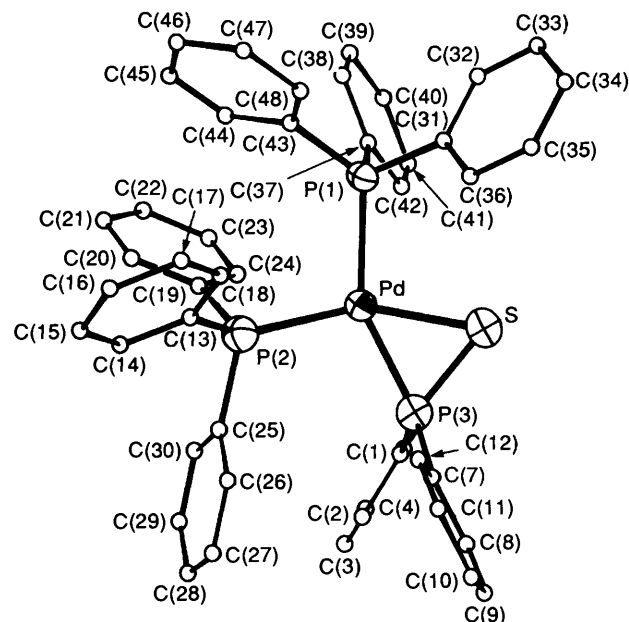
Fig. 3 Molecular structure of [Pd(SPPh$_2$)(PPh$_3$)$_2$]$^+$

$O,O')(PR_3)],$[5] [PdCl(C$_6$F$_5$)(PPh$_3$)$_2$],[14] [NBu$_4$]$_2$[Pd(μ-Cl)-(C$_6$F$_5$)$_2$]$_2$][15] and [NBu$_4$]$_2$[\{Pd(μ-C$_6$F$_5$)(C$_6$F$_5$)$_2$\}$_2$][16] were prepared following the previously reported methods. The complexes [M(acac-O,O')(PPh$_3$)$_2$]ClO$_4$ (M = Pd or Pt) were prepared by adding Tl(acac) to a CH$_2$Cl$_2$ suspension of the corresponding dinuclear complex [\{M(μ-Cl)(PPh$_3$)$_2$\}$_2$][ClO$_4$]$_2$ (M = Pd or Pt).

Preparations.—[\{Pd(μ-SPPh$_2$)(C$_6$F$_5$)(PPh$_3$)\}$_2$] **1**. (a) *From* [Pd(C$_6$F$_5$)(acac-O,O')(PPh$_3$)]. To a colourless solution of [Pd(C$_6$F$_5$)(acac-O,O')(PPh$_3$)] (0.086 g, 0.135 mmol) in CH$_2$Cl$_2$ (20 cm^3) at room temperature was added HP(S)Ph$_2$ (0.029 g, 0.135 mmol). The resulting deep yellow solution was stirred for 1.5 h and evaporated to small volume (ca. 2 cm^3). Addition of hexane (20 cm^3) gave a yellow precipitate of complex **1**. Yield: 0.080 g (80%) (Found: C, 57.75; H, 3.85. C$_{72}$H$_{50}$F$_{10}$P$_4$Pd$_2$S$_2$ requires C, 57.40; H, 3.55%). v(P=S) 565 cm^{-1}.

(b) *From* [Pd(C$_6$F$_5$)(Me$_2$CO)(PPh$_3$)$_2$]ClO$_4$. To an acetone solution (20 cm^3) of [PdCl(C$_6$F$_5$)(PPh$_3$)$_2$] (0.300 g, 0.360 mmol) at room temperature, AgClO$_4$ (0.074 g, 0.360 mmol) was added. After stirring for 30 min, the resulting solution was filtered through Celite to remove the AgCl precipitated and the filtrate was used as a [Pd(C$_6$F$_5$)(Me$_2$CO)(PPh$_3$)$_2$]ClO$_4$ solution. Diphenylthiophosphinic acid (0.078 g, 0.360 mmol) was added and the solution stirred at room temperature for 16 h. Yellow solid complex **1** 0.080 g (30% yield) was obtained.

(c) *From* [PdCl(C$_6$F$_5$)(PPh$_3$)$_2$]. To a solution of HP(S)Ph$_2$ (0.081 g, 0.371 mmol) in toluene (5 cm^3) at room temperature were added LiBu^n (0.82 mol dm^{-3} in hexane, 0.5 cm^3, 0.410 mmol, 10% excess) and thf (15 cm^3). To the resulting pale yellow solution was added [PdCl(C$_6$F$_5$)(PPh$_3$)$_2$] (0.310 g, 0.371 mmol). The mixture was stirred for 1 h at room temperature and then evaporated to dryness. Benzene (15 cm^3) was added to the residue and the resulting suspension was filtered through Celite to remove the precipitated LiCl. The resulting solution was evaporated to dryness. Addition of Et$_2$O (20 cm^3) rendered complex **1**. Yield: 0.140 g (50%).

Complexes [\{M(μ-SPPh$_2$)(C$_6$F$_5$)(PR$_3$)\}$_2$] **2** (M = Pd, PR$_3$ = PPh$_2$Et), **3** (M = Pt, PR$_3$ = PPh$_3$) and **4** (M = Pt, PR$_3$ = PPh$_2$Et) were prepared as for **1** following method (a). Preparative details: **2**; [Pd(C$_6$F$_5$)(acac-O,O')(PPh$_2$Et)] (0.139 g, 0.236 mmol), HP(S)Ph$_2$ (0.052 g, 0.236 mmol), yield 0.103 g (62%) (Found: C, 53.55; H, 3.45. C$_{64}$H$_{50}$F$_{10}$P$_4$Pd$_2$S$_2$ requires

Table 5 Fractional atomic coordinates (× 10⁴) for [Pd(SPPh₂)(PPh₃)₂]ClO₄·CH₂Cl₂

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pd	8 055(1)	349(1)	3 196(1)	C(27)	6 258	3 044	3 167
P(1)	6 754(1)	193(1)	3 845(1)	C(28)	6 755	3 124	3 891
P(2)	7 618(1)	1 311(1)	2 441(1)	C(29)	7 509	2 664	4 162
P(3)	9 583(1)	136(1)	3 086(1)	C(30)	7 766	2 125	3 709
S	9 153(2)	−492(1)	3 852(1)	C(31)	5 540(3)	434(3)	3 408(3)
C(1)	9 928(4)	−352(3)	2 346(3)	C(32)	5 252	1 146	3 371
C(2)	10 889	−459	2 297	C(33)	4 333	1 329	3 015
C(3)	11 133	−899	1 743	C(34)	3 701	800	2 696
C(4)	10 416	−1 230	1 237	C(35)	3 988	88	2 733
C(5)	9 455	−1 122	1 286	C(36)	4 908	−95	3 089
C(6)	9 211	−683	1 840	C(37)	6 977(3)	666(3)	4 734(2)
C(7)	10 447(3)	794(3)	3 419(3)	C(38)	6 236	922	5 074
C(8)	10 878	1 189	2 921	C(39)	6 444	1 263	5 761
C(9)	11 474	1 762	3 174	C(40)	7 394	1 347	6 109
C(10)	11 638	1 940	3 926	C(41)	8 136	1 092	5 770
C(11)	11 207	1 545	4 425	C(42)	7 927	751	5 082
C(12)	10 612	972	4 172	C(43)	6 648(4)	−733(2)	4 110(3)
C(13)	6 666(3)	1 182(3)	1 666(3)	C(44)	6 812	−1 261	3 609
C(14)	6 460	1 694	1 108	C(45)	6 673	−1 976	3 768
C(15)	5 710	1 584	516	C(46)	6 370	−2 165	4 428
C(16)	5 167	961	481	C(47)	6 207	−1 637	4 930
C(17)	5 374	448	1 038	C(48)	6 346	−922	4 771
C(18)	6 123	558	1 630	C(49)	2 689(10)	752(12)	507(12)
C(19)	8 559(3)	1 691(3)	1 992(3)	Cl(1)	1 868(4)	1 130(3)	865(3)
C(20)	9 029	2 324	2 234	Cl(2)	2 513(6)	−156(3)	287(4)
C(21)	9 739	2 593	1 868	Cl(3)	6 464(2)	−1 576(1)	1 473(1)
C(22)	9 978	2 228	1 260	O(1)	7 006(7)	−1 993(5)	1 997(4)
C(23)	9 508	1 596	1 019	O(2)	5 819(6)	−1 150(4)	1 754(6)
C(24)	8 798	1 327	1 385	O(3)	5 939(10)	−1 995(8)	983(7)
C(25)	7 270(4)	2 045(3)	2 985(3)	O(4)	6 936(8)	−1 264(9)	981(9)
C(26)	6 516	2 505	2 714				

C, 54.50; H, 3.55%), v(P=S) 565 cm⁻¹; 3 [Pt(C₆F₅)(acac-O,O′)(PPh₃)] (0.150 g, 0.207 mmol), HP(S)Ph₂ (0.045 g, 0.207 mmol), yield 0.055 g (30%) (Found: C, 50.45; H, 3.00. C₇₂H₅₀F₁₀P₄Pt₂S₂ requires C, 51.35; H, 3.00%), v(P=S) 570 cm⁻¹; 4, [Pt(C₆F₅)(acac-O,O′)(PPh₂Et)] (0.200 g, 0.296 mmol), HP(S)Ph₂ (0.065 g, 0.296 mmol), yield 0.12 g (51%) (Found: C, 44.00; H, 3.50. C₆₄H₅₀F₁₀P₄Pt₂S₂·3CH₂Cl₂ requires C, 43.70; H, 3.05%), v(P=S) 569 cm⁻¹.

[NBu₄]₂[{Pd(μ-SPPh₂)(C₆F₅)₂}₂] 5. (a) From [NBu₄]₂-[{Pd(μ-C₆F₅)(C₆F₅)₂}₂]. To a CH₂Cl₂ (20 cm³) solution of [NBu₄]₂[{Pd(μ-C₆F₅)(C₆F₅)₂}₂] (0.170 g, 0.100 mmol) under nitrogen was added HP(S)Ph₂ (0.044 g, 0.200 mmol) and the mixture was stirred at room temperature for 14 h and then evaporated to dryness. Addition of hexane (25 cm³) gave a pale yellow solid. Yield: 0.130 g (73%) (Found: C, 53.15; H, 5.35; N, 1.45: C₈₀H₉₂F₁₀N₂P₂Pd₂S₂ requires C, 53.35; H, 5.15; N, 1.55%), v(P=S) 566 cm⁻¹.

(b) From [NBu₄]₂[{Pd(μ-Cl)(C₆F₅)₂}₂]. To a solution of LiSPPh₂ (0.358 mmol) in thf–toluene (3:1, 20 cm³) at room temperature under nitrogen, was added [NBu₄]₂[{Pd(μ-Cl)(C₆F₅)₂}₂] (0.258 g, 0.179 mmol). After 3 h of stirring the solution was evaporated almost to dryness (ca. 2 cm³); the addition of PrⁱOH (20 cm³) gave a pale yellow solid. Yield: 0.172 g (53%). Alternatively to a thf solution (25 cm³) of [NBu₄]₂[{Pd(μ-Cl)(C₆F₅)₂}₂] (0.400 g, 0.278 mmol) were added NEt₃ (0.1 cm³, 0.723 mmol) and HP(S)Ph₂ (0.121 g, 0.556 mmol). The mixture was stirred for 14 h at room temperature and then evaporated almost to dryness (ca. 2 cm³); the addition of PrⁱOH (15 cm³) rendered complex 5. Yield: 0.220 g (44%).

[Pd(SPPh₂)(PPh₃)₂]ClO₄ 6. To a CH₂Cl₂ solution (20 cm³) of [Pd(acac-O,O′)(PPh₃)₂]ClO₄ (0.155 g, 0.187 mmol) was added HP(S)Ph₂ (0.041 g, 0.187 mmol). The mixture was stirred at room temperature for 5 h; afterwards the solution was evaporated to dryness and the addition of Et₂O gave a deep yellow solid. Yield: 0.162 g (91%) (Found: C, 60.00; H, 4.30.

C₄₈H₄₀ClO₄P₃PdS requires C, 60.85; H, 4.25%), v(P=S) 598 cm⁻¹.

[Pt(SPPh₂)(PPh₃)₂]ClO₄. Complex 7 was prepared in a similar way from [Pt(acac-O,O′)(PPh₃)₂]ClO₄ (0.200 g, 0.218 mmol) and HP(S)Ph₂ (0.048 g, 0.218 mmol). Yield: 0.180 g (80%) (Found: C, 55.90; H, 4.00. C₄₈H₄₀ClO₄P₃PtS requires C, 55.65; H, 3.90%) v(P=S) 593 cm⁻¹.

Crystal Structure Determinations.—Suitable crystals of compounds 1 and 6 were obtained by slow diffusion of hexane into a CH₂Cl₂ solution of the corresponding crude products. Intensity data were recorded at room temperature using graphite-monochromated Mo-Kα X-radiation. For 1 data were collected on a Siemens STOE/AED-2 four-circle diffractometer (4 ≤ 2θ ≤ 50°). Accurate lattice parameters were determined from accurate positions of 25 reflections (10 ≤ 2θ ≤ 25°). Intensity data were corrected for Lorentz and polarization effects. For compound 6·CH₂Cl₂, an Enraf-Nonius CAD4 diffractometer was employed (2 ≤ 2θ ≤ 44°). Accurate lattice parameters determined from the positions of 25 reflections (26 ≤ 2θ ≤ 28°). Intensity data were corrected for Lorentz and polarization effects.

Crystal data. C₇₂H₅₀F₁₀P₄Pd₂S₂, 1 M = 1505.89, monoclinic, space group C2/c, a = 21.361(2), b = 12.336(1), c = 25.234(2) Å, β = 91.14(1)°, U = 6648.1 Å³, Z = 4 (C₂ symmetry imposed), Dc = 1.50 g cm⁻³, F(000) = 3024, μ = 7.57 cm⁻¹, 5204 unique data, 3434 observed data [F > 5σ(F)] for the refinement of 346 parameters, scan method 2θ–ω, w = 1.2344/[σ²(F) + 0.001 32F²], R = 0.048, R′ = 0.048, Δ/σ = 0.001, largest difference peaks 0.68, −0.48 e Å⁻³.

C₄₉H₄₂Cl₃P₃PdSO₄, 6 M = 1032.62, monoclinic, space group P2₁/c, a = 14.173(5), b = 18.758(6), c = 18.280(9) Å, β = 99.99(3)°, U = 4786.2 Å³, Z = 4, Dc = 1.43 g cm⁻³, F(000) = 2104, μ = 7.33 cm⁻¹, 5851 unique data, 4583 observed data [F > 4σ(F)] for the refinement of 454 parameters, scan method 2θ–ω, w = 1.8525/[σ²(F) + 0.001 47F²], R = 0.055,

$R' = 0.062$, $\Delta/\sigma = 0.002$, largest difference peaks 0.95, $-0.72e$ Å^{-3}.

Structure solution and refinement. The structures were solved by the use of Patterson and Fourier methods. All calculations were carried out with SHELX 76[17] and 86.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters. The carbon atoms of the Ph groups were refined as rigid rings. Hydrogen atoms were omitted. Calculations by full-matrix least squares were performed on a Micro-VAX 8300 computer.

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

Acknowledgements

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