Different Co-ordination Modes of the Ligand $[SPPh_2]^-$ in Complexes of Pd^{II} and Pt^{II}. Crystal Structures of $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ and $[Pd(SPPh_2)(PPh_3)_2]ClO_4{\cdot}CH_2Cl_2$†

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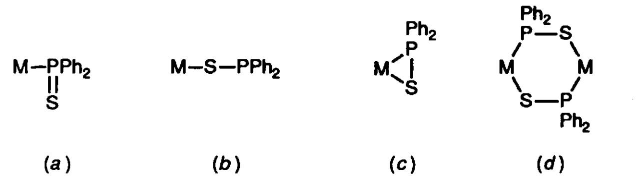
The neutral complexes $[\{M(\mu\text{-}SPPh_2)(C_6F_5)(PR_3)\}_2]$ (M = Pd or Pt; PR_3 = PPh_3 or PPh_2Et) containing the P,S-bridging $[SPPh_2]^-$ have been synthesised by reaction of the corresponding acetylacetonate (acac) derivatives $[M(C_6F_5)(acac\text{-}O,O')(PR_3)]$ with $HP(S)Ph_2$. However, the reaction of the cationic complexes $[M(acac\text{-}O,O')(PPh_3)_2]ClO_4$ (M = Pd or Pt) with $HP(S)Ph_2$ affords mononuclear $[M(SPPh_2)(PPh_3)_2]ClO_4$ in which the $[SPPh_2]^-$ ligand is co-ordinated as a P,S-chelate. The anionic complex $[NBu_4]_2[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)_2\}_2]$ has also been synthesised. The crystal structures of $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ and $[Pd(SPPh_2)(PPh_3)_2]ClO_4{\cdot}CH_2Cl_2$ have been determined by X-ray diffraction methods; the former adopts a boat conformation.

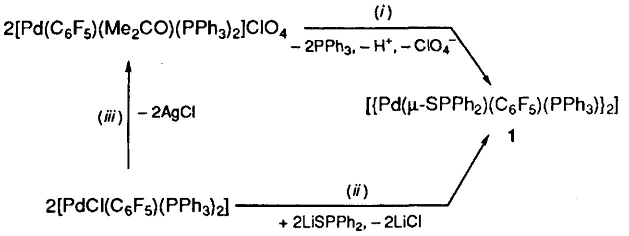
The anionic ligand $[SPPh_2]^-$ (diphenylthiophosphinite) can be co-ordinated to metal centres as: (*a*) P-monodentate,[1] (*b*) S-monodentate,[1a,2] (*c*) P,S-chelate[1a,3c,4] or (*d*) di-μ-P,S-bridge,[1,3] the last representing the most numerous group, probably due to the stability of the six-membered ring generated.[1a]



In the course of our current research on the reactivity of perhalogenophenyl derivatives of Pd^{II} and Pt^{II} with polyfunctional anionic ligands such as $[Ph_2PCHPPh_2]^-$ or $[C(PPh_2)_3]^-$ 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 $HP(S)Ph_2$ with neutral or cationic acac-*O,O′* derivatives of Pd^{II} or Pt^{II} which render di- or mono-nuclear $SPPh_2$ complexes depending on the starting materials.

Results and Discussion

Neutral Complexes $[\{M(\mu\text{-}SPPh_2)(C_6F_5)(PR_3)\}_2]$.—The reaction of the neutral derivatives $[M(C_6F_5)(acac\text{-}O,O')(PR_3)]$ (M = Pd or Pt; PR_3 = PPh_3 or PPh_2Et) with $H(S)PPh_2$ in CH_2Cl_2 solution, at room temperature, results in displacement of the $acac^-$ group as Hacac and co-ordination of the $[SPPh_2]^-$ anion as a bridging ligand, yielding the corresponding neutral dinuclear derivatives $[\{M(\mu\text{-}SPPh_2)(C_6F_5)(PR_3)\}_2]$ (M = Pd, PR_3 = PPh_3 **1** or PPh_2Et **2**; M = Pt, PR_3 = PPh_3 **3** or PPh_2Et **4**) [equation (1)]. Complex **1** can also be obtained, although in lower yields, through two other synthetic procedures (Scheme 1): (*a*) $[Pd(C_6F_5)(Me_2CO)(PPh_3)_2]ClO_4$ reacts with $H(S)PPh_2$ in acetone; (*b*) the reaction between $[PdCl(C_6F_5)(PPh_3)_2]$ and $LiSPPh_2$ in tetrahydrofuran (thf)–toluene.



Scheme 1 (*i*) $2Ph_2P(S)H$, Me_2CO; (*ii*) thf–toluene, N_2; (*iii*) $2AgClO_4$, Me_2CO

$$2[M(C_6F_5)(acac\text{-}O,O')(PR_3)] + 2Ph_2P(S)H \longrightarrow [\{M(\mu\text{-}SPPh_2)(C_6F_5)(PR_3)\}_2] + 2Hacac \quad (1)$$

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 $[SPPh_2]^-$; it appears at lower wavenumbers than for unco-ordinated diphenylphosphine sulfide (640 cm^{-1}).[6] Characteristic absorptions assignable to the presence of C_6F_5 groups[5,7] are observed. The analytical and IR data are not sufficiently informative to infer the structural configuration of these compounds, but the $^{31}P\text{-}\{^1H\}$ and ^{19}F NMR data do (Table 1).

The $^{31}P\text{-}\{^1H\}$ 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 $^2J(P_a\text{–}P_b)$ (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 $(\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ **1** confirms geometry **B**, and shows that the central portion of the molecule adopts a boat conformation.

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Fluorine-19 and ^{31}P-{^{1}H} 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 $CDCl_3$. ^{c} ^{19}F NMR spectrum measured at −80 °C in CD_2Cl_2. ^{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.

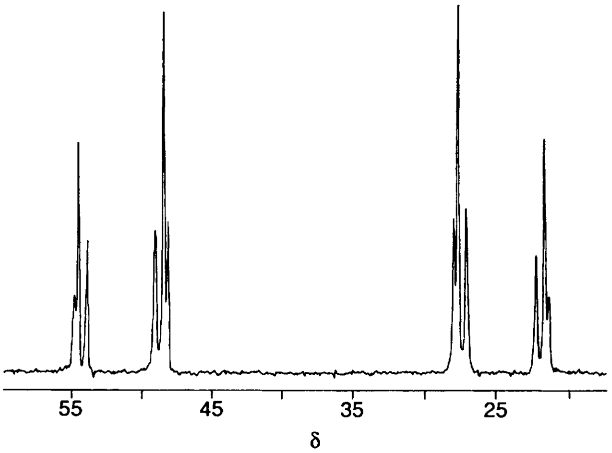
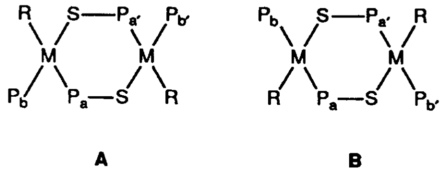


Fig. 1 ^{31}P-{^{1}H} NMR spectrum of complex **1**



Scheme 2

Table 2 Selected bond lengths (Å) and angles (°) for [{Pd(μ-$SPPh_2$)(C_6F_5)(PPh_3)}$_2$]

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)

(signals due to *m*- and *p*-F overlap), revealing: (*a*) that both C_6F_5 groups are equivalent (from the geometry of the molecule, point group C_2), and (*b*) that both halves of each C_6F_5 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-$SPPh_2$)(C_6F_5)(PPh_3)}$_2$] **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(C_6F_5)(PPh_3) moieties connected by two bridging [$SPPh_2$]$^-$ 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 [$Pt_2H_2(PBu^t_3)_2$(μ-$SPPh_2$)$_2$],[1b] but in [{Pt($S_2CNPr^i_2$)(μ-$SPPh_2$)}$_2$][10a] and [Pd_2(μ-$SPBu^t_2$)$_2$($SPBu^t_2$)$_2$][3c] the M_2(μ-SPR_2)$_2$ 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(C_6F_5), Pd–P(PPh_3), Pd–P($SPPh_2$), Pd–S($SPPh_2$) and P–S($SPPh_2$) 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-$SPPh_2$)$_2$ 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.

[NBu_4]$_2$[{Pd(μ-$SPPh_2$)(C_6F_5)$_2$}$_2$] **5**.—The reactions of [NBu_4]$_2$[{Pd(μ-X)(C_6F_5)$_2$}$_2$] with HP(S)Ph_2 [X = C_6F_5, Cl (in the presence of NEt_3)] or with Li$SPPh_2$ (X = Cl) (Scheme 3) allow the synthesis of the anionic dinuclear derivative [NBu_4]$_2$[{Pd(μ-$SPPh_2$)(C_6F_5)$_2$}$_2$] **5**. However, when similar reactions are carried out with the analogous platinum derivatives [NBu_4]$_2$[{Pt(μ-X)(C_6F_5)$_2$}$_2$] (X = C_6F_5 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 C_6F_5 groups disposed mutually *cis*.[12]

The ^{31}P-{^{1}H} 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 C_6F_5 groups. Both halves of each

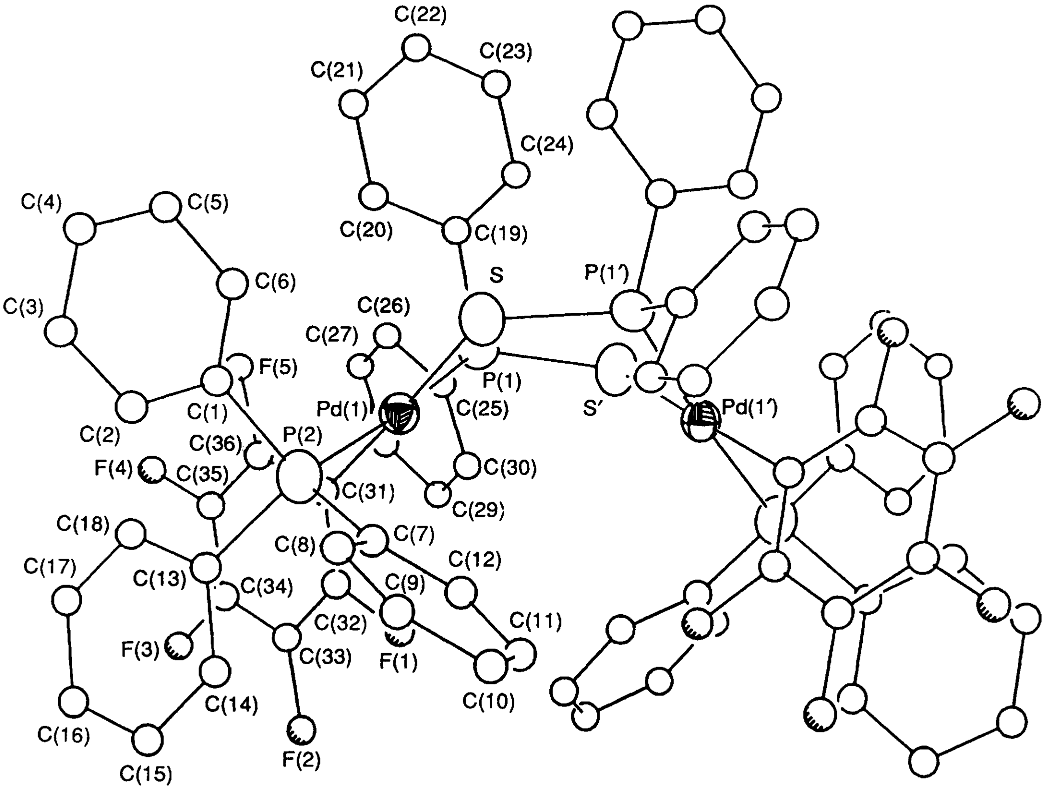


Fig. 2 Molecular structure of the complex $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ **1**

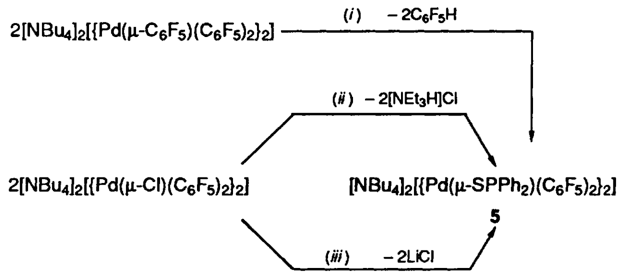
Table 3 Fractional atomic coordinates ($\times 10^4$) for $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$

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)				

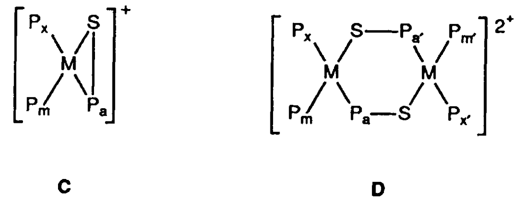
C_6F_5 group behave as equivalent which can be explained by assuming the existence of a dynamic process similar to that displayed by the neutral complexes.

Cationic Complexes $[M(SPPh_2)(PPh_3)_2]ClO_4$.—The reaction between $[M(acac\text{-}O,O')(PPh_3)_2]ClO_4$ (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 ν(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**)



Scheme 3 (*i*) $2Ph_2P(S)H$, CH_2Cl_2; (*ii*) $2Ph_2P(S)H$, NEt_3; (*iii*) thf, N_2, $2LiSPPh_2$



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 $[Pd(SPPh_2)(PPh_3)_2]ClO_4 \cdot CH_2Cl_2$.—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 $[Pd_2(\mu\text{-}SPBu^t{}_2)_2(SPBu^t{}_2)_2]$.[3c]

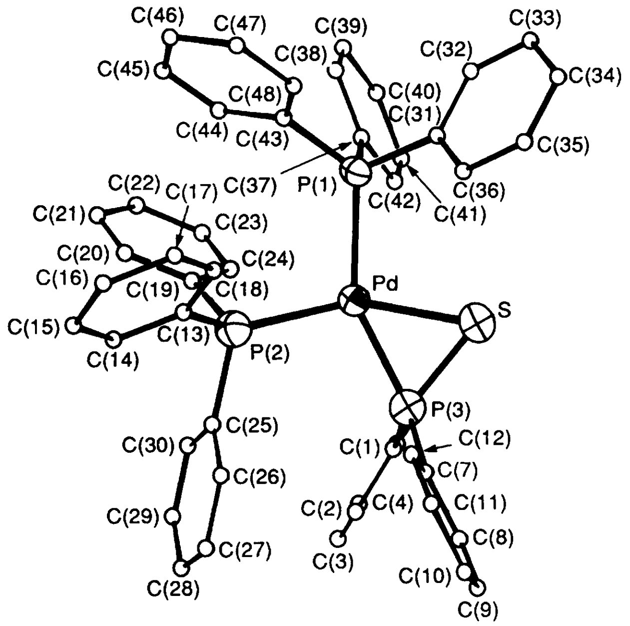


Fig. 3 Molecular structure of $[Pd(SPPh_2)(PPh_3)_2]^+$

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_6F_5)(acac-*O,O′*)(PR_3)],[5] [PdCl(C_6F_5)(PPh_3)$_2$],[14] $[NBu_4]_2[Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2]$[15] and $[NBu_4]_2[\{Pd(\mu\text{-}C_6F_5)(C_6F_5)_2\}_2]$[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_2Cl_2 suspension of the corresponding dinuclear complex $[\{M(\mu\text{-}Cl)(PPh_3)_2\}_2][ClO_4]_2$ (M = Pd or Pt).

Preparations.—$[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ **1**. (*a*) *From* [Pd(C_6F_5)(acac-*O,O′*)(PPh_3)]. To a colourless solution of [Pd(C_6F_5)(acac-*O,O′*)(PPh_3)] (0.086 g, 0.135 mmol) in CH_2Cl_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. $C_{72}H_{50}F_{10}P_4Pd_2S_2$ requires C, 57.40; H, 3.55%). ν(P=S) 565 cm^{-1}.

(*b*) *From* $[Pd(C_6F_5)(Me_2CO)(PPh_3)_2]ClO_4$. To an acetone solution (20 cm^3) of $[PdCl(C_6F_5)(PPh_3)_2]$ (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 $[Pd(C_6F_5)(Me_2CO)(PPh_3)_2]ClO_4$ 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* $[PdCl(C_6F_5)(PPh_3)_2]$. 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 $[PdCl(C_6F_5)(PPh_3)_2]$ (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_2O (20 cm^3) rendered complex **1**. Yield: 0.140 g (50%).

Complexes $[\{M(\mu\text{-}SPPh_2)(C_6F_5)(PR_3)\}_2]$ **2** (M = Pd, PR_3 = PPh_2Et), **3** (M = Pt, PR_3 = PPh_3) and **4** (M = Pt, PR_3 = PPh_2Et) were prepared as for **1** following method (*a*). Preparative details: **2**; [Pd(C_6F_5)(acac-*O,O′*)(PPh_2Et)] (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. $C_{64}H_{50}F_{10}P_4Pd_2S_2$ requires

Table 5 Fractional atomic coordinates (× 10^4) for $[Pd(SPPh_2)(PPh_3)_2]ClO_4{\cdot}CH_2Cl_2$

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

C, 54.50; H, 3.55%), ν(P=S) 565 cm^{-1}; **3** $[Pt(C_6F_5)$(acac-*O,O'*)$(PPh_3)]$ (0.150 g, 0.207 mmol), $HP(S)Ph_2$ (0.045 g, 0.207 mmol), yield 0.055 g (30%) (Found: C, 50.45; H, 3.00. $C_{72}H_{50}F_{10}P_4Pt_2S_2$ requires C, 51.35; H, 3.00%), ν(P=S) 570 cm^{-1}; **4**, $[Pt(C_6F_5)$(acac-*O,O'*)$(PPh_2Et)]$ (0.200 g, 0.296 mmol), $HP(S)Ph_2$ (0.065 g, 0.296 mmol), yield 0.12 g (51%) (Found: C, 44.00; H, 3.50. $C_{64}H_{50}F_{10}P_4Pt_2S_2{\cdot}3CH_2Cl_2$ requires C, 43.70; H, 3.05%), ν(P=S) 569 cm^{-1}.

$[NBu_4]_2[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)_2\}_2]$ **5**. (*a*) *From* $[NBu_4]_2[\{Pd(\mu\text{-}C_6F_5)(C_6F_5)_2\}_2]$. To a CH_2Cl_2 (20 cm^3) solution of $[NBu_4]_2[\{Pd(\mu\text{-}C_6F_5)(C_6F_5)_2\}_2]$ (0.170 g, 0.100 mmol) under nitrogen was added $HP(S)Ph_2$ (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 cm^3) gave a pale yellow solid. Yield: 0.130 g (73%) (Found: C, 53.15; H, 5.35; N, 1.45: $C_{80}H_{92}F_{10}N_2P_2Pd_2S_2$ requires C, 53.35; H, 5.15; N, 1.55%), ν(P=S) 566 cm^{-1}.

(*b*) *From* $[NBu_4]_2[\{Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2]$. To a solution of $LiSPPh_2$ (0.358 mmol) in thf–toluene (3 : 1, 20 cm^3) at room temperature under nitrogen, was added $[NBu_4]_2[\{Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ (0.258 g, 0.179 mmol). After 3 h of stirring the solution was evaporated almost to dryness (*ca.* 2 cm^3); the addition of Pr^iOH (20 cm^3) gave a pale yellow solid. Yield: 0.172 g (53%). Alternatively to a thf solution (25 cm^3) of $[NBu_4]_2[\{Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ (0.400 g, 0.278 mmol) were added NEt_3 (0.1 cm^3, 0.723 mmol) and $HP(S)Ph_2$ (0.121 g, 0.556 mmol). The mixture was stirred for 14 h at room temperature and then evaporated almost to dryness (*ca.* 2 cm^3); the addition of Pr^iOH (15 cm^3) rendered complex **5**. Yield: 0.220 g (44%).

$[Pd(SPPh_2)(PPh_3)_2]ClO_4$ **6**. To a CH_2Cl_2 solution (20 cm^3) of [Pd(acac-*O,O'*)$(PPh_3)_2]ClO_4$ (0.155 g, 0.187 mmol) was added $HP(S)Ph_2$ (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 Et_2O gave a deep yellow solid. Yield: 0.162 g (91%) (Found: C, 60.00; H, 4.30. $C_{48}H_{40}ClO_4P_3PdS$ requires C, 60.85; H, 4.25%), ν(P=S) 598 cm^{-1}.

$[Pt(SPPh_2)(PPh_3)_2]ClO_4$. Complex **7** was prepared in a similar way from [Pt(acac-*O,O'*)$(PPh_3)_2]ClO_4$ (0.200 g, 0.218 mmol) and $HP(S)Ph_2$ (0.048 g, 0.218 mmol). Yield: 0.180 g (80%) (Found: C, 55.90; H, 4.00. $C_{48}H_{40}ClO_4P_3PtS$ requires C, 55.65; H, 3.90%) ν(P=S) 593 cm^{-1}.

Crystal Structure Determinations.—Suitable crystals of compounds **1** and **6** were obtained by slow diffusion of hexane into a CH_2Cl_2 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 ($4 \leqslant 2\theta \leqslant 50°$). Accurate lattice parameters were determined from accurate positions of 25 reflections ($10 \leqslant 2\theta \leqslant 25°$). Intensity data were corrected for Lorentz and polarization effects. For compound **6**$\cdot CH_2Cl_2$, an Enraf-Nonius CAD4 diffractometer was employed ($2 \leqslant 2\theta \leqslant 44°$). Accurate lattice parameters determined from the positions of 25 reflections ($26 \leqslant 2\theta \leqslant 28°$). Intensity data were corrected for Lorentz and polarization effects.

Crystal data. $C_{72}H_{50}F_{10}P_4Pd_2S_2$, **1** $M = 1505.89$, monoclinic, space group $C2/c$, $a = 21.361(2)$, $b = 12.336(1)$, $c = 25.234(2)$ Å, $\beta = 91.14(1)°$, $U = 6648.1$ Å^3, $Z = 4$ (C_2 symmetry imposed), $D_c = 1.50$ g cm^{-3}, $F(000) = 3024$, $\mu = 7.57$ cm^{-1}, 5204 unique data, 3434 observed data [$F > 5\sigma(F)$] for the refinement of 346 parameters, scan method 2θ–ω, $w = 1.2344/[\sigma^2(F) + 0.001\,32F^2]$, $R = 0.048$, $R' = 0.048$, $\Delta/\sigma = 0.001$, largest difference peaks 0.68, −0.48 e Å^{-3}.

$C_{49}H_{42}Cl_3P_3PdSO_4$, **6** $M = 1032.62$, monoclinic, space group $P2_1/c$, $a = 14.173(5)$, $b = 18.758(6)$, $c = 18.280(9)$ Å, $\beta = 99.99(3)°$, $U = 4786.2$ Å^3, $Z = 4$, $D_c = 1.43$ g cm^{-3}, $F(000) = 2104$, $\mu = 7.33$ cm^{-1}, 5851 unique data, 4583 observed data [$F > 4\sigma(F)$] for the refinement of 454 parameters, scan method 2θ–ω, $w = 1.8525/[\sigma^2(F) + 0.001\,47F^2]$, $R = 0.055$,

$R' = 0.062$, $\Delta/\sigma = 0.002$, 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.

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