Bis(perhalogenophenyl) Derivatives of Palladium(II) and Platinum(II) containing $S_2CP(C_6H_{11})_3$ as a Mono- or Bi-dentate Ligand. Crystal Structures of *cis*-$[Pd(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$ and *cis*-$[Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(CO)]$†

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Addition of $S_2CP(C_6H_{11})_3$ to solutions of $[M(C_6X_5)_2(OC_4H_8)_2]$ (M = Pd or Pt; X = F or Cl) affords the derivatives $[M(C_6X_5)_2\{S_2CP(C_6H_{11})_3\}]$, which are the first containing $S_2CP(C_6H_{11})_3$ chelate-bonded to palladium or platinum. Reaction of the above complexes with 1 mol equivalent of a neutral monodentate ligand L leads to $[M(C_6X_5)_2\{SC(S)P(C_6H_{11})_3\}L]$ (L = PPh_3, X = F, M = Pd or Pt; L = CO, X = F or Cl, M = Pt; L = pyridine, X = F, M = Pt) where $S_2CP(C_6H_{11})_3$ is monodentate. The structure of one example of each of these types has been determined by single-crystal *X*-ray crystallography: *cis*-$[Pd(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$, space group $C2/c$, $a = 26.654(8)$, $b = 11.519(3)$, $c = 24.223(7)$ Å, $\beta = 116.93(3)°$, $Z = 8$, and $R = 0.045$; *cis*-$[Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(CO)]$, space group $P\bar{1}$, $a = 9.864(2)$, $b = 14.202(3)$, $c = 14.638(5)$ Å, $\alpha = 93.44(3)$, $\beta = 103.11(2)$, $\gamma = 105.45(2)°$, $Z = 2$, and $R = 0.042$. The co-ordination at the metal atoms is planar. In the palladium derivative the chelating S_2CP group makes a dihedral angle of 12.3° to the ligand plane; in the platinum derivative the corresponding angle formed by the monodentate ligand is 55.3°.

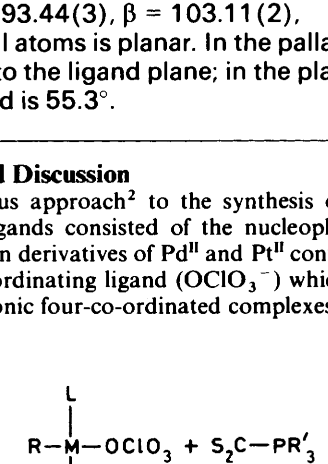
The zwitterionic moieties $R_3P^+{-}CS_2^-$ have nucleophilic character and a series of complexes with different electrophiles (L_nM) containing transition metals have been described. They are very versatile ligands, capable of acting as a monodentate σ-S donor,[1,2] as a bidentate (bridging) σ-S,S′ donor,[3] as a chelate,[3–6] or even as a four-electron pseudo-allylic ligand.[1]

For M = Pd or Pt we have recently reported[2] the preparation of the cationic derivatives $[M(C_6F_5)\{SC(S)PR'_3\}(PR_3)_2]ClO_4$, containing monodentate $R_3P^+{-}CS_2^-$, and therefore four-co-ordinated square-planar Pd (or Pt), as confirmed by a single-crystal *X*-ray diffraction study of the complex with R = R′ = Et, M = Pd. On the other hand, other authors[7] have described the preparation of neutral and cationic palladium complexes and, on the basis of indirect spectroscopic data (i.r. and n.m.r.) (which, however, are compatible with monodentate R_3PCS_2 and therefore with four-co-ordinated palladium) have proposed structures with five- or six-co-ordinated Pd {*i.e.* the proposed six-co-ordinated complex $[Pd(C_6H_5)(SCS)(S_2CPMe_3)(PMe_3)_2]BPh_4$ with bidentate S_2CPMe_3 could also be $[Pd(C_6H_5)(S_2CPMe_3)(PMe_3)_2]BPh_4{\cdot}CS_2$, with monodentate S_2CPMe_3 and unco-ordinated crystal CS_2}.

In the present paper we describe the preparation and reactivity of four-co-ordinated complexes of Pd^{II} and Pt^{II} that contain either a genuine chelate-bonded $R_3P^+{-}CS_2^-$ ligand or a monodentate $R_3P^+{-}CS_2^-$ ligand. The structures of *cis*-$[Pd(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$ and *cis*-$[Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(CO)]$ have been established by *X*-ray diffraction.

Results and Discussion

Our previous approach[2] to the synthesis of complexes with $R_3P{\cdot}CS_2$ ligands consisted of the nucleophilic attack of the betaine upon derivatives of Pd^{II} and Pt^{II} containing an anionic, weakly co-ordinating ligand ($OClO_3^-$) which leads [equation (1)] to cationic four-co-ordinated complexes. In order to force the betaine to act as a chelate, it seems convenient to find precursors containing *two* substitution-labile groups, *i.e.* of the type MR_2L_2 (L = weak ligand), such as those we have recently prepared[8] [M = Pd or Pt; R = C_6F_5 or C_6Cl_5; L = tetrahydrofuran (thf)] and whose reactivity is presently being studied. Thus, the reaction [equation (2)] of these complexes with $(C_6H_{11})_3P^+{-}CS_2^-$ leads to the neutral compounds (**1**)—(**4**).



$$R-\underset{L}{\overset{L}{M}}-OClO_3 + S_2C-PR'_3 \longrightarrow \left[R-\underset{L}{\overset{L}{M}}-SC(S)-PR'_3\right]ClO_4 \qquad (1)$$

Complexes (**1**)—(**4**) and the betaine are insoluble in the reaction medium and the use of an excess of the betaine therefore precipitates mixtures that are difficult to separate {*i.e.* the formation of $[MR_2\{SC(S)P(C_6H_{11})_3\}_2]$ cannot be observed}. Employing a slight deficit of the betaine allows the

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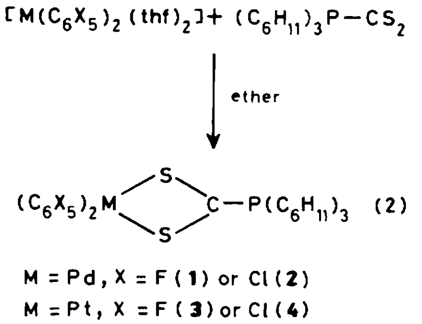
† *cis*-Bis(pentafluorophenyl)(tricyclohexylphosphoniodithioformate-*SS′*)palladium(II) and *cis*-carbonylbis(pentafluorophenyl)(tricyclohexylphosphoniodithioformate-*S*)platinum(II).

Supplementary data available: complete bond lengths and angles, structure factors, H-atom co-ordinates, thermal parameters can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, W. Germany. Please quote reference number CSD/51525 and a full literature citation.

Table 1. Analytical and i.r. data for complexes (**1**)—(**12**)

	Analysis(%)[a]			I.r. bands (cm^{-1})		
Complex	C	H	M[a]	C_6X_5	$S_2CP(C_6H_{11})_3$	L
(**1**) *cis*-$[Pd(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$	46.45 (46.7)	4.20 (4.70)	751 (797)	1 493vs, 1 048vs, 953vs, 788s, 778s	1 273m, 1 003s, 898m, 848s, 560s, 548m	
(**2**) *cis*-$[Pd(C_6Cl_5)_2\{S_2CP(C_6H_{11})_3\}]$	38.6 (38.7)	3.70 (3.45)	*b*	1 323s, 1 313s, 1 285s, 833w, 828w, 668s, 613m, 603m	1 218m, 1 005s, 898m, 848m, 553m, 535m	
(**3**) *cis*-$[Pt(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$	42.5 (42.05)	4.20 (3.75)	884 (886)	1 498vs, 1 053vs, 953vs, 800s, 790s	1 273m, 1 005s, 898m, 848s, 553m, 540m	
(**4**) *cis*-$[Pt(C_6Cl_5)_2\{S_2CP(C_6H_{11})_3\}]$	35.95 (35.45)	3.20 (3.15)	*b*	1 325s, 1 315s, 1 290s, 823w, 813w, 670m, 623m, 618m	1 218m, 1 003m, 895m, 848m, 552m, 538m	
(**5**) $[Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(CO)]$	42.3 (42.05)	3.60 (3.65)	917 (914)	1 503vs, 1 063vs, 958vs, 798s, 793s	1 273m, 1 033m, 898m, 848m, 558m, 538m	2 043vs
(**6**) $[Pt(C_6Cl_5)_2\{SC(S)P(C_6H_{11})_3\}(CO)]$	34.95 (35.65)	3.05 (3.10)	1 010 (1 078)	1 333s, 1 323s, 1 293vs, 838w, 833w, 673s, 623m, 613m	1 218m, 998m, 898m, 848m, 553m, 533m	2 045vs
(**7**) $[Pd(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(PPh_3)]$	55.65 (55.55)	4.45 (4.55)	1 133 (1 059)	1 493vs, 1 058vs, 948vs, 778s, 768s	1 268m, 1 038s, 895m, 848m, 558s, 533s	1 435vs, 1 098s, 748s, 703s, 693s, 523s
(**8**) $[Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(PPh_3)]$	50.40 (51.25)	3.90 (4.20)	1 192 (1 148)	1 498vs, 1 058vs, 953vs, 793s, 778s	1 268m, 1 038s, 898m, 848m, 555s, 530s	1 438vs, 1 098s, 738s, 708s, 693s, 508s
(**9**) $[Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(py)]$[c]	45.25 (44.8)	3.80 (3.95)	1 023 (965)	1 505vs, 1 060vs, 963vs, 803s, 790s	1 278m, 1 018m, 898m, 848m, 553m, 538m	1 603m, 1 218w, 1 035m
(**10**) $[\{PdCl_2[S_2CP(C_6H_{11})_3]\}_x]$	43.65 (42.75)	6.65 (6.25)	*b*		1 275m, 968s, 898m, 848m, 555s, 535s	
(**11**) $[\{PdBr_2[S_2CP(C_6H_{11})_3]\}_x]$	37.05 (36.65)	5.45 (5.30)	*b*		1 278m, 1 003m, 893s, 848s, 558s, 528s	
(**12**) $[\{PdI_2[S_2CP(C_6H_{11})_3]\}_x]$	31.55 (31.85)	4.85 (4.65)	*b*		1 268m, 998m, 893m, 848m, 558s, 523s	

[a] Calculated values are given in parentheses. [b] The very low solubility in chloroform prevents the determination of the molecular weight. [c] N 1.42 (1.45%).



separation of the precipitated complexes from the excess of $[MR_2(thf)_2]$, which remains in solution.

The elemental analyses and measured molecular weights of complexes (**1**)—(**4**) are listed in Table 1. Their i.r. spectra show absorptions from the C_6F_5[9] or C_6Cl_5[10] groups; the characteristic bands are also shown in Table 1. Complexes (**1**) and (**3**) exhibit two absorptions in the 760—800 cm^{-1} region assignable to the X-sensitive mode of the pentafluorophenyl group, whilst complexes (**2**) and (**4**) show two bands in the 800—850 cm^{-1} region (assignable to the X-sensitive mode of the pentachlorophenyl group) and two more in the 620—600 cm^{-1} region [assignable to v(M–C) vibration], thus confirming the *cis* configuration of the C_6F_5 or C_6Cl_5 groups respectively. The internal vibrations of the $P(C_6H_{11})_3$ groups prevent the assignment of the absorptions of the $-\mathrm{C}\begin{smallmatrix}\diagup\mathrm{S}\\ \diagdown\mathrm{S}\end{smallmatrix}$ moiety.

The ^{31}P n.m.r. spectra of complexes (**1**) and (**2**) show a peak at δ 31.96 or 30.68 p.p.m. respectively, whereas (**3**) and (**4**) show an absorption with corresponding platinum satellites {δ 44.37 [^3J(Pt–P) = 136] and 38.18 p.p.m. [^3J(Pt–P) = 137 Hz] respectively} indicating the presence of only one type of phosphorus nucleus.

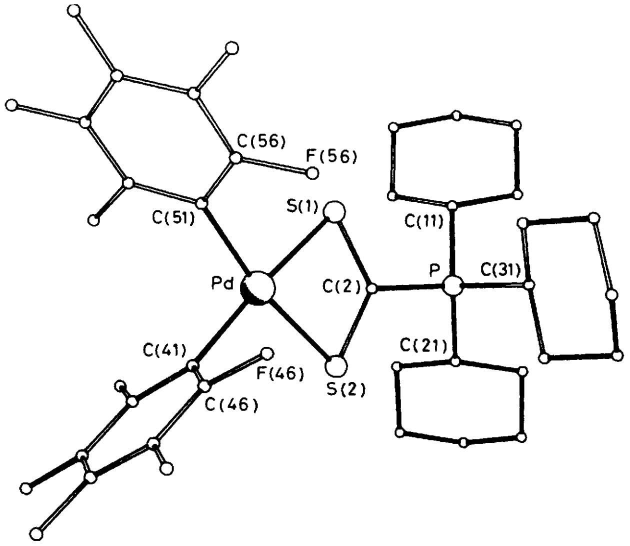
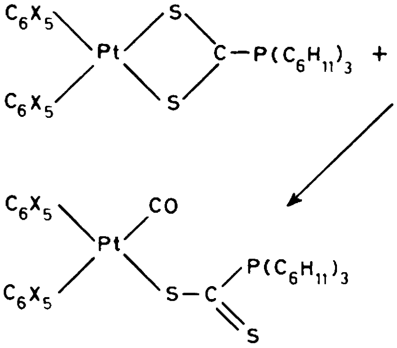


Figure 1. The molecule of (**1**) in the crystal (radii arbitrary, H atoms omitted)

The bidentate nature of the $S_2CP(C_6H_{11})_3$ ligand in complexes (**1**)—(**4**) has been established by *X*-ray diffraction studies on complex (**1**) (see Experimental section and Figure 1). Single crystals were grown by diffusion of n-hexane into a concentrated solution of (**1**) in CH_2Cl_2. Palladium is in a *cis* square-planar environment [root-mean square (r.m.s.) deviation 0.02 Å] formed by one carbon of each C_6F_5 group and the two sulphurs of the $S_2CP(C_6H_{11})_3$ group. The Pd–C bond lengths [2.029(4) and 2.012(6) Å] are shorter than in the $[Pd(C_6F_5)\{SC(S)PEt_3\}(PEt_3)_2]^+$ cation;[2] the C–S bond lengths are 1.662(6) and 1.672(4) Å. Because of the chelating nature of the betaine, the angle S(1)–Pd–S(2) is only 73.8(2)°; this is similar to corresponding angles in other $\overline{\text{PdSCS}}$ rings, *e.g.* 75.4° in $[Pd(S_2CNEt_2)(PPh_3)Cl]$,[11] 74.5° in $[Pd(S_2CPh)_2]$.[12] The planar S_2CP moiety forms a dihedral angle of 12.3° to the ligand plane, and its dimensions are in general agreement with those for similar chelated complexes.[3–6] The dihedral angles between the S_2CP plane and the C_6F_5 groups are 94.4° *trans* to S(1) and 113.3° *trans* to S(2).

Bubbling CO through dichloromethane solutions of the platinum complexes (**3**) and (**4**) causes the colour of the solution to change from dark red to orange with the formation of species of the general formula $[Pt(C_6X_5)_2\{SC(S)P(C_6H_{11})_3\}(CO)]$ [X = F (**5**) or Cl (**6**)] according to equation (3) where the betaine acts as a monodentate ligand. No reaction takes place with the palladium complexes (**1**) and (**2**); after treatment with CO, their solutions do not show any ν(CO) absorptions, and the unchanged starting materials are recovered. The i.r. spectra of complexes (**5**) and (**6**) show absorptions characteristic of the C_6F_5 or C_6Cl_5 group and the $S_2CP(C_6H_{11})_3$ ligand (see Table 1), and a strong absorption band at 2 043 (**5**) or 2 045 cm^{-1} (**6**) assignable to ν(CO).



(3)

Analogously, complexes (**1**) and (**3**) react with other neutral ligands L [PPh_3 or pyridine (py)] to give compounds of the general formula $[M(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}L]$ [M = Pd, L = PPh_3 (**7**); M = Pt, L = PPh_3 (**8**); M = Pt, L = py (**9**)], where the $(C_6H_{11})_3PCS_2$ moiety must be monodentate. The absorptions assignable to the X-sensitive mode of C_6F_5 (two in each case, see Table 1) do not distinguish *cis* from *trans* geometry since two bands are expected in both cases.

For complexes (**5**)—(**9**) the monodentate nature of the $S_2CP(C_6H_{11})_3$ ligand can be inferred from the structure of complex (**5**) as determined by *X*-ray diffraction [see Experimental section and Figure 2; single crystals obtained as for complex (**1**)]; a five-co-ordinate palladium or platinum environment may thus be ruled out. The metal is again in a *cis* square-planar environment (r.m.s. deviation 0.04 Å), less distorted than that of complex (**1**), as expected from the monodentate character of all four ligands. The distance Pt–S(1) is 2.348(2) Å; Pt–S(2) is 3.589 Å, therefore Pt–S(2) bonding may be ruled out. In agreement with this, C(2)–S(1) [1.682(6) Å] is somewhat longer than C(2)–S(2) [1.643(7) Å]. The small difference between the two bond lengths is a consequence of electron delocalisation within the SCS moiety.[2] As for other metal S_2CPR_3 complexes (*e.g.* ref. 6) there is no significant difference between the dimensions of the co-ordinated ligand and those of free S_2CPEt_3.[13] The distances Pt–C(41) and Pt–C(51) are 2.056(6) and 2.045(7) Å, similar to those found for other bis(pentafluorophenyl)platinum(II) derivatives.[14] The dihedral angle between the co-ordination plane and the S_2CP plane is 55.3°. The C_6F_5 group *trans* to S(1) forms a dihedral angle of 61.1° with the S_2CP group; this is in contrast to the corresponding angle of 4° in *trans*-$[Pd(C_6F_5)(S_2CPEt_3)(PEt_3)_2]^+$.[2]

The ^{31}P n.m.r. spectra of complexes (**5**) and (**6**) show a single signal with ^{195}Pt satellites {δ 33.89 [^3J(Pt–P) 79.2] and δ 32.79 p.p.m. [^3J(Pt–P) 75.5 Hz] respectively}. Compound (**7**) shows two signals with equal intensity: a broad multiplet (PPh_3 coupled to the F atoms of the C_6F_5 group, δ 24.08 p.p.m.) and a sharp singlet [$P(C_6H_{11})_3$, δ 27.85 p.p.m.].

The synthesis of complexes of the type $MX_2\{S_2CP(C_6H_{11})_3\}$, analogous to the compounds described above but containing a halogen instead of the perhalogenophenyl group, must be attempted by a different route, since no precursors of the type MX_2L_2 (L = weak ligand; X = Cl, Br, or I) are known. Treatment of acetone–dichloromethane solutions of $[NBu_4]_2[Pd_2X_6]$ (X = Cl, Br, or I) with stoicheiometric amounts of the betaine leads, according to equation (4), to the precipitation of dark red solids of the desired general formula, as confirmed by C and H analyses [see Table 1; X = Cl (**10**), Br (**11**), or I (**12**)]. The ^{31}P n.m.r. spectrum of the chloro derivative (**10**) shows a single signal (δ 39.2 p.p.m.) indicating the presence of only one type of

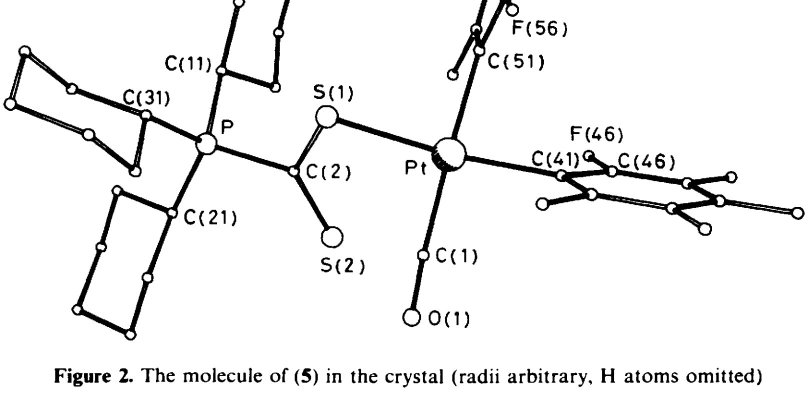
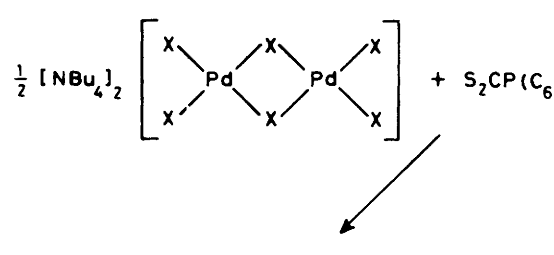
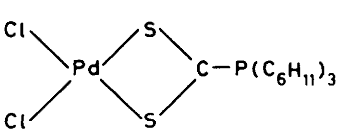


Figure 2. The molecule of (**5**) in the crystal (radii arbitrary, H atoms omitted)

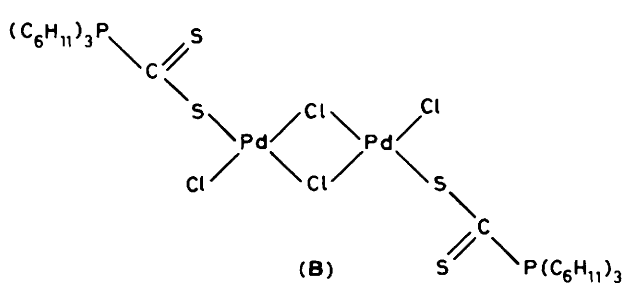


(4)

phosphorus nucleus, whilst its i.r. spectrum shows two bands with two shoulders in the 400—250 cm^{-1} region [340(sh), 325s, 290s, and 275(sh) cm^{-1}] characteristic of ν(Pd–Cl). These data do not allow a distinction between a square-planar geometry (**A**) with two mutually *cis* terminal chlorines (for which two bands are expected) and a binuclear structure (**B**) with unidentate betaine and a double chloro bridge, for which three absorptions[15] are expected.



(**A**)



(**B**)

The low solubility of these complexes has prevented both the determination of their molecular weights and the preparation of suitable crystals for *X*-ray diffraction studies. Neither does the reactivity of these compounds provide any useful indication of their structure; the complexes [{PdX$_2$[S$_2$CP(C$_6$H$_{11}$)$_3$]}$_x$] react with tris(cyclohexyl)phosphine or triphenylphosphine [equation (5)] to give *trans*-[PdX$_2${P(C$_6$H$_{11}$)$_3$}(PR$_3$)] (X = Cl or Br; R = C$_6$H$_{11}$ or Ph), where elimination of CS$_2$ has taken place, as shown by quantitative C and H and qualitative S analyses.

$$[\{PdX_2[S_2CP(C_6H_{11})_3]\}_x] + PR_3 \longrightarrow [PdX_2\{P(C_6H_{11})_3\}(PR_3)] \quad (5)$$

In the case of [PdCl$_2${P(C$_6$H$_{11}$)$_3$}$_2$] the i.r. spectrum is identical to that of the *trans* isomer prepared by a standard procedure,[16] showing a single band at 348 cm^{-1}.

Experimental

The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyser. Infrared spectra (4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets, n.m.r. spectra on a Varian XL-200. Molecular weights were determined with a Knauer 11.00 vapour-pressure osmometer.

The complexes [M(C$_6$X$_5$)$_2$(thf)$_2$] were prepared as described elsewhere.[8]

Preparations.—[M(C$_6$X$_5$)$_2${S$_2$CP(C$_6$H$_{11}$)$_3$}] (M = Pd *or* Pt; X = F *or* Cl). The ligand S$_2$CP(C$_6$H$_{11}$)$_3$ (0.0713 g, 0.20 mmol) was added to a yellow solution containing the corresponding complex [M(C$_6$X$_5$)$_2$(thf)$_2$] (0.25 mmol) in diethyl ether (30 cm^3), and stirred (45 min when X = F, 3 h when X = Cl). The resulting orange to red precipitate was filtered off and washed with Et$_2$O (3 × 5 cm^3). Yields: M = Pd, X = F, 83; X = Cl, 61%; M = Pt, X = F, 80; X = Cl, 65%.

[{PdX$_2$[S$_2$CP(C$_6$H$_{11}$)$_3$]}$_x$] (X = Cl, Br, *or* I). To a solution containing [NBu$_4$]$_2$[Pd$_2$X$_6$] (0.25 mmol) in acetone–dichloromethane (30 cm^3 : 40 cm^3) was added S$_2$CP(C$_6$H$_{11}$)$_3$ (0.1783 g,

Table 2. Atomic co-ordinates (× 10^4) for complex (**1**)

Atom	*x*	*y*	*z*
Pd	3 651.3(0.1)	4 571.5(0.3)	1 604.0(0.1)
P	4 066.5(0.4)	2 426(1)	3 346.9(0.4)
S(1)	4 396.4(0.4)	4 000(1)	2 565.9(0.5)
S(2)	3 280.9(0.4)	3 041(1)	1 996.8(0.5)
C(2)	3 916(1)	3 134(3)	2 607(2)
C(11)	4 824(1)	2 226(3)	3 768(2)
C(12)	5 091(1)	1 498(4)	3 445(2)
C(13)	5 730(2)	1 575(4)	3 802(2)
C(14)	5 937(2)	1 181(4)	4 466(2)
C(15)	5 664(2)	1 856(4)	4 786(2)
C(16)	5 019(2)	1 789(4)	4 433(2)
C(21)	3 640(2)	1 122(3)	3 181(2)
C(22)	3 760(2)	222(4)	2 792(2)
C(23)	3 318(2)	−731(4)	2 604(3)
C(24)	3 299(2)	−1 297(4)	3 160(3)
C(25)	3 200(2)	−407(4)	3 553(2)
C(26)	3 634(2)	557(4)	3 754(2)
C(31)	3 856(2)	3 469(3)	3 768(2)
C(32)	4 126(2)	4 664(4)	3 808(2)
C(33)	3 968(2)	5 536(4)	4 178(2)
C(34)	3 338(2)	5 629(5)	3 926(2)
C(35)	3 078(2)	4 448(5)	3 905(2)
C(36)	3 217(2)	3 593(4)	3 508(2)
C(41)	2 971(2)	4 980(4)	799(2)
C(42)	2 817(2)	4 309(4)	274(2)
C(43)	2 367(2)	4 598(4)	−288(2)
C(44)	2 061(2)	5 579(4)	−333(2)
C(45)	2 191(2)	6 248(4)	173(2)
C(46)	2 647(2)	5 942(4)	733(2)
F(42)	3 105(1)	3 344(2)	292(1)
F(43)	2 230(1)	3 905(3)	−783(1)
F(44)	1 631(1)	5 851(3)	−881(1)
F(45)	1 877(1)	7 191(3)	128(2)
F(46)	2 753(1)	6 658(3)	1 212(1)
C(51)	4 069(2)	5 862(4)	1 432(2)
C(52)	4 270(2)	5 755(4)	1 009(2)
C(53)	4 558(2)	6 621(4)	881(2)
C(54)	4 663(2)	7 650(4)	1 192(2)
C(55)	4 470(2)	7 808(4)	1 619(2)
C(56)	4 183(2)	6 912(4)	1 742(2)
F(52)	4 195(1)	4 760(2)	685(1)
F(53)	4 745(1)	6 477(3)	450(1)
F(54)	4 942(1)	8 513(3)	1 076(2)
F(55)	4 546(2)	8 817(3)	1 923(2)
F(56)	4 009(1)	7 090(3)	2 173(1)

0.5 mmol). After stirring for 20 h, the precipitate was filtered off and washed (with acetone for X = Cl, CH_2Cl_2 for X = Br, and hexane for X = I). The resulting red solids were recrystallised from CH_2Cl_2–EtOH (X = Cl) or CH_2Cl_2–Et_2O (X = I). Yields: X = Cl, 72; X = Br, 95; X = I, 70%.

$[Pt(C_6X_5)_2\{SC(S)P(C_6H_{11})_3\}(CO)]$. Carbon monoxide was bubbled through a red solution containing $[Pt(C_6X_5)_2\{S_2CP(C_6H_{11})_3\}]$ (0.125 mmol) in CH_2Cl_2 (30 cm^3) for 30 min while the solution slowly turned orange. The solvent was partially evaporated under vacuum and Et_2O was added to precipitate a pink (X = F) or pale pink (X = Cl) solid. Yields: X = F, 49; X = Cl, 66%.

$[Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}L]$ [L = PPh_3 *or* $P(C_6H_{11})_3$]. To a dark red solution containing $[Pt(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$ (0.125 mmol, 0.1107 g) was added an equivalent amount of the neutral ligand L. The stirred solution slowly became paler [L = PPh_3, 1 h, yellow; L = $P(C_6H_{11})_2$, 24 h, pale red] and, after partially evaporating the solvent, methanol was added to precipitate a yellow solid, which was washed with MeOH (2 × 5 cm^3). Yields: L = PPh_3, 69; L = $P(C_6H_{11})_3$, 66%.

Table 3. Selected bond lengths (Å) and angles (°) for complex (**1**)

Pd–S(1)	2.368(2)	C(11)–P	1.819(4)
C(2)–P	1.838(5)	C(21)–P	1.815(5)
C(2)–S(2)	1.672(4)	C(31)–P	1.823(6)
Pd–S(2)	2.415(2)	C(41)–Pd	2.029(4)
C(2)–S(1)	1.662(6)	C(51)–Pd	2.012(6)
S(1)–Pd–S(2)	73.8(2)	S(2)–Pd–C(41)	101.6(2)
S(1)–Pd–C(41)	175.3(2)	S(2)–Pd–C(51)	169.9(2)
S(1)–Pd–C(51)	96.5(2)	C(2)–P–C(11)	107.5(3)
C(41)–Pd–C(51)	88.0(3)	C(11)–P–C(21)	116.3(3)
C(2)–P–C(21)	108.2(3)	C(11)–P–C(31)	108.3(3)
C(2)–P–C(31)	105.5(3)	Pd–S(1)–C(2)	84.3(2)
C(21)–P–C(31)	110.4(3)	P–C(2)–S(1)	119.4(3)
Pd–S(2)–C(2)	82.6(3)	S(1)–C(2)–S(2)	119.0(3)
P–C(2)–S(2)	121.3(4)		

$[Pd(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(PPh_3)]$. The complex $[Pd(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$ (0.0996 g) was suspended in ether (20 cm^3) and PPh_3 (0.0328 g, 0.125 mmol) was added. On stirring, the orange solid gave way to a yellow solution which was evaporated to dryness. Addition of MeOH (15 cm^3) afforded a yellow solid which was filtered off and washed with MeOH (2 × 5 cm^3).

$[Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(py)]$. To a dark red solution of $[Pt(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$ (0.0886 g, 0.1 mmol) in CH_2Cl_2 (20 cm^3) was added an excess (0.20 cm^3) of pyridine. The solution became paler and, after stirring for 12 h, the solvent was partially removed under vacuum. Methanol was added to precipitate a yellow solid, which was filtered off and washed with methanol (2 × 5 cm^3). Yield: 56%.

X-Ray Structure Determination of Complex (**1**).—*Crystal data.* $C_{31}H_{33}F_{10}PPdS_2$, M = 796.4, monoclinic, a = 26.654(8), b = 11.519(3), c = 24.223(7) Å, β = 116.93(3)°, U = 6 630.4 $Å^3$ (by refinement of 2θ values for 41 reflections in the range 20—23°), space group $C2/c$, Z = 8, D_c = 1.595 g cm^{-3}, $F(000)$ = 3 216, red prism, 0.5 × 0.35 × 0.25 mm, $\mu(Mo\text{-}K_\alpha)$ = 0.8 mm^{-1}.

Data collection and processing. Stoe-Siemens four-circle diffractometer, monochromated Mo-K_α radiation (λ = 0.710 69 Å). 8 828 Profile-fitted [17] reflections ($2\theta_{max.}$ 50°, $+h$ $+k$ $\pm l$ and $+h$ $-k$ $+l$ equivalents), 5 818 unique, 4 338 with $F > 4\sigma(F)$ used for all calculations. Absorption correction (ψ scans) with transmission factors 0.51—0.97; three check reflections, no decay.

Structure analysis and refinement. Heavy-atom method. Refinement on F to R 0.045, R' 0.039 {all non-H atoms anisotropic; H atoms included with riding model [C–H 0.96 Å, H–C–H 109.5°, U(H) = 1.2 U_{eq}(CC)]; weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,15F^2$; 406 parameters}. Program system SHELXTL.[18] Final atomic co-ordinates and derived parameters are given in Tables 2 and 3.

X-Ray Structure Determination of Complex (**5**).—*Crystal data.* $C_{32}H_{33}F_{10}PPtS_2O{\cdot}CH_2Cl_2$, M = 999, triclinic, a =

Table 4. Atomic co-ordinates (× 10^4) for complex (**5**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	7 830.8(0.2)	7 277.5(0.1)	2 424.8(0.2)	C(41)	8 868(5)	8 615(3)	2 078(4)
P	5 331(1)	3 700(1)	2 438(1)	C(42)	10 020(6)	9 276(4)	2 696(4)
S(1)	6 492(2)	5 849(1)	2 904(1)	C(43)	10 713(7)	10 187(5)	2 490(5)
S(2)	7 247(2)	4 829(1)	1 318(1)	C(44)	10 210(7)	10 453(4)	1 619(6)
C(1)	9 536(7)	6 857(4)	2 515(5)	C(45)	9 068(6)	9 806(4)	973(5)
O(1)	10 585(5)	6 661(4)	2 568(5)	C(46)	8 420(6)	8 908(4)	1 210(4)
C(2)	6 474(5)	4 864(3)	2 198(3)	F(42)	10 578(4)	9 044(3)	3 561(3)
C(11)	3 433(5)	3 640(3)	1 934(3)	F(43)	11 847(5)	10 815(3)	3 127(3)
C(12)	3 153(6)	3 790(4)	886(4)	F(44)	10 858(4)	11 343(3)	1 407(4)
C(13)	1 528(6)	3 616(5)	463(4)	F(45)	8 588(4)	10 077(3)	124(3)
C(14)	929(7)	4 291(5)	976(5)	F(46)	7 299(4)	8 308(3)	545(2)
C(15)	1 216(6)	4 159(5)	2 035(5)	C(51)	6 013(6)	7 746(4)	2 276(4)
C(16)	2 835(6)	4 331(4)	2 467(4)	C(52)	4 790(7)	7 347(5)	1 540(5)
C(21)	5 733(5)	2 682(3)	1 840(4)	C(53)	3 555(7)	7 647(7)	1 430(6)
C(22)	7 246(5)	2 578(4)	2 279(4)	C(54)	3 523(11)	8 388(8)	2 048(9)
C(23)	7 591(7)	1 806(5)	1 666(5)	C(55)	4 700(11)	8 814(6)	2 783(8)
C(24)	6 438(7)	824(4)	1 528(5)	C(56)	5 935(7)	8 494(4)	2 898(5)
C(25)	4 935(6)	918(4)	1 107(5)	F(52)	4 775(4)	6 610(3)	912(3)
C(26)	4 557(6)	1 680(3)	1 697(4)	F(53)	2 399(5)	7 218(5)	703(4)
C(31)	5 626(5)	3 712(4)	3 723(3)	F(54)	2 327(6)	8 698(5)	1 927(6)
C(32)	4 692(7)	2 792(4)	4 001(4)	F(55)	4 673(7)	9 547(4)	3 407(5)
C(33)	4 812(8)	2 949(6)	5 061(4)	F(56)	7 057(5)	8 937(3)	3 641(3)
C(34)	6 383(8)	3 208(6)	5 639(4)	C(3)	538(11)	2 009(8)	4 792(8)
C(35)	7 322(7)	4 101(5)	5 339(4)	Cl(1)	838(3)	3 148(2)	4 422(3)
C(36)	7 226(6)	3 952(4)	4 284(4)	Cl(2)	−1 092(4)	1 216(2)	4 236(2)

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

Pt-S(1)	2.348(2)	C(2)-P	1.840(6)
C(1)-O(1)	1.128(10)	C(2)-S(2)	1.643(7)
C(2)-S(1)	1.682(6)	C(11)-P	1.828(6)
C(41)-Pt	2.056(6)	C(21)-P	1.823(7)
C(51)-Pt	2.045(7)	C(31)-P	1.835(6)
C(1)-Pt	1.910(9)		
S(1)-Pt-C(1)	95.2(3)	S(1)-Pt-C(41)	173.3(3)
C(1)-Pt-C(41)	90.6(3)	S(1)-Pt-C(51)	86.5(3)
C(1)-Pt-C(51)	177.7(4)	C(41)-Pt-C(51)	87.9(3)
C(2)-P-C(11)	107.9(3)	C(2)-P-C(21)	108.5(3)
C(11)-P-C(21)	108.6(3)	C(2)-P-C(31)	108.7(3)
C(11)-P-C(31)	108.4(3)	C(21)-P-C(31)	114.6(3)
Pt-S(1)-C(2)	108.6(3)	Pt-C(1)-O(1)	176.2(6)
P-C(2)-S(1)	113.0(4)	P-C(2)-S(2)	118.1(4)
S(1)-C(2)-S(2)	128.8(4)		

9.864(2), b = 14.202(3), c = 14.638(5) Å, α = 93.44(3), β = 103.11(2), γ = 105.45(2)°, U = 1 909.0 Å^3 (by refinement of 2θ values of 49 reflections in the range 20—23°), space group $P\bar{1}$, Z = 2, D_c = 1.738 g cm^{-3}, $F(000)$ = 980, violet prism, 0.29 × 0.27 × 0.23 mm, μ(Mo-K_α) = 4.1 mm^{-1}.

Data collection and processing. As for complex (**1**) with the following differences: 8 079 reflections measured (2$\theta_{max.}$ 53°; $+h$ $\pm k$ $\pm l$ and some $-h$ equivalents), 7 902 unique, 6 606 with $F > 4\sigma(F)$. Transmission factors 0.59—0.76.

Structure analysis and refinement. Heavy-atom method. Refinement on F to R 0.042, R' 0.037 [non-H atoms anisotropic except for C(3), H atoms as for complex (**1**); weighting scheme $w^{-1} = \sigma^2(F) + 0.000\ 2F^2$; 446 parameters]. See Tables 4 and 5 for final parameters.

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