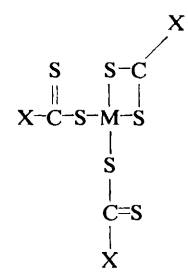
Synthesis of Cationic Palladium(II) and Platinum(II) Complexes with a Monodentate Trialkylphosphoniumdithiocarboxylate Ligand: Molecular Structure of *trans*-$[Pd(C_6F_5)(PEt_3)_2(S_2C–PEt_3)]ClO_4·CHCl_3$ †

Rafael Usón, Juan Forniés, Rafael Navarro, and Miguel A. Usón
Department of Inorganic Chemistry, University of Zaragoza, Zaragoza, Spain
Maria P. Garcia
Colegio Universitario de Logroño, Logroño, Spain
Alan J. Welch
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

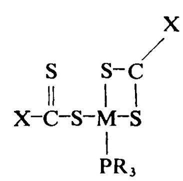
Reaction of *trans*-$[M(OClO_3)(C_6F_5)(PR_3)_2]$ with the zwitterion $S_2C–PR'_3$ affords the complexes *trans*-$[M(C_6F_5)(PR_3)_2(S_2C–PR'_3)]ClO_4$ (M = Pd; $R_3 = R'_3 = Et_3$, Bu_3, or Et_2Ph; R = Bu, R' = cyclo-C_6H_{11}; R = Ph, R' = Et or cyclo-C_6H_{11}; M = Pt, R = R' = Et or Bu). *trans*-$[Pd(C_6F_5)(PEt_3)_2(S_2C–PEt_3)]ClO_4$ is also given by reaction of $[Pd(C_6F_5)(PEt_3)_3]ClO_4$ with CS_2. Reaction of $[M(OClO_3)(C_6F_5)(bipy)]$ (bipy = 2,2'-bipyridyl) with $S_2C–PR'_3$ affords $[M(C_6F_5)(bipy)(S_2C–PR'_3)]ClO_4$ (M = Pd or Pt; R' = Et, Bu, or cyclo-C_6A_{11}). A crystallographic study of *trans*-$[Pd(C_6F_5)(PEt_3)_2(S_2C–PEt_3)]ClO_4$ (as its 1 : 1 chloroform solvate) shows that the cation contains a unidentate triethylphosphoniumdithiocarboxylate ligand, and ^{31}P n.m.r. spectra of all products with two terminal phosphine ligands are consistent with *trans* stereochemistries. Crystals of *trans*-$[Pd(C_6F_5)(PEt_3)_2(S_2C–PEt_3)]ClO_4·CHCl_3$ are monoclinic, space group $P2_1/a$, with a = 14.596 5(18), b = 15.356(3), c = 19.324 2(16) Å, β = 109.257(8)°, and Z = 4. Using 4 093 amplitudes the structure has been refined to R = 0.1049. The non-bonding Pd · · · S distance is 3.644(4) Å.

Derivatives of carbon disulphide of the type $^-S_2C–X$ are known to display both uni- and bi-dentate co-ordination to transition metal centres, with the unidentate (one-electron function) less common overall but obviously relatively more favourable in low oxidation state species towards the right-hand side of the periodic table.

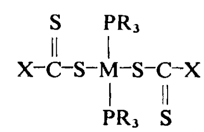
Established synthetic routes to structurally authenticated palladium or platinum complexes containing M–SC(S)X fragments involve cleavage of the M–S bonds in $[M(S_2C–X)_2]$, either by $^-S_2C–X$ [1] yielding the anionic $[M(S_2C–X)_3]^-$ (1), or by one [2] or two [3] moles of tertiary phosphine affording, respectively, the neutral molecules $[M(S_2C–X)_2(PR_3)]$ (2) and *trans*-$[M(S_2C–X)_2(PR_3)_2]$ (3). We now report two high-yield syntheses of *cationic* palladium and platinum complexes containing a unidentate trialkylphosphoniumdithiocarboxylate ligand.



(1) M = Pt; X = OEt or OPr^i



(2)



(3)

M = Pd or Pt; X = NMe_2, NPh_2, NEt_2, or NBu^i_2; R_3 = Et_3, Me_2Ph, $MePh_2$, or Ph_3

Results and Discussion

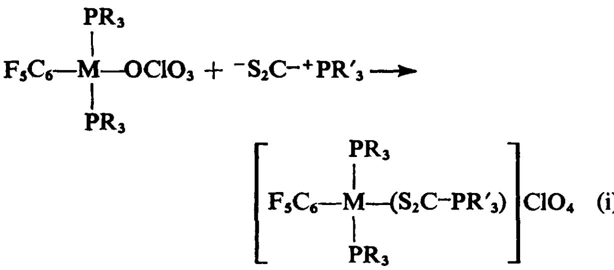
Reaction between benzene solutions of the neutral complexes *trans*-$[M(OClO_3)(C_6F_5)(PR_3)_2]$ and the zwitterionic adducts $^-S_2C–^+PR'_3$ gives rise (*ca.* 85% yield) to pink cationic derivatives (4a)—(4h) in which the poorly co-ordinating perchlorato-ligand has been displaced by the negative end of the zwitterion, according to equation (i) (C_6H_{11} = cyclohexyl). Acetone or dichloromethane solutions of the neutral complexes $[M(OClO_3)(C_6F_5)(bipy)]$ (bipy = 2,2'-bipyridyl) react analogously with $^-S_2C–^+PR'_3$ to give (*ca.* 80% yield) cationic derivatives (5a)—(5f), according to equation (ii). Moreover, the same product (4a) can also be obtained, albeit in lesser yield (*ca.* 60%) by insertion of CS_2 into the $M–PR_3$ bond *trans* to the aryl function of a related cationic species, according to equation (iii).

However, the dissociation $S_2C–PR'_3 \rightleftharpoons S_2C + PR'_3$ prevents in some cases the use of the zwitterionic $S_2C–PR'_3$ as a normal neutral ligand. For example, binuclear neutral palladium complexes react with $S_2C–PR'_3$ to give, according to equation (iv), neutral monomeric complexes of the type [PdYZLL'] instead of the expected $[PdYZL(S_2C–PR'_3)]$ neutral derivatives.

Bidentate co-ordination of the triphenylphosphonium-dithiocarboxylate ligand had been verified in the complexes $[Ir(CO)(PPh_3)_2(S_2C–PPh_3)]^+$ (ref. 4) and $[M\{(Ph_2PCH_2)_3C-$

† σ-Pentafluorophenylbis(triethylphosphine)(triethylphosphonio-dithioformate-*S*)palladium(II) perchlorate-chloroform (1/1).

Supplementary data available (No. SUP 23777, 23 pp.): observed and calculated structure factors, isotropic and anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.



(i)

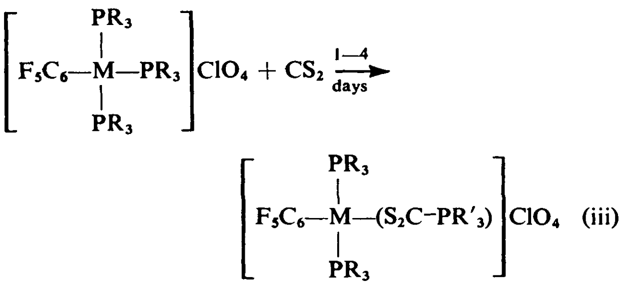
(4)

M	PR_3	PR'_3	
Pd	PEt_3	PEt_3	(4a)
Pd	PBu_3	PBu_3	(4b)
Pd	PEt_2Ph	PEt_2Ph	(4c)
Pd	PBu_3	$P(C_6H_{11})_3$	(4d)
Pd	PPh_3	PEt_3	(4e)
Pd	PPh_3	$P(C_6H_{11})_3$	(4f)
Pt	PEt_3	PEt_3	(4g)
Pt	PBu_3	PBu_3	(4h)

$$[M(OClO_3)(C_6F_5)(bipy)] + {}^-S_2C{-}^+PR'_3 \longrightarrow [M(C_6F_5)(bipy)(S_2C{-}PR'_3)]ClO_4 \quad (ii)$$

(5)

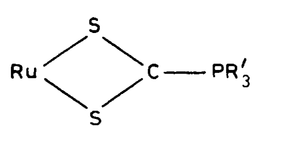
M	PR'_3	
Pd	PEt_3	(5a)
Pd	PBu_3	(5b)
Pd	$P(C_6H_{11})_3$	(5c)
Pt	PEt_3	(5d)
Pt	PBu_3	(5e)
Pt	$P(C_6H_{11})_3$	(5f)



(iii)

$$[\{Pd(\mu{-}Cl)(C_6F_5)(PPh_3)\}_2] + 2\ {}^-S_2C{-}^+P(C_6H_{11})_3 \longrightarrow 2\ [PdCl(C_6F_5)(PPh_3)\{P(C_6H_{11})_3\}] + 2\ CS_2 \quad (iv)$$

$Me\}(S_2C{-}PEt_3)]^{2+}$ (M = Co or Ni),[5] and suggested for other trialkyl derivatives on the basis of indirect (especially ^{31}P n.m.r.) data. Thus, Stephenson and co-workers [6] have postulated the existence of the moiety shown below in neutral and cation species, whilst Werner and Bertleff [7] have formulated



their cationic Pd^{II} complexes (6) as involving five-co-ordinated palladium.

In spite of the fact that five-co-ordinated Pd^{II} species are not unknown, it was of interest to obtain direct evidence for the structures of our complexes since, although their formation

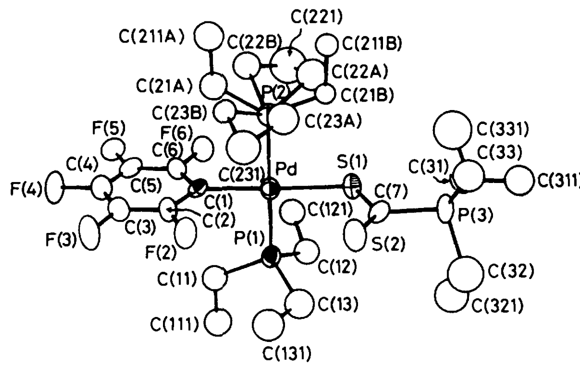
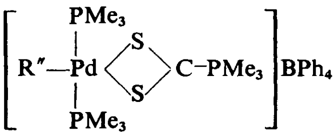


Figure. Perspective view of the cation *trans*-$[Pd(C_6F_5)(PEt_3)_2(S_2C{-}PEt_3)]^+$, with thermal ellipsoids constructed at the 30% electron probability level; C(31) is almost totally obscured by C(33)



(6) R″ = Me, C(O)Me, or Ph

via equation (i) seems compatible with structure (6), generation of the same compounds by equation (iii) indicates a simple 1,2-addition of $M{-}PR_3$ to one of the S=C bonds of CS_2, leading to a cation with a unidentate $S_2C{-}PR'_3$ ligand bonded to only a four-co-ordinate metal. Moreover, the capability of $S_2C{-}PR'_3$ to bond in a unidentate fashion to $M(CO)_5$ fragments (M = Cr, Mo, or W) has very recently been demonstrated [8] by crystallographic study.

Analytical data, conductivities, and melting points of all new complexes are given in Table 1. Phosphorus-31 n.m.r. spectra (see Table 2) of the compounds $[M(C_6F_5)(PR_3)_2(S_2C{-}PR'_3)]ClO_4$ (4a)—(4h) show two types of non-equivalent phosphines, in agreement with a *trans* configuration. The spectra of most of the palladium complexes show multiplet resonances; *i.e.*, for P in PR'_3 a triplet with J_{P-P} = *ca.* 3.5 Hz; for P in PR_3 a complicated multiplet doubtless due to the influence of the proximal C_6F_5 group. Platinum complexes show two single signals and the corresponding ^{195}Pt satellites. The different pattern of the spectra for Pd and Pt complexes is in agreement with the fact that J_{P-P} and J_{P-F} are larger in the former.[9,10]

I.r. spectra of all new complexes show characteristic absorptions due to the C_6F_5 group (*ca.* 1 500s, 950s cm^{-1}), to the ionic ClO_4^- (1 120—1 050vs br, 620s cm^{-1}), and to the neutral ligands. The broad absorption of the ClO_4^- group at 1 120—1 050 cm^{-1} prevents the assignment of ν(C–S).

In order unambiguously to establish the structures of our complexes, a single-crystal *X*-ray diffraction study of (4a) was undertaken, crystals being grown by chloroform evaporation. A perspective view of the cation, together with the atomic numbering scheme adopted, is presented in the Figure, and bond distances and angles are listed in Tables 3 and 4 respectively.

The *trans* arrangement of PR_3 ligands, suggested by the ^{31}P n.m.r. spectra of complexes (4), is confirmed. Given the chemical equivalence of the *trans* PEt_3 functions of (4a), it is unclear why the distances Pd–P(1) and Pd–P(2) should be so different [0.033(6) Å]. The $P(2)Et_3$ group is disordered in the crystal (and is modelled in terms of equal contributions from two components, A and B, related by a local mirror plane and sharing common methyl carbons 221 and 231) but there is no

Table 1. Analyses [a] (%), conductivities [b] (ohm^{-1} cm^2 mol^{-1}), and melting points (°C) for complexes (4) and (5)

Complex	C	N	H	Λ_M	M.p.
(4a) $[Pd(C_6F_5)(PEt_3)_2(S_2C-PEt_3)]ClO_4$	37.65 (37.35)		5.55 (5.65)	116	115
(4b) $[Pd(C_6F_5)(PBu_3)_2(S_2C-PBu_3)]ClO_4$	48.65 (48.9)		7.5 (7.75)	117	130
(4c) $[Pd(C_6F_5)(PEt_2Ph)_2(S_2C-PEt_2Ph)]ClO_4$	46.5 (46.9)		4.9 (4.8)	102	114
(4d) $[Pd(C_6F_5)(PBu_3)_2\{S_2C-P(C_6H_{11})_3\}]ClO_4$	51.65 (51.25)		7.55 (7.75)	145	130
(4e) $[Pd(C_6F_5)(PPh_3)_2(S_2C-PEt_3)]ClO_4{\cdot}C_6H$	56.75 (56.45)		4.55 (4.4)	130	136
(4f) $[Pd(C_6F_5)(PPh_3)_2\{S_2C-P(C_6H_{11})_3\}]ClO_4{\cdot}C_6H_6$	60.5 (60.4)		5.4 (5.2)	132	178
(5a) $[Pd(C_6F_5)(bipy)(S_2C-PEt_3)]ClO_4$	37.9 (38.2)	3.9 (3.85)	3.05 (3.2)	143	174
(5b) $[Pd(C_6F_5)(bipy)(S_2C-PBu_3)]ClO_4$	42.8 (43.15)	3.6 (3.45)	4.7 (4.35)	135	98
(5c) $[Pd(C_6F_5)(bipy)\{S_2C-P(C_6H_{11})_3\}]ClO_4$	47.0 (47.45)	3.15 (3.15)	4.7 (4.65)	136	143
(4g) $[Pt(C_6F_5)(PEt_3)_2(S_2C-PEt_3)]ClO_4$	34.05 (33.65)		5.0 (5.1)	140	154
(4h) $[Pt(C_6F_5)(PBu_3)_2(S_2C-PBu_3)]ClO_4$	45.1 (45.1)		6.8 (7.15)	143	142
(5d) $[Pt(C_6F_5)(bipy)(S_2C-PEt_3)]ClO_4$	34.1 (34.0)	3.9 (3.45)	3.1 (2.85)	150	219
(5e) $[Pt(C_6F_5)(bipy)(S_2C-PBu_3)]ClO_4$	39.35 (38.85)	2.95 (3.15)	4.25 (3.95)	145	157
(5f) $[Pt(C_6F_5)(bipy)\{S_2C-P(C_6H_{11})_3\}]ClO_4$	43.75 (43.15)	2.35 (2.9)	4.6 (4.25)	143	148—150 [c]

[a] Calculated values in parentheses. [b] In acetone. [c] Decomposes.

Table 2. Phosphorus-31 n.m.r. data * for complexes (4)

	$S_2C-PR'_3$			PR_3	
Complex	^{31}P (δ/p.p.m.)	$^4J_{PP}$	$^3J_{PtP}$	^{31}P (δ/p.p.m.)	J_{PtP}
(4a)	41.26 (t)	3.9		18.24 (m)	
(4b)	36.74 (t)	3.7		11.50 (m)	
(4c)	30.05 (t)	3.7		16.86 (m)	
(4d)	35.46 (t)	3.5		12.10 (m)	
(4e)	40.97 (s)			23.70 (m)	
(4f)	35.48 (s)			23.97 (m)	
(4g)	43.97 (s)		106.8	12.99 (s)	2 410.9
(4h)	39.26 (s)		107.4	6.12 (s)	2 403.6

* Spectra measured in $[^2H_1]$chloroform, coupling constants in Hz; reference is H_3PO_4.

evidence that the disorder involves P(2). Furthermore, the molecular environments of the *trans* phosphine ligands are very similar, since the C_6F_5 ligand and S_2CP fragment are closely coplanar and perpendicular to the palladium co-ordination plane (Table 5).

The triethylphosphoniumdithiocarboxylate ligand is unidentately bound to the metal, Pd–S(1) 2.342(3) Å, and adopts a *cisoidal* conformation (presumably a *transoidal* conformation would be sterically unrealistic). The non-bonding Pd ··· S(2) distance is 3.644(4) Å. Dimensions within the S_2CP moiety are in general agreement with those in $[Cr(CO)_5(S_2C-PEt_3)]$,[8] *i.e.* the C–S distance is somewhat longer to the co-ordinated sulphur, although the small difference between the two bond lengths is certainly consistent with electronic delocalisation in the SCS framework. Similar observations have previously been made for unidentate S_2C-X ligands in both *cisoidal* [8,11-12] and *transoidal* [13] conformations.

Other distances and angles in the cation, and those in the perchlorate anion and the molecule of chloroform solvate are unexceptional, and there are no serious interion or intermolecular contacts.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer. Conductivities were measured in 5×10^{-4} mol dm^{-3} acetone solutions with a Philips 9501/01 apparatus. Carbon, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyser. Phosphorus-31 n.m.r. spectra were run on a VARIAN FT-80-A instrument.

Preparation of the Adducts $S_2C-PR'_3$ [PR'_3 = PEt_3, PBu_3, PEt_2Ph, *or* $P(C_6H_{11})_3$].—Addition of CS_2 (small excess) to an ethanolic solution of the phosphine and cooling to −78 °C (when the adduct does not precipitate at room temperature) affords the adducts as red solids.

Preparation of $[MCl(C_6F_5)(PR_3)_2]$ *and* $[MCl(C_6F_5)(bipy)]$ (M = Pd *or* Pt) (PR_3 = PPh_3, PEt_3, PBu_3, *or* PEt_2Ph).—Reaction of acetone solutions (*ca.* 75 cm^3) of the binuclear compounds $[\{M(\mu-Cl)(C_6F_5)(PPh_3)\}_2]$ (0.5 mmol) (M = Pd [14] or Pt [15]) with a small excess (*ca.* 3%) of PR_3 (PR_3 = PPh_3, PEt_3, PBu_3, or PEt_2Ph) or bipy gives acetone solutions which, when partially evaporated, give the mononuclear compounds $[MCl(C_6F_5)(PR_3)_2]$ or $[MCl(C_6F_5)(bipy)]$, respectively in almost quantitative yields.

Preparation of $[Pd(OClO_3)(C_6F_5)(PR_3)_2]$.—Benzene solutions of $[Pd(OClO_3)(C_6F_5)(PR_3)_2]$ were obtained by reaction of stoicheiometric amounts of $[PdCl(C_6F_5)(PR_3)_2]$ and $Ag(ClO_4)$ (0.5 mmol, *ca.* 50 cm^3); the mix-ture was stirred for 30 min at room temperature and the precipitated AgCl was filtered off to obtain a benzene solution of $[Pd(OClO_3)(C_6F_5)(PR_3)_2]$.

Preparation of [Pd(C_6F_5)(PR_3)$_2$(S_2C–PR'_3)]ClO_4 [PR_3 = PR'_3 = PEt_3 (4a), PBu_3 (4b), *or* PEt_2Ph (4c)].—To a solution of 0.5 mmol of [Pd($OClO_3$)(C_6F_5)(PR_3)$_2$] [PR_3 = PEt_3 to synthesize (4a), PBu_3 for (4b), PEt_2Ph for (4c)] in benzene (50 cm^3) was added 0.5 mmol of the corresponding adduct S_2C–PR'_3 (PR'_3 = PEt_3, 0.097; PBu_3, 0.139; or PEt_2Ph, 0.233 g).

The solution was stirred for 4 h at room temperature and the resulting pink solution was concentrated to a few cm^3. A pink solid was obtained after adding ethanol (or diethyl ether) and cooling to −28 °C. The product was filtered off, washed with ethanol and vacuum dried. It was identified as [Pd(C_6F_5)(PR_3)$_2$(S_2C–PR'_3)]ClO_4.

Preparation of [Pd(C_6F_5)(PR_3)$_2$(S_2C–PR'_3)]ClO_4 [PR_3 = PBu_3, PR'_3 = P(C_6H_{11})$_3$ (4d); PPh_3, PEt_3 (4e); or PPh_3, P(C_6H_{11})$_3$ (4f)].—To a solution of 0.5 mmol of [Pd($OClO_3$)(C_6F_5)(PR_3)$_2$] [PR_3 = PBu_3 to synthesize (4d), PPh_3 for (4e) and (4f)] in benzene (50 cm^3) was added 0.5 mmol of S_2C–PR'_3 [PR'_3 = P(C_6H_{11})$_3$, 0.178; or PEt_3, 0.097 g].

A pink solid which precipitates immediately, when PR_3 = PPh_3 and PR'_3 = P(C_6H_{11})$_3$, was filtered off, washed with diethyl ether and vacuum dried; it was identified as (4f). In the other cases the solution was stirred for 2 h at room temperature and afterwards concentrated to a few cm^3. A pink solid was obtained after adding ethanol or diethyl ether. It was identified as (4d) and (4e) respectively.

Complexes (4e) and (4f) crystallize with one molecule of benzene.

Preparation of [Pd(C_6F_5)(bipy)(S_2C–PR'_3)]ClO_4 [PR'_3 = PEt_3 (5a), PBu_3 (5b), *or* P(C_6H_{11})$_3$ (5c)].—To a solution of [PdCl(C_6F_5)(bipy)] (0.233 g, 0.5 mmol) in acetone (75 cm^3) was added Ag(ClO_4) (0.104 g, 0.5 mmol). The mixture was stirred for 4 h at room temperature. The precipitated AgCl was filtered off.

To the resulting solution was added 0.5 mmol of S_2C–PR'_3 [PR'_3 = PEt_3 for (5a), 0.097 g; PBu_3 for (5b), 0.139 g; or P(C_6H_{11})$_3$ for (5c), 0.178 g]. It was stirred for 2 h at room temperature and concentrated to a few cm^3. The solid ob-

Table 3. Internuclear distances (Å) in the chloroform solvate of *trans*-[Pd(C_6F_5)(PEt_3)$_2$(S_2C–PEt_3)]ClO_4 (4a) with estimated standard deviations in parentheses

(*a*) Complex cation			
Pd–C(1)	2.057(12)	P(2)–C(22A)	1.82(4)
C(1)–C(2)	1.399(19)	P(2)–C(23A)	1.84(4)
C(2)–C(3)	1.394(19)	P(2)–C(21B)	1.80(3)
C(3)–C(4)	1.346(21)	P(2)–C(22B)	1.87(4)
C(4)–C(5)	1.352(21)	P(2)–C(23B)	1.84(3)
C(5)–C(6)	1.371(18)	C(21A)–C(211A)	1.57(5)
C(6)–C(1)	1.307(17)	C(22A)–C(221)	1.80(5)
C(2)–F(2)	1.344(17)	C(23A)–C(231)	1.51(4)
C(3)–F(3)	1.360(17)	C(21B)–C(211B)	1.47(4)
C(4)–F(4)	1.355(16)	C(22B)–C(221)	1.74(4)
C(5)–F(5)	1.331(15)	C(23B)–C(231)	1.58(4)
C(6)–F(6)	1.366(15)	Pd–S(1)	2.342(3)
Pd–P(1)	2.318(4)	S(1)–C(7)	1.699(16)
P(1)–C(11)	1.859(18)	C(7)–S(2)	1.632(15)
P(1)–C(12)	1.810(17)	C(7)–P(3)	1.838(15)
P(1)–C(13)	1.808(23)	P(3)–C(31)	1.793(17)
C(11)–C(111)	1.569(26)	P(3)–C(32)	1.926(31)
C(12)–C(121)	1.553(25)	P(3)–C(33)	1.887(24)
C(13)–C(131)	1.620(28)	C(31)–C(311)	1.607(25)
Pd–P(2)	2.351(4)	C(32)–C(321)	1.248(35)
P(2)–C(21A)	1.74(3)	C(33)–C(331)	1.314(33)
(*b*) Perchlorate anion			
Cl(4)–O(1)	1.40(2)	Cl(4)–O(3)	1.35(2)
Cl(4)–O(2)	1.31(3)	Cl(4)–O(4)	1.33(4)
(*c*) Chloroform solvent			
C(8)–Cl(1)	1.785(19)	C(8)–Cl(3)	1.722(20)
C(8)–Cl(2)	1.739(19)		

Table 4. Interbond angles (°) in the chloroform solvate of (4a), with estimated standard deviations in parentheses

(*a*) Complex cation					
S(1)–Pd–P(1)	88.8(1)	F(6)–C(6)–C(1)	119.5(12)	Pd–P(2)–C(23B)	114.1(9)
P(1)–Pd–C(1)	89.0(3)	Pd–P(1)–C(11)	115.8(6)	C(21B)–P(2)–C(22B)	105.5(14)
C(1)–Pd–P(2)	90.5(3)	Pd–P(1)–C(12)	112.6(6)	C(21B)–P(2)–C(23B)	104.3(12)
P(2)–Pd–S(1)	91.4(1)	Pd–P(1)–C(13)	111.3(7)	C(22B)–P(2)–C(23B)	101.3(14)
Pd–C(1)–C(2)	121.3(10)	C(11)–P(1)–C(12)	106.6(8)	P(2)–C(21B)–C(211B)	118.1(19)
Pd–C(1)–C(6)	123.3(11)	C(11)–P(1)–C(13)	107.6(9)	P(2)–C(22B)–C(221)	102.6(20)
C(2)–C(1)–C(6)	115.4(13)	C(12)–P(1)–C(13)	101.9(9)	P(2)–C(23B)–C(231)	107.5(18)
C(1)–C(2)–F(2)	121.7(12)	P(1)–C(11)–C(111)	113.5(13)	Pd–S(1)–C(7)	109.5(5)
C(1)–C(2)–C(3)	120.2(15)	P(1)–C(12)–C(121)	111.8(12)	S(1)–C(7)–S(2)	129.4(9)
F(2)–C(2)–C(3)	118.1(13)	P(1)–C(13)–C(131)	113.3(15)	S(1)–C(7)–P(3)	113.3(8)
C(2)–C(3)–F(3)	118.5(16)	Pd–P(2)–C(21A)	115.1(11)	S(2)–C(7)–P(3)	117.1(9)
C(2)–C(3)–C(4)	119.9(15)	Pd–P(2)–C(22A)	111.4(13)	C(7)–P(3)–C(31)	111.6(7)
F(3)–C(3)–C(4)	121.6(14)	Pd–P(2)–C(23A)	112.4(13)	C(7)–P(3)–C(32)	104.5(10)
C(3)–C(4)–F(4)	119.5(15)	C(21A)–P(2)–C(22A)	106.7(18)	C(7)–P(3)–C(33)	107.6(9)
C(3)–C(4)–C(5)	120.9(14)	C(21A)–P(2)–C(23A)	105.0(17)	C(31)–P(3)–C(32)	108.1(11)
F(4)–C(4)–C(5)	119.5(15)	C(22A)–P(2)–C(23A)	105.4(19)	C(31)–P(3)–C(33)	111.4(9)
C(4)–C(5)–F(5)	119.0(14)	P(2)–C(21A)–C(211A)	116.3(25)	C(32)–P(3)–C(33)	113.5(12)
C(4)–C(5)–C(6)	116.7(14)	P(2)–C(22A)–C(221)	102.3(23)	P(3)–C(31)–C(311)	111.3(12)
F(5)–C(5)–C(6)	124.2(15)	P(2)–C(23A)–C(231)	110.5(26)	P(3)–C(32)–C(321)	116.1(27)
C(5)–C(6)–F(6)	113.6(13)	Pd–P(2)–C(21B)	116.1(8)	P(3)–C(33)–C(331)	116.3(21)
C(5)–C(6)–C(1)	126.8(14)	Pd–P(2)–C(22B)	113.9(11)		
(*b*) Perchlorate anion					
O(1)–Cl(4)–O(2)	122.6(15)	O(1)–Cl(4)–O(4)	89.2(19)	O(2)–Cl(4)–O(4)	100.7(20)
O(1)–Cl(4)–O(3)	119.7(14)	O(2)–Cl(4)–O(3)	107.1(16)	O(3)–Cl(4)–O(4)	114.4(18)
(*c*) Chloroform solvent					
Cl(1)–C(8)–Cl(2)	108.2(10)	Cl(2)–C(8)–Cl(3)	113.5(11)	Cl(1)–C(8)–Cl(3)	109.1(10)

tained after adding diethyl ether was filtered off, washed with ether, vacuum dried and identified as $[Pd(C_6F_5)(bipy)(S_2C-PR'_3)]ClO_4$.

Reaction of $[Pd(C_6F_5)(PEt_3)_3]ClO_4$ *with* CS_2.—A freshly prepared colourless solution of $[Pd(C_6F_5)(PEt_3)_3]ClO_4$ (0.218 g, 0.3 mmol) in CS_2 (15 cm^3) was stirred overnight at room temperature, whereupon the colour of solution turned pink. The solvent was evaporated to dryness, the resulting pink solid was recrystallized from methanol–diethyl ether and identified as (4a).

Table 5. Least-squares planes data for the chloroform solvate of (4a)

(*a*) Coefficients (*P*, *Q*, *R*, and *S*), where the expression $Px + Qy + Rz = S$ (Å) defines the plane * (*x*, *y*, and *z* are atomic fractional co-ordinates)

	P	*Q*	*R*	*S*
Plane 1:				
Pd, S(1), P(1), C(1), P(2)	13.137	3.892	−12.128	−2.056
Plane 2:				
C(1)—C(6)	−4.202	14.691	1.040	−0.137
Plane 3:				
S(1), C(7), S(2), P(3)	−4.956	14.444	2.148	0.227

(*b*) Individual atomic deviations (Å) from each plane

Plane 1: Pd −0.078, S(1) 0.073, P(1) −0.041, C(1) 0.084, P(2) −0.038

Plane 2: C(1) 0.006, C(2) −0.004, C(3) 0.005, C(4) −0.008, C(5) 0.009, C(6) −0.008, Pd 0.037, F(2) 0.030, F(3) 0.052, F(4) −0.009, F(5) 0.031, F(6) 0.000

Plane 3: S(1) −0.012, C(7) 0.033, S(2) −0.012, P(3) −0.009, Pd −0.074

(*c*) Root-mean-square deviations (Å) of atoms defining each plane from the plane

Plane 1: 0.066 Plane 2: 0.007 Plane 3: 0.019

(*d*) Dihedral angles (°)

Plane 1–Plane 2	89.8
Plane 1–Plane 3	86.5
Plane 2–Plane 3	4.0

* All atoms have unit weights.

Preparation of $[Pt(OClO_3)(C_6F_5)(PR_3)_2]$ (PR_3 = PEt_3 *or* PBu_3) *or* $[Pt(OClO_3)(C_6F_5)](bipy)]$.—Solutions of these complexes were obtained by reaction of stoicheiometric amounts of $[PtCl(C_6F_5)(PR_3)_2]$ or $[PtCl(C_6F_5(bipy)]$ and $Ag(ClO_4)$ in dichloromethane (0.25 mmol, *ca.* 25 cm^3); the mixture was stirred for 3 h at room temperature and the precipitated AgCl was filtered off.

Preparation of $[Pt(C_6F_5)(PR_3)_2(S_2C-PR'_3)]ClO_4$ [PR_3 = PR'_3 = PEt_3 (4g) *or* PBu_3 (4h)].—To a solution of 0.25 mmol of $[Pt(OClO_3)(C_6F_5)(PR_3)_2]$ [PR_3 = PEt_3 to synthesize (4g), *or* PBu_3 for (4h)] in dichloromethane (30 cm^3) was added 0.25 mmol of $S_2C-PR'_3$ (PR'_3 = PEt_3, 0.0486 g; or PBu_3, 0.0686 g).

The mixture was stirred for 3 h at room temperature; the resulting red solution was concentrated to a few cm^3. A pink solid was obtained after adding benzene or ethanol. It was filtered off, washed with ethanol (2 × 5 cm^3), vacuum dried, and identified as $[Pt(C_6F_5)(PR_3)_2(S_2C-PR'_3)]ClO_4$.

Preparation of $[Pt(C_6F_5)(bipy)(S_2C-PR'_3)]ClO_4$ [PR'_3 = PEt_3 (5d), PBu_3 (5e), *or* $P(C_6H_{11})_3$ (5f)].—To a solution of $[Pt(OClO_3)(C_6F_5)(bipy)]$ (0.25 mmol) in dichloromethane (30 cm^3) was added 0.25 mmol of $S_2C-PR'_3$ [PR'_3 = PEt_3, 0.0486 g; PBu_3 0.0696 g; or $P(C_6H_{11})_3$, 0.0891 g].

The mixture was stirred for 1 h at room temperature and the solvent was evaporated to dryness. An ochre solid was obtained after adding ethanol (5 cm^3). It was filtered off, washed with ethanol, vacuum dried and identified as $[Pt(C_6F_5)(bipy)(S_2C-PR'_3)]ClO_4$.

Molecular Structure Determination of (4a) (*chloroform solvate*).—Slow evaporation of a chloroform solution of (4a)

Table 6. Fractional co-ordinates of atoms in the chloroform solvate of (4a), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.129 19(7)	0.007 62(6)	0.318 39(5)	C(22B) *	0.305 4(25)	−0.152 3(22)	0.319 7(18)
C(1)	0.229 9(10)	0.027 0(8)	0.420 5(7)	C(221)	0.300 5(23)	−0.105 9(21)	0.236 5(16)
C(2)	0.206 0(12)	0.015 0(8)	0.484 3(7)	C(23A) *	0.086 7(31)	−0.214 7(27)	0.330 8(23)
C(3)	0.274 9(13)	0.030 5(9)	0.552 8(8)	C(23B) *	0.182 8(21)	−0.197 8(18)	0.403 6(15)
C(4)	0.365 3(12)	0.055 2(9)	0.557 6(8)	C(231)	0.075 8(18)	−0.204 2(16)	0.405 4(13)
C(5)	0.389 8(10)	0.067 6(8)	0.496 7(9)	S(1)	0.030 66(26)	−0.003 62(24)	0.195 52(17)
C(6)	0.319 4(11)	0.050 9(8)	0.430 9(7)	C(7)	−0.081 6(11)	−0.038 4(11)	0.191 0(8)
F(2)	0.116 1(7)	−0.008 1(7)	0.481 7(4)	S(2)	−0.122 42(35)	−0.065 37(36)	0.257 17(23)
F(3)	0.247 9(9)	0.021 7(7)	0.613 4(5)	P(3)	−0.163 44(31)	−0.055 37(37)	0.096 73(21)
F(4)	0.432 1(8)	0.069 5(7)	0.624 4(5)	C(31)	−0.105 1(12)	−0.029 8(10)	0.030 8(9)
F(5)	0.479 2(6)	0.094 2(6)	0.503 8(5)	C(311)	−0.179 1(16)	−0.038 5(14)	−0.051 5(12)
F(6)	0.349 3(6)	0.064 2(6)	0.371 7(5)	C(32)	−0.266 8(23)	0.027 2(19)	0.085 1(17)
P(1)	0.085 82(30)	0.153 06(24)	0.316 12(19)	C(321)	−0.243 5(21)	0.105 6(19)	0.088 7(15)
C(11)	0.154 6(13)	0.218 3(12)	0.397 7(9)	C(33)	−0.205 1(18)	−0.172 4(16)	0.088 7(12)
C(111)	0.121 2(15)	0.315 9(13)	0.393 6(11)	C(331)	−0.136 7(22)	−0.231 9(20)	0.101 9(15)
C(12)	0.095 8(13)	0.210 0(11)	0.236 9(9)	Cl(4)	0.461 1(4)	0.251 2(4)	0.017 7(3)
C(121)	0.198 7(15)	0.201 0(12)	0.230 7(10)	O(1)	0.400 8(16)	0.216 3(14)	0.053 9(11)
C(13)	−0.041 8(16)	0.164 9(14)	0.303 8(11)	O(2)	0.541 1(21)	0.293 7(18)	0.052 1(14)
C(131)	−0.069 3(17)	0.137 7(15)	0.375 5(12)	O(3)	0.421 5(16)	0.289 6(14)	−0.048 2(12)
P(2)	0.178 01(32)	−0.138 49(23)	0.319 99(20)	O(4)	0.496 4(28)	0.171 6(28)	0.014 9(19)
C(21A) *	0.284 6(26)	−0.165 1(22)	0.389 7(18)	C(8)	0.500 3(14)	−0.059 1(12)	0.842 0(10)
C(211A) *	0.315 2(29)	−0.263 7(26)	0.395 6(21)	Cl(1)	0.383 5(4)	−0.040 6(4)	0.775 8(3)
C(21B) *	0.104 2(19)	−0.206 2(16)	0.246 3(13)	Cl(2)	0.530 9(5)	0.031 2(4)	0.899 3(3)
C(211B) *	0.133 1(21)	−0.297 7(19)	0.243 9(15)	Cl(3)	0.582 1(5)	−0.080 5(5)	0.797 1(4)
C(22A) *	0.195 6(30)	−0.168 8(27)	0.234 1(22)				

* Population parameter 0.5 (see text).

afforded pink blocks. A single crystal, *ca.* 0.03 × 0.03 × 0.025 cm, was cut from a larger one and mounted (epoxy-resin adhesive) on a thin glass fibre. Oscillation and zero- and first-layer (equi-inclination) Weissenberg photographs (Cu-K_α X-radiation) yielded space group and approximate unit-cell dimensions.

On transference to an Enraf-Nonius CAD4 diffractometer accurate cell parameters were determined *via* the centring of 25 strong, general reflections with θ between 12 and 13° (graphite-monochromated Mo-K_α X-radiation, λ = 0.710 69 Å).

Crystal data. $[C_{25}H_{45}F_5P_3PdS_2][ClO_4]\cdot CHCl_3$, M = 922.9, Monoclinic, a = 14.5965(18), b = 15.356(3), c = 19.324 2(16) Å, β = 109.257(8)°, U = 4 089.13 Å^3, Z = 4, D_c = 1.499 g cm^{-3}, $F(000)$ = 1 880, μ(Mo-K_α) = 8.95 cm^{-1}, space group $P2_1/a$ (non-standard setting of $P2_1/c$, C^5_{2h}, no. 14) from systematic absences.

Intensity data were recorded, at 289 ± 1 K, with the same crystal on the same instrument, using ω—2θ scans in the range 1.5 ⩽ θ ⩽ 25°. Omega scan widths were given by (0.85 + 0.35 tan θ)°, and only those reflections for which $I \geqslant 2.0\sigma(I)$ from a rapid prescan were remeasured, such that the final net intensity had $I > 33\sigma(I)$ subject to a maximum measuring time of 60 s. Two orientation and two intensity control reflections were remeasured every 100 reflections and every 3 600 s respectively. Although no crystal movement was detected, analysis of the intensity controls revealed some crystal decay ($I \longrightarrow 0.81I$ over the 82 h of X-ray exposure), and all intensities were appropriately scaled-up (*via* an exponential decay function). Data were not corrected for X-ray absorption.

Of 7 174 symmetry-independent reflections measured 4 093 had $F_o \geqslant 3.0\sigma(F_o)$ and were retained for structure solution (Patterson and difference-Fourier techniques) and refinement (full-matrix least squares; Pd, S, P, Cl, F, and aryl C atoms anisotropic, others isotropic, no H atoms included). Structure factors were weighted according to $w^{-1} = [\sigma^2(F_o) + 0.001\,55(F_o)^2]$. The $P(2)Et_3$ ligand is disordered in the crystal, and this has been modelled in terms of two components (A and B) of equal contribution.

Refinement was cycled to convergence, R = 0.1049, R' = 0.1256 for 307 variables.* A final ΔF synthesis revealed no peak >1.2 nor trough <−0.8 e Å^{-3}, and there was no unusual or systematic variation of the root-mean-square deviation of a reflection of unit weight *versus* parity group, (sinθ/λ), F_o, h, k, or l.

All calculations were executed with SHELX 76 [16] or XANADU [17] on the University of London Computer Centre CDC 7600 machine, using inlaid neutral scattering factors for all atoms except Pd; for this, coefficients for an analytical approximation were abstracted from 'International Tables'.[18] Table 6 lists the derived atomic fractional co-ordinates. The molecular plot was constructed using ORTEP-II.[18]

* The R values are somewhat higher than might have been anticipated. Possible contributory factors could include (*i*) our use of a non-severe OMIT parameter, (*ii*) somewhat imperfect modelling of the disorder in the $P(2)Et_3$ ligand, and (*iii*) a possibly non-stoicheiometric amount of solvate (solvate thermal parameters in the 1 : 1 model are rather high).

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