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Synthesis and characterization of trimethylplatinum(IV) complexes with diphenyldithiophosphinic acid. Crystal and molecular structures of $[PtMe_3(SSPPh_2)]_2$ and $[PtMe_3(py)(SSPPh_2)]$ *

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Abstract

The preparation and characterization of trimethylplatinum(IV) diphenyldithiophosphinates of the type $[PtMe_3(SSPPh_2)]_2$ and $[PtMe_3(L)(SSPPh_2)]$ (L = mono- or bi-dentate neutral donor ligands) have been reported. On the basis of NMR data (^1H, ^{31}P, ^{195}Pt), stereochemistry of these complexes has been discussed. The neutral donor ligands cleave the sulphur bridges of the dimeric complex $[PtMe_3(SSPPh)]_2$ to give mononuclear complexes. Crystal structures of two compounds $[PtMe_3(SSPPh)]_2$ and $[PtMe_3(py)(SSPPh_2)]$ have been reported. In the former complex, the dithio ligand acts in a chelating tridentate mode while in the latter complex it is symmetrically chelated.

Introduction

The trimethylplatinum(IV) complexes have been studied quite extensively. The central metal atom in these complexes invariably adopts an octahedral geometry [1] with a rigid or non-rigid structure depending on the ligands attached to

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platinum. Recently a number of triorganoplatinum(IV) compounds with neutral chalcogen ligands have been studied by Abel et al. [2] and many interesting fluxional processes have been demonstrated. The less studied trimethylplatinum(IV) complex with anionic thio ligands offers many interesting possibilities. For example $[PtMe_3(S_2CNR_2)]_2$ [3], $[PtMe_3(SSAsMe_2)]_2$ [4] and $[PtMe_3(thio\text{-}\beta\text{-}dik)]_2$ [5] (thio-β-dik = thio-β-diketonate anion) are stereochemically rigid, while $[PtMe_3(SSCOR)]_2$ is non-rigid at room temperature [3]. Additionally such ligands show a variety of bonding modes as we have shown in trimethylplatinum(IV) dialkyldithiophosphates [6]. In this paper we report on the synthesis and characterization of trimethylplatinum(IV) complexes with diphenyldithiophosphinic acid.

Results and discussion

Reaction of trimethylplatinum iodide with $NaSSPPh_2$ gave a dinuclear platinum(IV) complex $[PtMe_3(SSPPh_2)]_2$. Reaction of trimethylplatinum iodide in the presence of pyridine with diphenyldithiophosphinic acid afforded a mononuclear complex $[PtMe_3(py)(SSPPh_2)]$ (Scheme 1). Treatment of $[PtMe_3(SSPPh_2)]_2$ with neutral donor ligands resulted in bridge cleavage to give mononuclear complexes $[PtMe_3(L)(SSPPh_2)]$. The formation of $[PtMe_3(\alpha\text{-picoline})(SSPPh_2)]$ is reversible as on recrystallization α-picoline is lost but addition of excess α-picoline in solution stabilizes the complex. Physical data for these complexes are summarized in Table 1.

$$[PtMe_3I]_4 + 4Ph_2PSSNa \rightarrow 2[PtMe_3(SSPPh_2)]_2 + 4NaI$$

$$[PtMe_3I]_4 + 4Ph_2PSSH + py(excess) \rightarrow 4[PtMe_3(py)(SSPPh_2)] + 4py \cdot HI$$

$$[PtMe_3(SSPPh_2)]_2 + 2\overset{\frown}{NN} \rightarrow 2\left[PtMe_3(\overset{\frown}{NN})(SSPPh_2)\right]$$

Scheme 1.

Table 1

Analyses and melting points of trimethylplatinum(IV) complexes with diphenyldithiophosphinic acid

Complex [a]	m.p. (°C)	% Analyses found (calculated)		
		C	H	N
$[PtMe_3(SSPPh_2)]_2$	194 [b]	37.19 (36.81)	3.96 (3.91)	–
$[PtMe_3(py)(SSPPh_2)]$	172	41.90 (42.25)	4.20 (4.25)	2.20 (2.46)
$[PtMe_3(\alpha\text{-picoline})(SSPPh_2)]$ [c]				
$[PtMe_3(AsPh_3)(SSPPh_2)]$	172	50.36 (49.81)	4.38 (4.31)	–
$[PtMe_3(bip)(SSPPh_2)]$	208	45.90 (46.50)	4.10 (4.21)	4.43 (4.34)
$[PtMe_3(bipMe_2)(SSPPh_2)]$	210	48.93 (48.13)	4.44 (4.64)	3.96 (4.16)
$[PtMe_3(phen)(SSPPh_2)]$	226	48.86 (48.42)	4.07 (4.06)	3.23 (4.18)
$[PtMe_3(pz_2CH_2)(SSPPh_2)]$	173	41.58 (41.44)	4.20 (4.27)	8.50 (8.79)
$[PtMe_3(pypz)(SSPPh_2)]$	192	43.30 (43.53)	4.20 (4.13)	6.40 (6.62)

[a] Abbreviations: py = pyridine; bip = 2,2'-bipyridine; $bipMe_2$ = 4,4'-dimethyl-2,2'-bipyridine; phen = 1,10-phenanthroline; pz_2CH_2 = bis(1-pyrazolyl)methane; pypz = 1-(2-pyridyl)pyrazole. [b] Decomposed. [c] Analysis varied from sample to sample owing to partial conversion into $[PtMe_3(SSPPh_2)]_2$.

Table 2

^{1}H and $^{31}P\{^{1}H\}$ NMR data for trimethylplatinum(IV) complexes with diphenyldithiophosphinic acid

Complex	^{31}P NMR data [a]		^{1}H NMR data [b]
	δ (in ppm)	$^{2}J(^{195}Pt-^{31}P)$ (in Hz)	δ (Pt–Me protons)
Ph_2PSSH	56.2	–	–
$[PtMe_3(SSPPh_2)]_2$	71.9	63	0.86 (77.8) 2Me; 1.19 (72.2) 1Me [c]
$[PtMe_3(py)(SSPPh_2)]$	71.9 [c]	67	1.44 (75.0) 2Me; 2.22 (70.0) 1Me [c]
$[PtMe_3(\alpha\text{-picoline})(SSPPh_2)]$ [d]	74.0	54	
$[PtMe_3(AsPh_3)(SSPPh_2)]$	78.1	83	1.10 (75.0) 2Me; 1.59 (70.0) 1Me
$[PtMe_3(bip)(SSPPh_2)]$	57.3	58	1.23 (68.8) 2Me; 0.23 (68.9) 1Me
$[PtMe_3(bipMe_2)(SSPPh_2)]$	57.7	58	1.02 (68.5) 2Me; 0.23 (69.4) 1Me
$[PtMe_3(phen)(SSPPh_2)]$	57.6	57	1.42 (69.6) 2Me; 0.25 (69.0) 1Me
$[PtMe_3(pz_2CH_2)(SSPPh_2)]$	57.1	56	1.00 (70.0) 2Me; 0.60 (70.0) 1Me
$[PtMe_3(pypz)(SSPPh_2)]$	58.4	57	1.33 (76.9) 1Me; 1.18 (71.8) 1Me 0.33 (69.0) 1Me

[a] Recorded in CH_2Cl_2 solution containing a capillary (3 mm o.d.) of C_6D_6 for locking. [b] Ligand proton resonances appeared in the region 6.90–9.05 ppm as complex multiplets, for $bipMe_2$ complex a singlet at δ 2.51 ppm assignable to Me protons of the nitrogen donor ligand was also observed. [c] Recorded in benzene-d_6. [d] Excess α-picoline was used.

The ^{1}H, ^{31}P and ^{195}Pt NMR spectra of these complexes have been recorded in $CDCl_3$. The ^{195}Pt NMR spectrum of $[PtMe_3(SSPPh_2)]_2$ displayed a triplet at δ −2592 ppm with $^{2}J(^{195}Pt-^{31}P)$ 66 Hz suggesting a dimeric structure with two bridging dithiophosphinate ligands, as reported for analogous dialkayldithiophosphate derivatives [6] and $[PtMe_3(SSAsMe_2)]_2$ [4]. The ^{195}Pt NMR spectrum of $[PtMe_3(py)(SSPPh_2)]$ exhibited a doublet at δ −2632 ppm with $^{2}J(^{195}Pt-^{31}P)$ 63 Hz indicating its monomeric nature.

The ^{31}P NMR spectra of these complexes showed a single resonance which was deshielded with respect to the free ligand. Deshielding was maximum with chelated dithiophosphinic acid complexes and minimum with monodentate ligand moiety. However, analogous dialkyldithiophosphoric acid derivatives show the following trend of deshielding: tridentate < bidentate < monodentate < ionic. The magnitude of $^{2}J(Pt-P)$ for these complexes is of the order of 56–83 Hz. The complex $[PtMe_3(SSPPh_2)]_2$ showed $^{4}J(Pt-P)$ couplings (5.7 Hz).

The ^{1}H NMR spectrum of $[PtMe_3(SSPPh_2)]_2$ exhibited two Pt–Me triplets (200 MHz) (Table 2) indicating that either the two methyl signals overlap or the molecule is fluxional. The spectrum at high field (500 MHz), however, displayed three resonances at δ 1.19, 0.97 and 0.91 ppm. The platinum satellites for the latter two broad signals merged in the main resonances at room temperature could be resolved at −40°C [δ 1.18 ($^{2}J(Pt-H)$ 72.6 Hz); 0.95 ($^{2}J(Pt-H)$ 76.3 Hz); 0.86 ($^{2}J(Pt-H)$ 74.4 Hz)]. Three triplets for Pt–Me protons are expected for a rigid structure as has been observed in case of $[PtMe_3(SSAsMe_2)]_2$ [4]. The ^{1}H NMR spectra of the addition complexes consisted of two platinum-methyl triplets of relative intensity 2:1 (except for the complex containing pypz ligand for which three signals of equal intensity were observed as expected) together with expected ligand proton resonances. The low field signal for the complexes containing bidentate chelating ligands is assigned as the methyl groups *trans* to the neutral

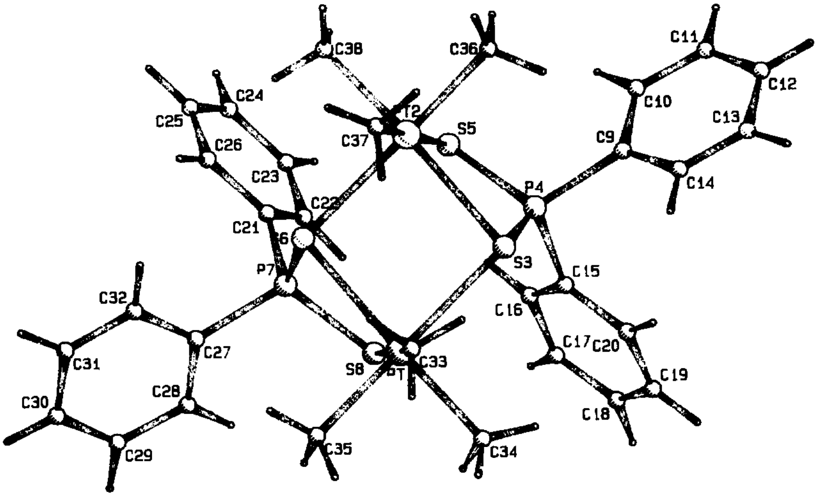

Fig. 1. Molecular structure of $[PtMe_3(SSPPh_2)]_2$ with the crystallographic numbering scheme for non-hydrogen atoms.

donor ligands. The resonance at low frequency is attributed to the methyl group *trans* to S of the monodentate dithio ligand moiety. The complexes containing monodentate neutral donor ligands with the chelating dithiophosphinic acid moiety displayed two resonances. The high field resonance corresponding to two methyl protons is assigned to the methyl groups *trans* to chelating Ph_2PSS ligand while the one appearing at the lower field is attributed to the methyl group *trans* to L.

Conclusions drawn from the spectroscopic data on these complexes were confirmed by single crystal X-ray diffraction studies of the representative compounds $[PtMe_3(SSPPh_2)]_2$ and $[PtMe_3(py)(SSPPh_2)]$.

The molecular structure of $[PtMe_3(SSPPh_2)]_2$ (I) is shown in Fig. 1 and is similar to the structure reported recently for an analogous compound $[PtMe_3(SSAsMe_2)]_2$ [4]. In the molecule, the dithiophosphorus moiety is attached to two platinum atoms giving rise to triconnective bridges. Both the platinum atoms show distorted octahedral geometry. Each of them is coordinated by three *fac* methyl groups and three *fac* sulphur atoms. The two phosphinic acid ligands are mutually *cis* to the four-membered Pt_2S_2 ring.

Selected geometrical parameters for I are listed in Table 3. The Pt–C distances at both platinum atoms lie in the range 2.06(2)–2.09(2) Å and agree with the sum of the covalent radii (2.08 Å) [7]. The dithiophosphinic ligand moiety is unsymmetrically chelated to the platinum atom. The Pt–S distance where sulphur is involved in bridge formation is longer than the one singly coordinated to platinum. The bridging Pt–S distances are nearly the same [2.530(4), 2.551(3) Å]. The Pt–S distances are in agreement with the Pt–S distances reported for $[PtMe_3(SSAsMe_2)]_2$ [4].

The geometry around each phosphorus atom is distorted tetrahedral with the interbond angles ranging from 103.2(2) to 113.7(5)°. The P–S bond lengths [1.985 and 2.05 Å] are in the range observed for metal complexes containing chelated

Table 3

Selected bond distances (Å) and angles (°) with e.s.d.s for $[PtMe_3SSPPh_2)]_2$ [a]

Pt(1)–S(3)	2.551(3)	Pt(2)–C(37)	2.06(2)
Pt(1)–S(6)	2.590(3)	Pt(2)–C(38)	2.09(2)
Pt(1)–S(8)	2.524(4)	S(3)–P(4)	2.052(5)
Pt(1)–C(33)	2.08(2)	S(5)–P(4)	1.985(5)
Pt(1)–C(34)	2.07(2)	S(6)–P(7)	2.051(5)
Pt(1)–C(35)	2.09(2)	S(8)–P(7)	1.985(6)
Pt(2)–S(3)	2.578(3)	P(4)–C(9)	1.82(1)
Pt(2)–S(5)	2.527(4)	P(4)–C(15)	1.82(1)
Pt(2)–S(6)	2.530(4)	P(7)–C(21)	1.82(1)
Pt(2)–C(36)	2.08(2)	P(7)–C(27)	1.81(1)
S(3)–Pt(1)–S(6)	85.2(2)	S(6)–Pt(2)–C(37)	83.2(5)
S(3)–Pt(1)–S(8)	98.3(1)	S(6)–Pt(2)–C(38)	91.2(5)
S(3)–Pt(1)–C(33)	84.7(6)	C(36)–Pt(2)–C(37)	88.2(7)
S(3)–Pt(1)–C(34)	92.3(5)	C(36)–Pt(2)–C(38)	88.8(6)
S(3)–Pt(1)–C(35)	170.2(5)	C(37)–Pt(2)–C(38)	86.2(7)
S(6)–Pt(1)–S(8)	80.0(1)	Pt(1)–S(3)–Pt(2)	94.3(2)
S(6)–Pt(1)–C(33)	96.2(5)	Pt(1)–S(3)–P(4)	114.3(2)
S(6)–Pt(1)–C(34)	172.4(5)	Pt(2)–S(3)–P(4)	82.1(1)
S(6)–Pt(1)–C(35)	95.1(5)	Pt(2)–S(5)–P(4)	84.7(2)
S(8)–Pt(1)–C(33)	175.0(6)	Pt(1)–S(6)–Pt(2)	94.6(1)
S(8)–Pt(1)–C(34)	93.3(6)	Pt(1)–S(6)–P(7)	81.9(2)
S(8)–Pt(1)–C(35)	91.4(6)	Pt(2)–S(6)–P(7)	113.5(2)
C(33)–Pt(1)–C(34)	90.8(8)	Pt(1)–S(8)–P(7)	84.9(2)
C(33)–Pt(1)–C(35)	85.7(8)	S(3)–P(4)–S(5)	108.3(3)
C(34)–Pt(1)–C(35)	88.6(7)	S(3)–P(4)–C(9)	107.6(5)
S(3)–Pt(2)–S(5)	79.8(2)	S(3)–P(4)–C(15)	111.9(5)
S(3)–Pt(2)–S(6)	85.9(2)	S(5)–P(4)–C(9)	111.9(5)
S(3)–Pt(2)–C(36)	94.9(5)	S(5)–P(4)–C(15)	113.7(5)
S(3)–Pt(2)–C(37)	99.1(5)	C(9)–P(4)–C(15)	103.2(6)
S(3)–Pt(2)–C(38)	173.6(5)	S(6)–P(7)–S(8)	109.0(2)
S(5)–Pt(2)–S(6)	97.9(1)	S(6)–P(7)–C(21)	113.1(5)
S(5)–Pt(2)–C(36)	90.8(5)	S(6)–P(7)–C(27)	106.4(5)
S(5)–Pt(2)–C(37)	178.4(6)	S(8)–P(7)–C(21)	112.7(6)
S(5)–Pt(2)–C(38)	95.1(5)	S(8)–P(7)–C(27)	111.5(5)
S(6)–Pt(2)–C(36)	171.3(5)	C(21)–P(7)–C(27)	103.7(6)

[a] $(C–C)_{av}$ for phenyl rings = 1.38(3) Å.

dithiophosphorus grouping [8,9]. The P–C distances are in agreement with the reported values for similar compounds.

The four-membered Pt_2S_2 ring (plane I) is planar. The four-membered chelated rings Pt(1)S(8)P(7)S(6) (plane II) and Pt(2)S(3)P(4)S(5) (plane III), however are not planar, the maximum deviations being 0.185 and 0.203 Å, respectively. Plane I is inclined to planes II and III by 75.43 and 104.16°, respectively, *i.e.* they are more or less perpendicularly disposed. The ring in plane II is inclined to the plane III by 28.8°. Individual phenyl rings are planar, maximum deviation being 0.02(2) Å.

The structure of $[PtMe_3(py)(SSPPh_2)]$ (II) shown in Fig. 2, consists of discrete monomeric molecules with octahedral geometry around the platinum atom. Selected bond lengths and angles are given in Table 4. The dithio ligand symmetrically chelates to the platinum atom, the Pt–S distances being 2.530(3) and 2.532(3)

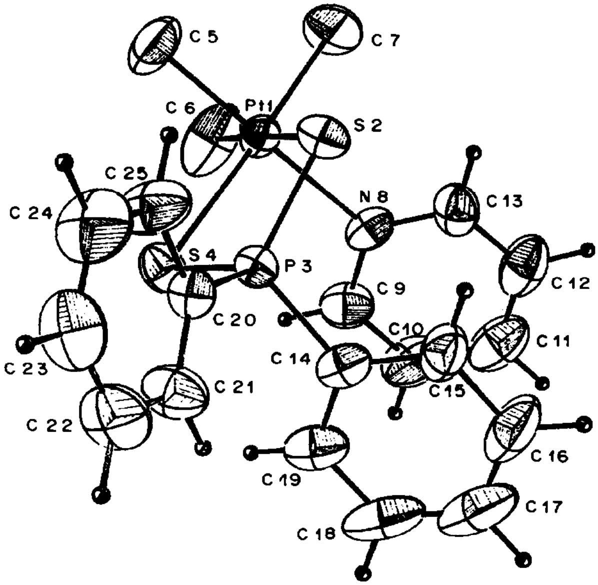

Fig. 2. Molecular structure of [PtMe$_3$(py)(SSPPh$_2$)] with the crystallographic numbering scheme for non-hydrogen atoms.

Å. The Pt–C distances [2.03(1) and 2.06(2) Å] *trans* to sulphur are essentially identical and are close to the values found for trimethylplatinum compounds. The Pt–C distance [2.10(1) Å] *trans* to nitrogen is somewhat longer than that *trans* to sulphur and also significantly longer than the Pt–C distance *trans* to N [2.032(5) Å]

Table 4

Selected bond distances (Å) and angles (°) with e.s.d.s for [PtMe$_3$(py)(SSPPh$_2$)] [a]

Pt(1)–S(2)	2.530(3)	S(2)–P(3)	1.994(3)
Pt(1)–S(4)	2.532(3)	S(4)–P(3)	2.015(4)
Pt(1)–N(8)	2.239(9)	P(3)–C(14)	1.83(1)
Pt(1)–C(5)	2.10(1)	P(3)–C(20)	1.82(1)
Pt(1)–C(6)	2.06(2)	N(8)–C(9)	1.36(1)
Pt(1)–C(7)	2.03(1)	N(8)–C(13)	1.33(1)
S(2)–Pt(1)–S(4)	79.99(9)	C(5)–Pt(1)–C(7)	88.1(6)
S(2)–Pt(1)–N(8)	89.4(3)	C(6)–Pt(1)–C(7)	86.1(7)
S(2)–Pt(1)–C(5)	91.0(5)	Pt(1)–S(2)–P(3)	83.7(1)
S(2)–Pt(1)–C(6)	177.5(5)	Pt(1)–S(4)–P(3)	83.3(1)
S(2)–Pt(1)–C(7)	96.3(5)	S(2)–P(3)–S(4)	108.5(2)
S(4)–Pt(1)–N(8)	91.8(2)	S(2)–P(3)–C(14)	111.3(4)
S(4)–Pt(1)–C(5)	88.9(4)	S(2)–P(3)–C(20)	111.8(3)
S(4)–Pt(1)–C(6)	97.6(5)	S(4)–P(3)–C(14)	110.4(4)
S(4)–Pt(1)–C(7)	175.2(5)	S(4)–P(3)–C(20)	110.4(4)
N(8)–Pt(1)–C(5)	179.2(6)	C(14)–P(3)–C(20)	104.6(6)
N(8)–Pt(1)–C(6)	91.2(6)	Pt(1)–N(8)–C(9)	119.2(8)
N(8)–Pt(1)–C(7)	91.2(5)	Pt(1)–N(8)–C(13)	120.8(8)
C(5)–Pt(1)–C(6)	88.5(7)		

[a] $(C-C)_{av}$ for pyridine ring 1.38(2) Å; $(C-C)_{av}$ for phenyl rings 1.39(2) Å.

reported for $[PtMe_3I\{(Me_2pz)_2CH_2\}]$ [10]. The Pt–N distance [2.239(9) Å] compares well with the reported values of 2.24 Å in $[PtMe_3I\{(Me_2pz)_2CH_2\}]$ [10] and $[PtMe_2I_2\{(Me_2pz)_2CH_2\}]$ [11].

Coordination around phosphorus is nearly tetrahedral. The P–C distances [1.83(1) and 1.82(1) Å] are essentially identical and are close to the values found for other similar compounds [8,9]. P–S bond lengths of 1.994(3) and 2.015(4) Å are intermediate between the double bond value (1.94 Å) and the single bond value (2.09 Å), confirming the partial double bond character as expected for isobidentate type of bonding of the ligand moiety.

The configuration about platinum is approximately octahedral with interbond angles in the range 79.99(9)–97.6(5)° for right angles and 175.2(5)–179.2(6)° for linear arrays. One of the right angles around platinum S–Pt–S is considerably reduced [79.99(9)°] owing to the small bite of the dithio ligand and consequently adjacent angles S(2)–Pt(1)–C(7) and S(4)–Pt(1)–C(6) are opened up.

The individual phenyl rings on phosphorus and pyridine ligand are planar, the maximum deviation of any of the atoms from the mean plane being 0.012, 0.003 and 0.008 Å, respectively. The four-membered PtSSP ring is distinctly non-planar, the maximum deviation of one of the atoms being 0.188 Å. This lies more or less perpendicular to the pyridine plane (dihedral angles of 70.9 and 114.7°). The phenyl rings on the phosphorus are inclined to each other at 79.9°; one ring is nearly parallel to the pyridine ring (dihedral angle of 12°) while the second ring is inclined at 69.4°.

Experimental

Trimethylplatinum iodide [12], 1-(2-pyridyl)pyrazole (pypz) [13], bis(1-pyrazolyl)methane (pz_2CH_2) [14] and diphenyldithiophosphinic acid [15] were prepared as mentioned in the literature. Analytical grade solvents were used throughout and dried and distilled before use. ^1H NMR spectra were recorded on a Bruker AC 200 spectrometer in $CDCl_3$ and chemical shifts are in ppm from an internal chloroform peak. ^{31}P and ^{195}Pt NMR spectra were recorded on a Varian FT-80A spectrometer operating at 32.203 and 17.01 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4 for ^{31}P and Na_2PtCl_6 in D_2O for ^{195}Pt. Microanalyses were performed by the Bio-organic and Analytical Chemistry Divisions of BARC. Melting points were determined in capillary tubes and are uncorrected.

Synthesis of $[PtMe_3(SSPPh_2)]_2$

A benzene solution of trimethylplatinum iodide (401 mg, 1.09 mmol) was added to a solution of $NaSSPPh_2$ (prepared from 26 mg (1.1 mmol) of Na in methanol and 274 mg (1.09 mmol) of Ph_2PSSH in benzene). The reaction mixture was stirred at room temperature for 3 h during which the colour of the reaction mixture changed from colourless to pale yellow. Solvents were removed under vacuum, the residue was dissolved in a minimum quantity of dichloromethane and filtered. The filtrate was concentrated *in vacuo* and the residue was recrystallized from benzene to give $[PtMe_3(SSPPh_2)]_2$ as a colourless crystalline solid in 62% yield (329 mg).

Preparation of [PtMe$_3$(py)(SSPPh$_2$)]

To a benzene solution of trimethylplatinum iodide (102 mg, 0.28 mmol) was added excess pyridine (0.2 ml) and the mixture was stirred for 30 min. To this a benzene solution of Ph_2PSSH (71 mg, 0.28 mmol) was added and the reactants stirred for an additional 1 h before filtering to remove pyridinium iodide. The filtrate was dried *in vacuo*. The residue was recrystallized from a benzene/hexane mixture to give a colourless crystalline solid (117 mg, 74%).

Reaction between [PtMe$_3$(SSPPh$_2$)]$_2$ and 2,2'-bipyridine

To a dichloromethane solution of $[PtMe_3(SSPPh_2)]_2$ (72 mg, 0.15 mmol) was added a dichloromethane solution of 2,2'-bipyridine (24 mg, 0.15 mmol); the mixture was stirred at room temperature for 2 h. The solvent was reduced to 3 ml and benzene (3 ml) was added. The mixture was left aside to crystallize giving colourless crystals in 53% (52 mg) yield. Other addition complexes were prepared similarly and recrystallized from appropriate solvents.

Crystallography

Intensity data were measured at room temperature on an Enraf-Nonius CAD-4 diffractometer fitted with graphite monochromated Mo-K_α radiation, $\lambda = 0.71068$ Å in the range $4 < 2\theta < 52°$ and zigzag mode of data collection. Three control reflections were monitored after every 3600 s of X-ray exposure for decay and three other orientations after every 200 reflections (maximum decay = 0.7% during

Table 5

Crystal data and refinement details for $[PtMe_3(SSPPh_2)]_2$ and $[PtMe_3(py)(SSPPh_2)]$

	$[PtMe_3(SSPPh_2)]_2$	$[PtMe_3(py)(SSPPh_2)]$
Formula	$C_{30}H_{38}P_2S_4Pt_2$	$C_{20}H_{24}NPS_2Pt$
Mol. wt.	979.0	568.6
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	10.045(1)	15.055(1)
b (Å)	20.027(2)	9.844(1)
c (Å)	16.691(2)	15.770(2)
β (°)	92.19(1)	114.58(1)
V (Å^3)	3355.3(6)	2125.3(7)
Z	4	4
D_c (g cm^{-3})	1.937	1.774
$F(000)$	1872	1104
μ (cm^{-1})	87.7	69.3
θ limits (°)	2.0–26.0	2.0–26.0
No. of data collected	5374	3731
No. of unique reflections used with $I \geqslant 3\sigma(I)$	3648	2893
R	0.040	0.037
R_w	0.048	0.048
Transmission factors		
Minimum	37.43	34.38
Maximum	99.98	99.95
Average	76.15	71.72

Table 6

Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms with e.s.d.s in parentheses for [PtMe$_3$SSPPh$_2$)]$_2$ [a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Pt(1)	0.77940(6)	0.19864(3)	0.24597(3)	3.59(1)
Pt(2)	1.09865(6)	0.20778(3)	0.37080(3)	3.30(1)
S(3)	0.9585(4)	0.2859(2)	0.2783(2)	3.15(8)
S(5)	0.9756(4)	0.2736(2)	0.4739(2)	3.40(8)
S(6)	0.9208(4)	0.1211(2)	0.3397(2)	3.34(8)
S(8)	0.6517(4)	0.2088(2)	0.3727(2)	3.73(8)
P(4)	0.9342(4)	0.3360(2)	0.3840(2)	2.88(8)
P(7)	0.7575(4)	0.1300(2)	0.4091(2)	2.99(8)
C(9)	1.046(1)	0.4073(7)	0.3854(8)	3.4(3)
C(10)	1.101(2)	0.4304(8)	0.4585(8)	4.0(4)
C(11)	1.176(2)	0.4875(9)	0.461(1)	5.2(4)
C(12)	1.199(2)	0.5222(9)	0.392(1)	5.8(5)
C(13)	1.148(2)	0.4987(9)	0.320(1)	6.0(5)
C(14)	1.075(2)	0.4417(8)	0.3159(9)	4.9(4)
C(15)	0.771(1)	0.3741(7)	0.3878(8)	3.4(3)
C(16)	0.688(1)	0.3606(7)	0.4506(9)	4.1(4)
C(17)	0.565(2)	0.392(1)	0.452(1)	6.2(5)
C(18)	0.529(2)	0.438(1)	0.394(1)	7.6(6)
C(19)	0.610(2)	0.453(1)	0.334(1)	6.7(6)
C(20)	0.731(2)	0.4210(9)	0.3302(9)	4.9(4)
C(21)	0.800(1)	0.1318(8)	0.5160(8)	3.6(3)
C(22)	0.743(2)	0.1781(8)	0.5645(8)	4.1(4)
C(23)	0.773(2)	0.1768(9)	0.6482(9)	5.4(5)
C(24)	0.852(2)	0.126(1)	0.6802(9)	6.1(5)
C(25)	0.904(2)	0.079(1)	0.632(1)	6.7(6)
C(26)	0.880(2)	0.0796(9)	0.5488(9)	5.1(4)
C(27)	0.664(1)	0.0533(7)	0.3959(7)	3.3(3)
C(28)	0.526(2)	0.0553(8)	0.3995(9)	4.3(4)
C(29)	0.455(2)	−0.0031(9)	0.396(1)	5.4(5)
C(30)	0.517(2)	−0.0627(9)	0.3897(9)	6.0(5)
C(31)	0.654(2)	−0.0647(8)	0.385(1)	5.9(5)
C(32)	0.728(2)	−0.0073(7)	0.3892(9)	4.3(4)
C(33)	0.886(2)	0.181(1)	0.1436(9)	6.5(5)
C(34)	0.660(2)	0.2675(8)	0.185(1)	6.4(5)
C(35)	0.653(2)	0.1235(8)	0.203(1)	5.8(5)
C(36)	1.261(2)	0.2724(8)	0.382(1)	4.7(4)
C(37)	1.200(2)	0.1566(9)	0.285(1)	5.6(5)
C(38)	1.194(2)	0.1441(9)	0.454(1)	5.4(5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\times[a^2\times B(1,1)+b^2\times B(2,2)+c^2\times B(3,3)+ab\cos\gamma\times B(1,2)+ac\cos\beta\times B(1,3)+bc\cos\alpha\times B(2,3)]$.

data collection which was corrected during data reduction). Data were corrected for Lorentz and polarization factors. Absorption corrections were applied. The unit cell dimensions were refined using 25 arbitrarily chosen higher order reflections around θ of 15–16°. Relevant crystal data for **I** and **II** are given in Table 5, and fractional atomic coordinates are listed in Tables 6 and 7.

A three-dimensional sharpened origin Patterson map yielded the positions of the platinum atoms. Least-squares method with difference Fourier syntheses gave

Table 7

Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms with e.s.d.s in parentheses [$PtMe_3(py)(SSPPh_2)$] [a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Pt(1)	0.13376(3)	0.09802(4)	0.90392(3)	3.03(1)
S(2)	0.1477(2)	0.0031(3)	0.7609(2)	3.42(7)
S(4)	0.3172(2)	0.1078(3)	0.9572(2)	3.63(7)
P(3)	0.2890(2)	−0.0137(3)	0.8462(2)	2.64(7)
N(8)	0.1418(6)	−0.1136(9)	0.9587(6)	3.3(3)
C(5)	0.124(1)	0.296(1)	0.853(1)	5.8(5)
C(6)	0.129(1)	0.178(1)	1.023(1)	6.8(6)
C(7)	−0.0147(8)	0.095(2)	0.850(1)	6.2(5)
C(9)	0.2129(9)	−0.145(1)	1.0435(8)	4.3(4)
C(10)	0.221(1)	−0.277(2)	1.0770(9)	5.6(5)
C(11)	0.158(1)	−0.374(1)	1.026(1)	5.8(5)
C(12)	0.085(1)	−0.341(1)	0.940((1)	5.5(5)
C(13)	0.0803(8)	−0.209(1)	0.9079(9)	4.2(4)
C(14)	0.3214(8)	−0.189(1)	0.8838(8)	3.4(3)
C(15)	0.2669(9)	−0.294(1)	0.823(1)	4.6(4)
C(16)	0.290(1)	−0.428(1)	0.853(1)	6.6(6)
C(17)	0.365(1)	−0.453(2)	0.942(1)	6.9(6)
C(18)	0.416(1)	−0.352(2)	0.999(1)	6.7(5)
C(19)	0.3947(9)	−0.217(1)	0.9707(9)	4.8(4)
C(20)	0.3669(7)	0.031(1)	0.7879(7)	2.9(3)
C(21)	0.4563(9)	−0.022(1)	0.8133(8)	4.5(4)
C(22)	0.5146(9)	0.016(2)	0.769(1)	5.4(5)
C(23)	0.480(1)	0.109(2)	0.697(1)	5.5(5)
C(24)	0.390(1)	0.160(2)	0.670(1)	6.2(5)
C(25)	0.330(1)	0.125(1)	0.714(1)	5.3(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\times[a^2 \times B(1,1) + b^2 \times B(2,2) + c^2 \times B(3,3) + ab \cos\gamma \times B(1,2) + ac \cos\beta \times B(1,3) + bc \cos\alpha \times B(2,3)]$.

the positions of all the non-hydrogen atoms. A weighted anisotropic refinement by BLOKLS of all the non-hydrogen atoms, while keeping all the hydrogen atoms in stereochemically acceptable positions, with a unit weighting scheme with a Dunitz–Seiler factor [16], yielded the final *R* values. The refinement was deemed to be over when the shift to the standard deviation ratio in scale, and the positional and thermal parameters of non-hydrogen atoms reached 0.01. The final difference map has ripples of 1.68–1.00 Å around the heavy atoms. The scattering factors for platinum, phosphorus and sulphur were from volume IV of the *International Tables for Crystallography* [17] while those of hydrogen were from Stewart *et al.* [18]. The computations were carried out using the SDP package available for PDP-11/73 [19] and NORSK data computers.

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References

1 V.K. Jain, G.S. Rao and L. Jain, Adv. Organomet. Chem., 27 (1987) 113.

2 E.W. Abel, A.R. Khan, K. Kite, K.G. Orrell and V. Sik, J. Chem. Soc., Chem. Commun., (1979) 713; E.W. Abel, M. Booth, K.G. Orrell and G.M. Pring, J. Chem. Soc., Chem. Commun., (1981) 29; E.W. Abel, S.K. Bhargava and K.G. Orrell, Prog. Inorg. Chem., 32 (1984) 1; E.W. Abel, T.P.J. Coston, K.G. Orrell, V. Sik and D. Stephenson, J. Magn. Res., 70 (1986) 34.

3 B.W. Brown, K. Kite, A.J. Nettle and A.F. Psaila, J. Organomet. Chem., 139 (1977) C1.

4 E.W. Abel, M.A. Beckett, P.A. Bates and M.B. Hursthouse, Polyhedron, 7 (1988) 1853.

5 J.R. Hall and G.A. Swile, J. Organomet. Chem., 47 (1973) 195.

6 R. Visalakshi and V.K. Jain, Transition Met. Chem., 15 (1990) 278.

7 L. Pauling, The Nature of Chemical Bond, 3rd ed., Cornell University Press, Ithaca, NY, 1960.

8 K.C. Molloy, M.B. Hossain, D. van der Helm, J.J. Zuckerman and F.P. Mullins, Inorg. Chem., 20 (1981) 2172.

9 I. Haiduc, Rev. Inorg. Chem., 3 (1981) 353.

10 H.C. Clark, G. Ferguson, V.K. Jain and M. Parvez, J. Organomet. Chem., 270 (1984) 365.

11 H.C. Clark, G. Ferguson, V.K. Jain and M. Pervez, Organometallics, 2 (1983) 806.

12 J.C. Baldwin and W.C. Kaska, Inorg. Chem., 14 (1975) 2020.

13 M.A. Khan and J.P. Polya, J. Chem. Soc. C, (1970) 85.

14 S. Trofimenko, J. Am. Chem. Soc., 92 (1970) 5118.

15 W.A. Higgins, P.W. Vogel and W.G. Graig, J. Am. Chem. Soc., 77 (1955) 1894.

16 J.D. Dunitz and P. Seiler, Acta Crystallogr., A24 (1968) 351.

17 International Tables for X-Ray Crystallography, Vol. IV, D. Reidel, Dordrecht, 1979.

18 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 48 (1965) 3175.

19 SDP programs for PDP-11/73, Enraf Nonius Ltd, Delft, Holland, 1986.