Synthesis and Characterization of Methylplatinum(II) *O,O'*-Dialkyl Dithiophosphates. Crystal Structure of $[PtMe\{S_2P(OPr^i)_2\}(AsPh_3)]$†

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Methylplatinum(II) *O,O'*-dialkyl dithiophosphates of the type $[PtMe\{S_2P(OR)_2\}L]$ and $[PtMe\{S_2P(OR)_2\}(L\text{–}L)]$ [R = Et or Pr^i; L = PPh_3, $P(C_6H_4Me\text{-}p)_3$, $P(OPh)_3$ or $AsPh_3$; L–L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2AsPh_2$] have been synthesized. They were characterized by elemental analyses and NMR (^1H and ^{31}P) data. A single-crystal X-ray structure determination of $[PtMe\{S_2P(OPr^i)_2\}(AsPh_3)]$ has established a chelated dithiophosphate ligand moiety. The four-membered metallacyclic PtS_2P ring is planar.

During the last two decades or so a number of palladium(II) and platinum(II) complexes with anionic dithio ligands R_2NCS_2, $ROCS_2$, RCS_2, R_2PS_2, and $(RO)_2PS_2$ (R = alkyl or aryl) have been synthesized and their reaction chemistry with Group 15 donor ligands has been investigated.[1–5] In these reactions various products containing chelating, monodentate and ionic dithio ligands are formed and even in some cases dealkylation[6,7] of dithiocarbonate and dithiophosphate takes place depending on the stoichiometry of the neutral donor. Interestingly the oxidation of dithiocarboxylate complexes readily affords the corresponding binuclear platinum(III) derivatives.[5] Despite extensive studies on classical coordination complexes of platinum(II) with dithio ligands, organometallic platinum complexes have received little attention.[8] In this paper we describe the synthesis and characterization of methylplatinum dialkyl dithiophosphates.

Experimental

The compounds [Pt(Me)I(cod)][9] (cod = cycloocta-1,5-diene), [Pt(Me)I(dppe)][10] [dppe = 1,2-bis(diphenylphosphino)ethane], [Pt(Me)I(dadpe)] (dadpe = 1-diphenylarsino-2-diphenylphosphinoethane) and $NH_4[S_2P(OR)_2]$[11] were prepared by the published methods. Proton NMR spectra were recorded on a Varian FT-80A, Bruker AC-200 or AMX-500 spectrometer operating at 80, 200 and 500 MHz, respectively. Chemical shifts are relative to the internal chloroform peak (δ 7.26); ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer operating at 32.203 MHz and chemical shifts are in ppm from external 85% H_3PO_4. Elemental analyses were performed by the Analytical Chemistry Division of Bhabha Atomic Research Centre (BARC).

Preparations.—$[PtMe\{S_2P(OPr^i)_2\}(PPh_3)]$. To a propan-2-ol solution (5 cm^3) of $NH_4[S_2P(OPr^i)_2]$ (60 mg, 0.26 mmol) was added a benzene solution (10 cm^3) of [Pt(Me)Cl(cod)] (92 mg, 0.26 mmol) with stirring which was continued for 1 h at room temperature. To this a benzene solution (10 cm^3) of triphenylphosphine (68 mg, 0.26 mmol) was added and the whole was stirred for an additional 5 h. The solvents were evaporated *in vacuo* and the residue was extracted with dichloromethane–hexane (1:1, v/v) and filtered. The filtrate was concentrated and on cooling in a freezer gave colourless crystals of the product (85 mg, 61%). The other complexes were prepared in a similar manner by dissolving the ammonium salt in the appropriate alcohol. Pertinent data are given in Table 1.

$[PtMe\{S_2P(OPr^i)_2\}(dppe)]$. A propan-2-ol solution of $NH_4[S_2P(OPr^i)_2]$ (32 mg, 0.14 mmol) was added to a vigorously stirred benzene solution of [Pt(Me)I(dppe)] (101 mg, 0.14 mmol) at room temperature. The whole was stirred for 11 h. The solvents were removed *in vacuo* and the residue was recrystallized from toluene–hexane as a colourless crystalline solid in 72% (82 mg) yield. The other related complexes were prepared in a similar manner.

Crystallography.—Crystallographic data together with data collection details are given in Table 2. All the data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data by measuring intensities of four reflections with χ near 90 for different ψ values (0 < ψ < 360, every 10) and using the EAC program from the Enraf-Nonius package. The maximum and minimum correction factors for absorption were 0.99 and 0.65. Two standard reflections (1 7 3 and −1 −3 −7) measured every 1800 s showed no intensity variation.

The structure was solved by routine heavy-atom methods. The non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were omitted. The final cycle of full-matrix least-squares refinement converged with unweighted and weighted agreement factors of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.029$ and $R' = [(\Sigma w|F_o| - |F_c|)^2/|\Sigma w F_o{}^2]^{\frac{1}{2}} = 0.041$. A final difference map had maximum density of 0.52 e Å^{-3} near platinum. Programs from Enraf-Nonius SDP Plus Package[12] were run on a PDP 11/73 computer. Fractional atomic coordinates are listed in Table 3.

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

Results and Discussion

Reaction of [Pt(Me)X(cod)] (X = Cl or I, cod = cycloocta-1,5-diene) with 1 mole equivalent of $NH_4[S_2P(OR)_2]$ in the presence of 1 equivalent of Group 15 donor afforded complexes of the type $[PtMe\{S_2P(OR)_2\}L]$ **1** [(L = PPh_3, $P(C_6H_4Me\text{-}p)_3$, $P(OPh)_3$ or $AsPh_3$]. Treatment of [Pt(Me)I(L–L)] [L–L = $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Ph_2PCH_2CH_2AsPh_2$ (dadpe)]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Melting-point and analytical data for $[PtMe\{S_2P(OR)_2\}(L)]$ and $[PtMe\{S_2P(OR)_2\}(L\text{-}L)]$

Complex	Recrystallization solvent (% yield)	m.p./ °C	Analysis* (%) C	H
1a $[PtMe\{S_2P(OEt)_2\}(AsPh_3)]$	CH_2Cl_2–hexane (33)	112	39.0 (39.4)	4.0 (4.0)
1b $[PtMe\{S_2P(OEt)_2\}(PPh_3)]$	Acetone–hexane (53)	125	41.7 (42.0)	4.2 (4.3)
1c $[PtMe\{S_2P(OEt)_2\}\{P(C_6H_4Me\text{-}p)_3\}]$	Hexane (66)	110	44.2 (44.6)	4.8 (4.9)
1d $[PtMe\{S_2P(OPr^i)_2\}(AsPh_3)]$	CH_2Cl_2–hexane (42)	133	40.6 (41.1)	4.4 (4.4)
1e $[PtMe\{S_2P(OPr^i)_2\}(PPh_3)]$	CH_2Cl_2–hexane (48)	138	43.6 (43.8)	4.8 (4.7)
1f $[PtMe\{S_2P(OPr^i)_2\}\{P(C_6H_4Me\text{-}p)_3\}]$	Hexane (56)	80	46.7 (46.2)	5.1 (5.2)
1g $[PtMe\{S_2P(OPr^i)_2\}\{P(OPh)_3\}]$	Hexane (45)	77	41.3 (40.9)	4.5 (4.4)
2a $[PtMe\{S_2P(OEt)_2\}(dppe)]$	Acetone–hexane (76)	78	46.0 (46.9)	4.5 (4.7)
2b $[PtMe\{S_2P(OEt)_2\}(dadpe)]$	Acetone–hexane (70)	70	44.1 (44.4)	4.3 (4.4)
2c $[PtMe\{S_2P(OPr^i)_2\}(dppe)]$	Toluene–hexane (72)	150	47.3 (48.2)	5.0 (5.0)
2d $[PtMe\{S_2P(OPr^i)_2\}(dadpe)]$	Toluene–hexane (53)	158	44.9 (45.8)	4.5 (4.8)

* Required values are given in parentheses.

with 1 equivalent of ammonium dialkyl dithiophosphate yields $[PtMe\{S_2P(OR)_2\}(L\text{-}L)]$ **2** (Scheme 1).

$$[Pt(Me)X(cod)] + NH_4[S_2P(OR)_2] + L \longrightarrow [PtMe\{S_2P(OR)_2\}L] + NH_4X + cod$$

	R	L
1a	Et	$AsPh_3$
1b	Et	PPh_3
1c	Et	$P(C_6H_4Me\text{-}p)_3$
1d	Pr^i	$AsPh_3$
1e	Pr^i	PPh_3
1f	Pr^i	$P(C_6H_4Me\text{-}p)_3$
1g	Pr^i	$P(OPh)_3$

$$[Pt(Me)I(L\text{-}L)] + NH_4[S_2P(OR)_2] \longrightarrow [PtMe\{S_2P(OR)_2\}(L\text{-}L)] + NH_4I$$

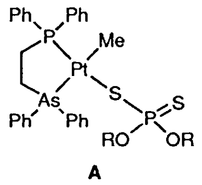
	R	L–L
2a	Et	dppe
2b	Et	dadpe
2c	Pr^i	dppe
2d	Pr^i	dadpe

Scheme 1

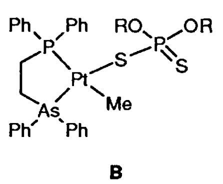
The ^{31}P NMR spectra of **2b**, **2d** and **1b**, **1c**, **1e**–**1g** containing neutral phosphorus donor ligands displayed 1:4:1 triplets of doublets for each of the dithio and neutral phosphorus ligands. The ^1J(Pt–P) values (Table 4) are much greater than those reported for analogous dialkyldithiocarbamate complexes.[8] The spectra of the complexes **2a** and **2c** exhibited 1:4:1 triplets of doublets of doublets [^3J(P–P) = 8 and 26 ± 1 Hz] due to coupling with platinum and two magnetically different phosphorus nuclei (dppe) for the dithio group. For the dppe ligand two triplets of doublets were observed; one phosphorus atom being *trans* to the methyl group [^1J(Pt–P) = 1701, ^3J(P–P) = 25 Hz] while the other one is *trans* to sulfur [^1J(Pt–P) ≈3700, ^3J(P–P) = 8 Hz]. This suggests that dppe acts in a chelating fashion and the dithiophosphate behaves in a monodentate manner. Based on the magnitude of ^2J(Pt–P) (72–79 Hz), a similar structure can be suggested for the

Table 2 Crystal data and data collection parameters for $[PtMe\{S_2P(OPr^i)_2\}(AsPh_3)]$

Crystal data	
Formula	$C_{25}H_{32}AsO_2PPtS_2$
M	729.6
Crystal habit	Colourless plates
Crystal size/mm	0.10 × 0.35 × 0.25
Symmetry, space group	Monoclinic, $P2_1/c$ (no. 14)
a/Å	8.467(1)
b/Å	15.846(3)
c/Å	21.541(2)
β/°	98.03(1)
U/Å^3	2 861.8
Z	4
D_c/g cm^{-3}	1.693
F(000)	1 424
μ(Mo-Kα)/cm^{-1}	63.13
Intensity measurements	
Diffractometer	Enraf-Nonius CAD-4
Radiation (λ/Å)	0.710 69
Monochromator	Graphite
Scan technique	θ–2θ
Scan width/°	0.70 + 0.35 tan θ
No. of data collected	5 501
No. of unique data	5 232
No. of unique reflections used [$I > 3\sigma(I)$]	3 831
No. of reflections used to determine cell constants	25 (7 < θ < 10°)
No. of parameters refined	289
Final largest shift/e.s.d.	0.16



A



B

Table 3 Fractional atomic coordinates for non-hydrogen atoms with estimated standard deviations (e.s.d.s.) in parentheses for [PtMe{$S_2P(OPr^i)_2$}($AsPh_3$)] **1d**

Atom	x	y	z	Atom	x	y	z
Pt	0.326 88(3)	0.201 69(2)	0.178 61(1)	C(10)	0.853(1)	0.155 2(6)	0.382 3(4)
As	0.499 00(7)	0.100 53(4)	0.228 91(3)	C(11)	0.931(1)	0.223 1(6)	0.360 4(4)
S(1)	0.304 4(2)	0.150 9(1)	0.071 11(8)	C(12)	0.881(1)	0.253 6(6)	0.300 7(4)
S(2)	0.145 3(2)	0.303 7(1)	0.134 19(9)	C(13)	0.749(1)	0.215 5(5)	0.263 6(4)
P	0.149 1(2)	0.245 1(1)	0.052 15(8)	C(14)	0.611 5(7)	0.024 2(4)	0.180 3(3)
O(1)	0.185 3(6)	0.306 3(3)	−0.001 9(2)	C(15)	0.520 7(8)	−0.021 9(5)	0.132 6(3)
O(2)	−0.018 9(6)	0.217 5(3)	0.017 8(2)	C(16)	0.599(1)	−0.078 4(5)	0.096 0(4)
C(1)	0.327 9(9)	0.258 0(5)	0.265 7(3)	C(17)	0.765(1)	−0.085 2(5)	0.106 2(4)
C(2)	0.393 1(7)	0.022 6(4)	0.278 1(3)	C(18)	0.853(1)	−0.040 3(6)	0.152 5(4)
C(3)	0.234 7(7)	0.039 4(5)	0.286 4(3)	C(19)	0.774 3(9)	0.016 4(5)	0.190 5(3)
C(4)	0.156 8(8)	−0.017 4(6)	0.321 1(4)	C(20)	0.330(1)	0.359 6(6)	0.005 4(4)
C(5)	0.234 0(9)	−0.090 5(5)	0.347 4(4)	C(21)	0.270(1)	0.450 3(7)	0.009 4(6)
C(6)	0.387 4(9)	−0.106 2(5)	0.339 4(4)	C(22)	0.411(1)	0.344 7(8)	−0.049 7(5)
C(7)	0.468 2(8)	−0.049 3(5)	0.302 2(3)	C(23)	−0.111 7(8)	0.148 2(5)	0.040 9(4)
C(8)	0.672 0(7)	0.148 3(4)	0.285 9(3)	C(24)	−0.253(1)	0.185 8(7)	0.065 4(6)
C(9)	0.722 1(9)	0.117 1(5)	0.345 1(3)	C(25)	−0.156(1)	0.091 4(6)	−0.015 4(5)

Table 4 $^{31}P-\{^1H\}$ NMR data for [PtMe{$S_2P(OR)_2$}L] and [PtMe{$S_2P(OR)_2$}(L–L)] in $CDCl_3$

	Phosphine ligand		Dithio ligand	
Complex	δ	J/Hz	δ	J/Hz
1a	—	—	—	—
1b	21.0 (d)	^1J(Pt–P) 4512	97.9 (d)	^2J(Pt–P) 223
		^3J(P–P) 9		^3J(P–P) 9
1c	18.7 (d)	^1J(Pt–P) 4509	98.0 (d)	^2J(Pt–P) 216
		^3J(P–P) 9		^3J(P–P) 9
1d	—	—	94.3 (s)	^2J(Pt–P) 268
1e	21.1 (d)	^1J(Pt–P) 4479	93.9	^2J(Pt–P) 220
		^3J(P–P) 8		^3J(P–P) 8
1f	18.7 (d)	^1J(Pt–P) 4468	93.8 (d)	^2J(Pt–P) 215
		^3J(P–P) 8		^3J(P–P) 8
1g	76.8 (d)	^1J(Pt–P) 7488	95.5 (d)	^2J(Pt–P) 212
		^3J(P–P) 20		^3J(P–P) 18
2a	44.7 (d)	^1J(Pt–P) 1701	102.1 (d,d)	^2J(Pt–P) 72
	(*trans* to Me)	^3J(P–P) 25		^3J(P–P) 8,25
	47.6 (d)	^1J(Pt–P) 3694		
	(*trans* to S)	^3J(P–P) 8		
2b	49.1 (d)	^1J(Pt–P) 3709	102.1 (d)	^2J(Pt–P) 73
		^3J(P–P) 8		^3J(P–P) 8
2c	44.3 (d)	^1J(Pt–P) 1692	100.1 (d,d)	^2J(Pt–P) 79
	trans to Me	^3J(P–P) 27		^3J(P–P) 8,27
	47.6 (d)	^1J(Pt–P) 3680		
	trans to S	^3J(P–P) 8		
2d	48.8 (d)	^1J(Pt–P) 3690	99.1 (d)	^2J(Pt–P) 72
		^3J(P–P) 8		^3J(P–P) 8

* s = Singlet, d = doublet, d,d = doublet of doublets.

complexes containing the dadpe ligand. Interestingly the latter complexes formed exclusively in one isomeric form with the methyl group *trans* to the arsenic (**A**), although another isomer (**B**) with the methyl *trans* to the phosphorus is also expected.

The ^1H NMR spectra (Table 5) of these complexes showed expected multiplicities and integration. The spectra of **1a** and **1d** displayed a singlet for the Pt–Me protons with platinum coupling. The spectra of [PtMe{$S_2P(OR)_2$}L] [L = PPh_3, $P(C_6H_4Me\text{-}p)_3$ or $P(OPh)_3$] and [PtMe{$S_2P(OR)_2$}(dadpe)] showed a 1:4:1 triplet of doublets for Pt–Me protons. The complexes containing dppe displayed a triplet of doublets of doublets due to coupling with platinum and the two magnetically different phosphorus nuclei. The methyl groups of the OPr^i moiety are anisochronous as two doublets were observed for **1d**–**1g**.

The structure of one of the complexes, [PtMe{$S_2P(OPr^i)_2$}($AsPh_3$)] **1d** was established by single-crystal X-ray diffraction analysis. The molecular structure shown in Fig. 1 consists of discrete monomeric molecules with square-planar configuration around platinum. Selected bond lengths and angles are given in Table 6. The various bond lengths are normal within experimental error.[13,14] The dithiophosphate ligand is asymmetrically chelated to the platinum atom, the Pt–S distance [2.434(2) Å] *trans* to the methyl group is longer than that [2.341(2) Å] *trans* to the triphenylarsine. The latter distance is in accord with the reported value in platinum(II) dithio acid complexes,[7,15] however the former is the longest known Pt–S (dithio ligand) distance. This variation in Pt–S distances illustrates the stronger *trans* influence of the methyl group than that of the $AsPh_3$ ligand.[16] The P–S bond lengths of 1.994(3) and 2.001(3) Å are intermediate between the double (1.94 Å) and single bond values (2.09 Å), confirming the partial double bond character as expected.

Because of the four-membered chelate ring various angles around platinum deviate from the normal value of 90°. Thus S(1)–Pt–S(2) angle has been compressed to 83.10(7)°, while the adjacent angle As–Pt–S(1) has opened to 100.12(5)°. The other angles, As–Pt–C(1) [87.2(3)°] and S(2)–Pt–C(1) [89.6(2)°], show little deviation. In metal complexes the four-membered MS_2P ring has been shown to adopt either a planar[17] or non-

Table 5 ^{1}H NMR data for [PtMe{$\mathrm{S_2P(OR)_2}$}L] and [PtMe{$\mathrm{S_2P(OR)_2}$}(L–L)] in CDCl$_3$

	Pt–Me		
Complex	δ	J/Hz	Ligand protons
1a	0.55 (s)	^2J(Pt–H) 80	1.35 (t, J = 7, CH$_3$), 4.20 (m, OCH$_2$), 7.45 (br m, Ph)
1b	0.50 (d)	^2J(Pt–H) 80 ^3J(P–H) 4.4	1.35 (t, J = 7, CH$_3$), 4.15 (m, OCH$_2$), 7.40 (br m, Ph)
1c	0.47(d)	^2J(Pt–H) 80 ^3J(P–H) 4.5	1.30 (t, J = 7, CH$_3$), 2.35 (s, C$_6$H$_4$*Me*), 4.15 (m, OCH$_2$), 7.10–7.65 (m, C$_6$$H_4$Me)
1d	0.57 (s)	^2J(Pt–H) 79	1.37 (d, J = 6, CH$_3$), 1.41 (d, J = 6, CH$_3$), 4.90 (m, OCH), 7.35–7.65 (br m, Ph)
1e	0.53 (d)	^2J(Pt–H) 80 ^3J(P–H) 4.5	1.34 (d, J = 6, CH$_3$), 1.39 (d, J = 6, CH$_3$), 4.85 (m, OCH), 7.40–7.75 (br m, Ph)
1f	0.48 (d)	^2J(Pt–H) 80 ^3J(P–H) 4.5	1.32 (d, J = 6, CH$_3$), 1.37 (d, J = 6, CH$_3$), 2.38 (s, C$_6$H$_4$*Me*), 4.90 (m, OCH), 7.10–7.60 (m, C$_6$$H_4$Me)
1g	0.70 (d)	^2J(Pt–H) 79 ^3J(P–H) 3.7	1.26 (d, J = 6, CH$_3$), 1.29 (d, J = 6, CH$_3$), 4.59 (m, OCH), 7.14–7.33 (m, Ph)
2a	0.86 (d,d)	^2J(Pt–H) 61 ^3J(P–H) *cis* 5.2 ^3J(P–H) *trans* 7.2	1.21 (t, J = 7, CH$_3$), 2.24 (m, CH$_2$CH$_2$), 4.05 (m, OCH$_2$), 7.40–7.80 (br m, Ph)
2b	0.93 (d)	^2J(Pt–H) 70 ^3J(P–H) *cis* 5	1.16 (t, J = 7, CH$_3$), 1.95–2.37 (br m, CH$_2$CH$_2$), 4.00 (m, OCH$_2$), 7.40–7.75 (br m, Ph)
2c	0.91 (d,d)	^2J(Pt–H) 62	1.25 (d, J = 6, CH$_3$), 2.32 (m, CH$_2$CH$_2$), 4.72 (m, OCH), 7.40–7.80 (br m, Ph)
2d	1.00 (d)	^2J(Pt–H) 71 ^3J(P–H) 5	1.26 (d, J = 6, CH$_3$), 1.92–2.42 (br m, CH$_2$CH$_2$), 4.79 (m, OCH), 7.41–7.76 (br m, Ph)

* s = singlet, d = doublet, d,d = doublet of doublets, t = triplet, m = multiplet, br = broad.

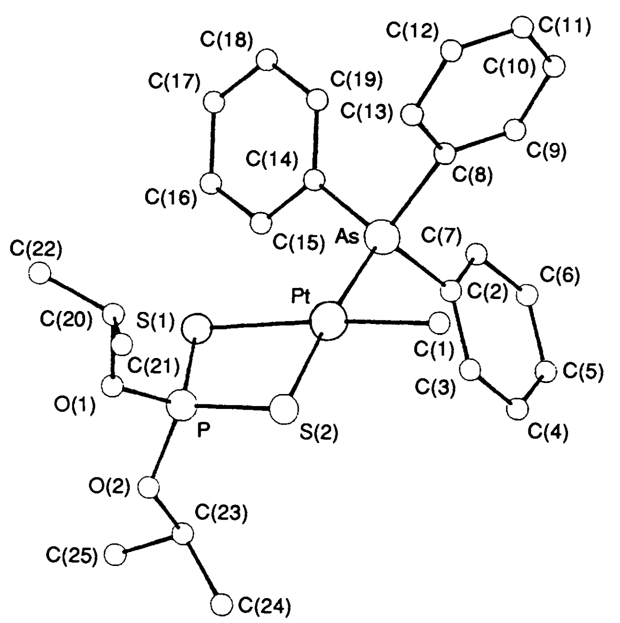


Fig. 1 Molecular structure of **1a**

Table 6 Selected bond distances (Å) and angles (°) for [PtMe{$\mathrm{S_2P(OPr^i)_2}$}(AsPh$_3$)] **1d**

Pt–S(1)	2.434(2)	P–O(1)	1.577(5)
Pt–S(2)	2.341(2)	P–O(2)	1.572(5)
Pt–C(1)	2.077(7)	O(1)–C(20)	1.48(1)
Pt–As	2.3293(6)	O(2)–C(23)	1.476(9)
As–C(2)	1.930(6)	C(20)–C(21)	1.53(1)
As–C(8)	1.929(6)	C(20)–C(22)	1.48(1)
As–C(14)	1.936(6)	C(23)–C(24)	1.50(1)
P–S(1)	1.994(3)	C(23)–C(25)	1.51(1)
P–S(2)	2.001(3)	av. C–C (phenyl)	1.395
As–Pt–S(1)	100.12(5)	Pt–S(1)–P	84.78(9)
As–Pt–S(2)	176.11(5)	Pt–S(2)–P	87.12(9)
As–Pt–C(1)	87.2(3)	S(1)–P–S(2)	105.0(2)
S(1)–Pt–S(2)	83.10(7)	S(1)–P–O(1)	114.9(2)
S(1)–Pt–C(1)	172.6(2)	S(1)–P–O(2)	114.6(3)
S(2)–Pt–C(1)	89.6(2)	S(2)–P–O(1)	113.4(2)
Pt–As–C(2)	112.8(2)	S(2)–P–O(2)	114.8(2)
Pt–As–C(8)	113.3(2)	O(1)–P–O(2)	94.6(3)
Pt–As–C(14)	120.1(2)	P–O(1)–C(20)	121.1(4)
		P–O(2)–C(23)	122.6(4)

planar[18,19] conformation. In the present case the PtS$_2$P ring is planar [the phosphorus atom shows maximum deviation (0.0158 ± 0.0018 Å) from the plane formed by the Pt, S(1), S(2) and P atoms]. This ring is co-planar with the square plane of the platinum atom.

It is noteworthy that in spite of structural similarity of **1d** with [Pt{$\mathrm{S_2P(OEt)_2}$}$_2$(PPh$_3$)][15] (the monodentate dithio ligand is substituted by a methyl group) and also the longer Pt–S distance *trans* to methyl group in **1d**, organoplatinum dialkyl dithiophosphates are inert to neutral donor ligands. The ^{31}P NMR spectrum of [PtMe{$\mathrm{S_2P(OPr^i)_2}$}(PPh$_3$)] was unaffected when treated with an excess of PPh$_3$ at room temperature. Insertion of the Pt–Me bond into acetylenes is well documented.[20,21] However, no insertion of phenylacetylene or dimethylacetylene dicarboxylate was observed when treated with **1e** as revealed by ^{1}H NMR spectroscopy.

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