

Synthesis and characterization of binuclear arylthiolato- and phenylselenolato-bridged organoplatinum(II) complexes: crystal structure of $[\text{Pt}_2\text{Ph}_2(\mu\text{-SPh})_2(\text{PMe}_2\text{Ph})_2]$

Vimal K. Jain

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085 (India)

S. Kannan

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085 (India)

R.J. Butcher

Department of Chemistry, Howard University, Washington, DC 20059 (USA)

J.P. Jasinski

Keene State College, Keene, NH 03431 (USA)

(Received July 15, 1993)

Abstract

Binuclear organoplatinum(II) complexes of the type $[\text{Pt}_2\text{Ar}_2(\mu\text{-EAr}')_2(\text{PR}_3)_2]$ (Ar = Ph or *p*-tol; E = S or Se; Ar' = Ph or *p*-tol; $\text{PR}_3 = \text{PPr}_3$, PBu_3 or PMe_2Ph) have been synthesized and characterized by elemental analysis and nuclear magnetic resonance (^1H and ^{31}P) spectroscopy. Some of these complexes were isolated exclusively as the *trans* isomer, but others were present at a mixture of *cis* and *trans* isomers. An X-ray diffraction study of $[\text{Pt}_2\text{Ph}_2(\mu\text{-SPh})_2(\text{PMe}_2\text{Ph})_2]$ has shown that it has *sym-trans* geometry, with a planar four-membered Pt_2S_2 ring.

Key words: Platinum; Thiolate; Selenolate; Aryl

1. Introduction

Binuclear complexes of platinum(II) of the type $[\text{Pt}_2\text{X}_2(\mu\text{-Y})(\mu\text{-Z})(\text{PR}_3)_2]$ are of much current interest [1]. Compounds containing $\mu\text{-ER}$ bridges (E = S, Se or Te) offer many structural possibilities [2]. For example, the four-membered “ Pt_2YZ ” ring may adopt a planar or non-planar (bent or “butterfly”) conformation (Scheme 1). As well as *cis* and *trans* isomerism, these complexes exhibit another type of geometrical iso-

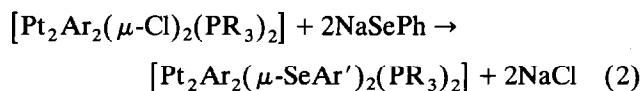
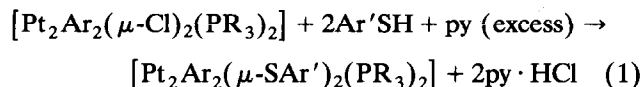
merism, namely *syn* and *anti*. For X = Cl, Y = Z = SR, it has been reported that alkylthiolato-bridged complexes prefer the *cis* geometry with a non-planar Pt_2S_2 conformation [3]. The arylthiolato-bridged palladium(II) complexes are found to be *trans* species, with a planar four-membered ring [4]. However, the complex $[\text{Pt}_2\text{Cl}_2(\mu\text{-SPh})_2(\text{Ptol}_3)_2]$, despite having an arylthiolato bridge, exists as a mixture of *cis* and *trans* isomers [5]. Evidently subtle changes in the nature of the ligand trans to the thiolato group can determine the thermodynamically preferred configurations. We have now synthesized a series of complexes containing a strong *trans*-influencing X, an aryl group, *trans* to

Correspondence to: Dr. V.K. Jain.

bridging Y, Z (Y = Z = arylthiolato or phenylselenolato group) and characterized the resulting complexes by nuclear magnetic resonance (NMR) spectroscopy.

2. Results and discussion

Arylthiolato- and phenylselenolato-bridged dinuclear organoplatinum(II) complexes of the type $[Pt_2Ar_2(\mu-EAr')_2(PR_3)_2]$ have been prepared by the following reactions:



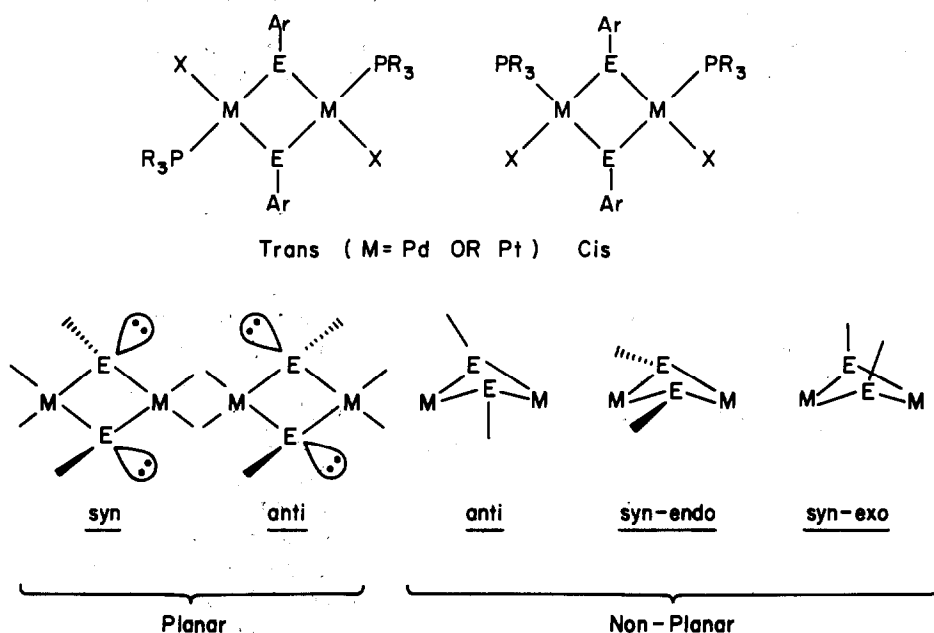
(where Ar = Ph or C_6H_4Me-4 (*p*-tol); Ar' = Ph or *p*-tol; $PR_3 = P^nPr_3$, P^nBu_3 or PMe_2Ph).

These complexes are cream to yellow air-stable crystalline solids. They can exist in *cis* and *trans* forms. Some, notably the bridged *p*-tolS compounds, could be isolated exclusively as the *trans* isomers, while others gave mixtures of both isomers, with the *trans* form predominating. It has been reported that $^1J(^{195}Pt-^{31}P)$ values are larger for the *cis* isomer than for the *trans* form, whereas $^3J(^{195}Pt-^{31}P)$ is larger for the *trans* (about 50 Hz) than for the corresponding *cis* isomer (15–20 Hz) [5]. Although $^3J(^{195}Pt-^{31}P)$ values for the two isomers are not very different in the present case (24–32 Hz) (Table 1), the higher values of $^1J(Pt-P)$ and

$^3J(Pt-P)$ (about 30 Hz) are attributed to the *cis* isomer and smaller values of $^3J(^{195}Pt-^{31}P)$ (about 25 Hz) to the *trans* isomer.

The 1H NMR spectra are consistent with the isomeric forms deduced from ^{31}P NMR data. In general, the peak multiplicities and their integration are as expected. Each isomer of the complexes containing dimethylphenylphosphine exhibited a single doublet for PMe_2 protons, indicating a planar conformation of the four-membered "Pt₂E₂" ring. Complexes having a bent configuration, such as $[Pt_2Cl_2(\mu-X)(\mu-SR)(PMe_2Ph)_2]$ (R = alkyl; X = Cl or SR) show two doublets for PMe_2 protons [5,6], whereas complexes with planar conformation, as in case of arylthiolato-bridged complexes [4], exhibit a single doublet for PMe_2 group [5]. Possibly the strong *trans*-influencing groups Ar or PR_3 , *trans* to the bridging EAr' ligand, increases the rate of inversion at E (sulfur or selenium), leading to fluxionality in the molecule and resulting in a planar "Pt₂E₂" conformation.

The low temperature 1H NMR spectrum of *trans*- $[Pt_2Ph_2(\mu-Stol)_2(PMe_2Ph)_2]$ was recorded in CD_2Cl_2 at 500 MHz. The spectrum did not change when the temperature was lowered to $-60^\circ C$ except for gradual shielding of the PMe_2 ($\delta = 1.20$ (d) ppm at room temperature (RT); $\delta = 1.15$ (d) ppm at $-60^\circ C$), the methyl protons of the $SC_6H_4CH_3-p$ (Stol) group ($\delta = 2.27$ (s) ppm at RT; $\delta = 2.22$ (s) ppm at $-60^\circ C$) and the *ortho* protons of the Stol moiety ($\delta = 7.26$ (d) ppm at RT; $\delta = 7.20$ (d) ppm at $-60^\circ C$). The changes in the chemical shifts are too small (shielding of about 0.05 ppm at



Scheme 1.

TABLE 1. ¹H and ³¹P{¹H} nuclear magnetic resonance spectral data for [Pt₂Ar₂(μ-X)₂(PR₃)₂] in CDCl₃

Complex	³¹ P{ ¹ H} NMR data			¹ H NMR data ^a , δ (ppm)
	δ (ppm)	¹ J (¹⁹⁵ Pt- ³¹ P) (Hz)	Other couplings (Hz)	
[Pt ₂ Ph ₂ (μ-Cl) ₂ (PPR ₃) ₂]	0.8 ^b 0.3 ^c	4748 4757		0.90(br), 1.45(br)(Pr); 6.85(m), 7.25(m)(Ph)
[Pt ₂ Ph ₂ (μ-SePh) ₂ (PPR ₃) ₂]	<i>trans</i>	-0.8	3585	³ J(Pt-P) = 26 0.80(br), 1.30(m)(Pr); 6.50-8.00(m, Ph)
[Pt ₂ Ph ₂ (μ-Cl) ₂ (PBu ₃) ₂]	1.3 ^b 1.0 ^c	4754	-	0.90(br), 1.50(br)(Bu); 6.80-7.35 (br, m, ph)
[Pt ₂ Ph ₂ (μ-Stol) ₂ (PBu ₃) ₂]	<i>trans</i>	2.8	3555	³ J(Pt-P) = 24 0.80(br), 1.20(br)(Bu); 2.20(s, Me); 6.60-8.80(br, m, Ph + C ₆ H ₄)
[Pt ₂ Ph ₂ (μ-SePh) ₂ (PBu ₃) ₂]	<i>trans</i> <i>cis</i>	0.1 ^b -0.7 ^c	3588 3606	³ J(Pt-P) = 25 ³ J(Pt-P) = 32 ⁴ J(P-P) = 6 0.78(br), 1.29(br)(Bu); 6.71-7.70(m, Ph)
[Pt ₂ tol ₂ (μ-Cl) ₂ (PBu ₃) ₂]	<i>trans</i> <i>cis</i>	1.3 ^b 0.9 ^c	4757 4770	- 0.85(br), 1.45(br)(Bu); 2.12(s, Me); 6.62-7.50(m, C ₆ H ₄)
[Pt ₂ tol ₂ (μ-SePh) ₂ (PBu ₃) ₂]	<i>trans</i> <i>cis</i>	0.03 ^b -0.8 ^c	3597 3606	³ J(Pt-P) = 25 0.80(br), 1.25(br)(Bu); 2.05(s, Me); 6.50-7.60(m, Ph + C ₆ H ₄)
[Pt ₂ Ph ₂ (μ-Cl) ₂ (PMe ₂ Ph) ₂] ^d		-13.1	4875	- 1.54(d, J = 11 Hz, PMe ₂); ³ J(Pt-H) = 27 Hz ^b ; 1.58(d, J = 11 Hz, PMe ₂); ³ J(Pt-H) = 27 Hz ^c ; 6.70-7.80(br, m, Ph)
[Pt ₂ Ph ₂ (μ-SPh) ₂ (PMe ₂ Ph) ₂]	<i>trans</i>	-11.0	3642	³ J(Pt-P) = 25 1.21(d, J = 10.2 Hz, PMe ₂); ³ J(Pt-H) = 25 Hz ^b ; 1.33(d, J = 10.2 Hz, PMe ₂) ^c ; 6.53-7.39(br, m, Ph)
[Pt ₂ Ph ₂ (μ-Stol) ₂ (PMe ₂ Ph) ₂]	<i>trans</i>	-10.9	3616	³ J(Pt-P) = 25 1.21(d, J = 10 Hz, PMe ₂); ³ J(Pt-H) = 41 Hz; 2.28(s, Me); 6.66-7.30(m, Ph + C ₆ H ₄)
[Pt ₂ Ph ₂ (μ-SePh) ₂ (PMe ₂ Ph) ₂]	<i>trans</i> <i>cis</i>	-14.0 ^b -13.5 ^c	3642 3722	³ J(Pt-P) = 25 0.98(d, J = 10.2 Hz, PMe ₂); ³ J(Pt-H) = 21 Hz ^b ; 1.11(d, J = 10.2 Hz, PMe ₂) ^c ; 6.76-7.84(br, m, Ph)
[Pt ₂ tol ₂ (μ-Cl) ₂ (PMe ₂ Ph) ₂]	<i>trans</i> <i>cis</i>	-13.7 ^b -13.9 ^c	4906 4940	- 1.52(d, J = 11 Hz, PMe ₂); ³ J(Pt-H) = 27 Hz ^b ; 1.57(d, J = 11 Hz, PMe ₂); ³ J(Pt-H) = 27 Hz ^c ; 2.20(br, s, Me); 6.65-7.80(br, m, Ph + C ₆ H ₄)
[Pt ₂ tol ₂ (μ-SPh) ₂ (PMe ₂ Ph) ₂]	<i>trans</i> <i>cis</i>	-11.2 ^b -10.6 ^c	3655 3738	³ J(Pt-P) = 25 1.20(d, J = 10.2 Hz, PMe ₂); ³ J(Pt-H) = 21 Hz ^b ; 1.30(d, J = 10.2 Hz, PMe ₂) ^c ; 1.99(s, Me) ^c ; 2.09(s, Me) ^b (ratio, 1:2.4); 6.38-7.40(m, Ph + C ₆ H ₄)
[Pt ₂ tol ₂ (μ-Stol) ₂ (PMe ₂ Ph) ₂]	<i>trans</i>	-11.2	3633	³ J(Pt-H) = 25 1.22(d, J = 10 Hz, PMe ₂); ³ J(Pt-H) = 39 Hz; 2.11(s, Me, Pt tol); 2.28(s, Me, Stol); 6.50-7.31(m, Ph + C ₆ H ₄)
[Pt ₂ tol ₂ (μ-SePh) ₂ (PMe ₂ Ph) ₂]	<i>trans</i> ^c <i>cis</i> ^c	-13.9 ^b -13.5 ^c	3656 3738	³ J(Pt-P) = 24 1.32(d, J = 10.2 Hz, PMe ₂); ³ J(Pt-H) = 21 Hz ^b ; 2.14(br, s, Me); 6.45-7.90(br, m, Ph + C ₆ H ₄)
[Pt ₂ tol ₂ (μ-SePh) ₂ (PMe ₂ Ph) ₂] ^a		-13.7	3658	

^a Recorded in CDCl₃; s, singlet; d, doublet; m, multiplet; br, broad. ^b Major isomer more than 70%. ^c Minor isomer less than 30%. ^d In CH₂Cl₂. ^e In C₆H₆ + C₆D₆.

-60°C) to be attributed to different conformations. However, small changes of about 0.25 ppm, in ¹⁹F NMR chemical shifts for [Pt₂(μ-SCF₃)₂(PR₃)₄]²⁺ complexes have been interpreted as due to *syn* and *anti* isomers [7].

To confirm the conclusions drawn from NMR data the structure of one representative complex was determined by X-ray diffraction. The molecular structure of [Pt₂Ph₂(μ-SPh)₂(PMe₂Ph)₂] depicted in Fig. 1, shows that the compound has a *sym-trans* configuration. The

coordination around each platinum atom is distorted square planar. The central four-membered "Pt₂S₂" ring is planar, in contrast with non-planar bridges found in *cis*-[Pt₂Cl₂(μ-SEt)₂(PPR₃)₂] [3], *cis*-[Pt₂(SBz)₂(μ-SBz)₂(PMePh₂)₂] [8] and [Pt₂(NO₂)₂(μ-SMe)₂(PPh₃)₂] [9]. There is a centre of inversion in the middle of this four-membered ring. The geometry around sulfur is distorted tetrahedral, with relevant angles as follows: Pt-S-Pt*, 97.2(1)°; Pt-S-C(1A), 104.9(5)°; Pt*-S-C(1A), 111.9(5)°. The phenyl groups of the SPh ligands adopt an *anti* configuration.

The Pt-S distance *trans* to phosphine (2.371(4) Å) is slightly shorter than that *trans* to phenyl although the difference is barely significant. The Pt-S distance *trans* to phosphine is in good agreement with the reported value [3,8,9]. Lengthening of the Pt-S bond *trans* to the phenyl group reflects the strong *trans* influence of the aryl group [10]. The Pt-S distances *trans* to C(1) and NO₂, known to be weaker *trans*-influencing ligands, are 2.27 Å [3,5] and 2.29 Å [9] respectively for thiolato-bridged platinum(II) complexes. The bond lengths Pt-P (2.232(4) Å) [3,5,8,9] and Pt-C (2.00(2) Å) [11] are in good agreement with the reported values. The average P-C distance (1.82(2) Å) is normal. The average C-C distance in the phenyl rings attached to phosphorus, sulfur and platinum is 1.39 Å, with individual values ranging between 1.33(2) and 1.45(2) Å.

The S-Pt-S* angle (Table 2) (82.8(1)°) is considerably smaller than the normal value, indicating strain in the four-membered ring. The Pt-S-Pt angle (97.2(1)°) is significantly larger than that reported for any thio-

TABLE 2. Selected bond distances and angles with estimated standard deviations for $[Pt_2Ph_2(\mu-SPh)_2(PMe_2Ph)_2]^a$

Bond distance (Å)		Bond distance (Å)	
Pt-S	2.371(4)	S-C(1A)	1.78(2)
Pt-S *	2.386(4)	P-C(1)	1.84(2)
Pt-P	2.232(4)	P-C(2)	1.82(2)
Pt-C(1B)	2.00(2)	P-C(1C)	1.81(1)
Bond angle (°)		Bond angle (°)	
S-Pt-S *	82.8(1)	Pt-P-C(1C)	115.4(4)
S-Pt-P	177.4(1)	Pt-P-C(2)	115.1(7)
S-Pt-C(1B)	89.7(4)	C(1)-P-C(1C)	102.8(7)
S*-Pt-P	98.5(1)	C(1)-P-C(2)	104.7(9)
S*-Pt-C(1B)	171.6(4)	C(1C)-P-C(2)	104.1(8)
P-Pt-C(1B)	89.2(4)	Pt-C(1B)-C(2B)	120(1)
Pt-S-Pt*	97.2(1)	Pt-C(1B)-C(6B)	120(1)
Pt-S-C(1A)	104.9(5)	P-C(1C)-C(2C)	122(1)
Pt*-S-C(1A)	111.9(5)	P-C(1C)-C(6C)	119(1)
Pt-P-Cl	113.3(6)		

^a The symmetry element indicated by an asterisk (*) is 1 - x, 1 - y, 1 - z.

TABLE 3. Melting point and analytical data for $[Pt_2Ar_2(\mu-EAr')(PR_3)_2]$

Complex ^a	Melting point (°C)	Analyses: found (calculated)	
		C	H
$[Pt_2Ph_2(\mu-SePh)_2(PPR_3)_2]$	165-166	42.4 (42.9)	5.4 (5.3)
$[Pt_2Ph_2(\mu-Stol)_2(PBu_3)_2]$	101-103	49.7 (50.2)	6.5 (6.6)
$[Pt_2Ph_2(\mu-SePh)_2(PBu_3)_2]$	127-129	44.7 (45.7)	5.8 (5.9)
$[Pt_2tol_2(\mu-SePh)_2(PBu_3)_2]$	115-117	46.6 (46.6)	6.2 (6.2)
$[Pt_2Ph_2(\mu-SPh)_2(PMe_2Ph)_2]$	182-183	46.7 (46.2)	4.1 (4.1)
$[Pt_2Ph_2(\mu-Stol)_2(PMe_2Ph)_2]$	203-204	47.2 (47.3)	4.3 (4.3)
$[Pt_2Ph_2(\mu-SePh)_2(PMe_2Ph)_2]$	162-164	41.8 (42.4)	3.8 (3.7)
$[Pt_2tol_2(\mu-SPh)_2(PMe_2Ph)_2]$	158-160	47.0 (47.3)	4.4 (4.3)
$[Pt_2tol_2(\mu-Stol)_2(PMe_2Ph)_2]$	192-194	47.8 (48.3)	4.6 (4.6)
$[Pt_2tol_2(\mu-SePh)_2(PMe_2Ph)_2]$	160-162	43.2 (43.4)	3.9 (4.0)

^a All the complexes were recrystallized from dichloromethane-ethanol with a 55-80% yield.

lato-bridged palladium(II) and platinum(II) complex [3-5,8,9].

3. Experimental details

The complexes $[Pt_2Cl_2(\mu-Cl)_2(PR_3)_2]$ [12], *cis*- $[PtCl_2(CH_2=CH_2)(PR_3)_2]$ [13], $[Pt_2Ar_2(\mu-Cl)_2(PR_3)_2]$ [14] and Me₃SnAr [15] were prepared as described previously, and gave satisfactory microanalyses. Methods and spectroscopic techniques are similar to those used previously [16].

3.1. Preparation of $[Pt_2tol_2(\mu-SPh)_2(PMe_2Ph)_2]$

Pyridine (0.2 ml) was added to a dichloromethane solution of $[Pt_2tol_2(\mu-Cl)_2(PMe_2Ph)_2]$ (120 mg, 0.13 mmol) and the mixture was stirred for 30 min. Thiophenol (28 mg, 0.255 mmol) in benzene (5 ml) was then added and the mixture was stirred for 5 h at room temperature. The solvent was removed *in vacuo* and the residue extracted with dichloromethane. After evaporation of the extract, the residue was recrystallized from dichloromethane-ethanol to give cream crystals (95 mg (68%)). Other compounds were prepared similarly, and the pertinent data are summarized in Table 3.

3.2. Preparation of $[Pt_2Ph_2(\mu-SePh)_2(PMe_2Ph)_2]$

To a vigorously stirred solution of NaSePh prepared from Ph₂Se₂ (42 mg, 0.135 mmol) in benzene-methanol by reduction with NaBH₄ as described previously [13], was added under nitrogen, a suspension of $[Pt_2Ph_2(\mu-Cl)_2(PMe_2Ph)_2]$ (121 mg, 0.135 mmol) in benzene (10 ml). The mixture was stirred at room temperature for 5 h and the solvents then evaporated off *in vacuo*. The residue was extracted with dichloromethane, the extract was filtered and concentrated to 5 ml, and 1 ml of

TABLE 4. Crystal data and refinement details for $[\text{Pt}_2\text{Ph}_2(\mu\text{-SPh})_2(\text{PMe}_2\text{Ph})_2]$

Empirical formula	$\text{C}_{40}\text{H}_{42}\text{S}_2\text{P}_2\text{Pt}_2$
Formula weight	1039.03
Crystal dimensions (mm × mm × mm)	0.4 × 0.2 × 0.6
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
<i>a</i> (Å)	9.802(2)
<i>b</i> (Å)	8.490(2)
<i>c</i> (Å)	22.788(4)
β (°)	97.93(2)
<i>Z</i>	2
D_c (g cm ⁻³)	1.837
F_{000}	1000
μ (Mo K α) (cm ⁻¹)	77.35
λ (Mo K α) (Å)	0.71069
Number of data collected	3769
Number of unique reflections	3550 ($R_{\text{int}} = 0.152$)
Number of observations ($I > 3.00\sigma(I)$)	2420
Number of variables	293
<i>R</i>	0.065
R_w	0.071

ethanol was added. Slow evaporation afforded pale-yellow crystals (105 mg (67%)). Other complexes containing a bridging PhSe group were prepared similarly.

TABLE 5. Fractional coordinates and equivalent isotropic parameters for non-hydrogen atoms with estimated standard deviations in parentheses for $[\text{Pt}_2\text{Ph}_2(\mu\text{-SPh})_2(\text{PMe}_2\text{Ph})_2]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Pt	0.34807(5)	0.42134(6)	0.45802(2)	2.53(2)
S	0.4963(4)	0.6411(4)	0.4551(2)	2.8(1)
P	0.2008(4)	0.2220(5)	0.4611(2)	3.2(2)
C(1)	0.023(2)	0.287(2)	0.4643(9)	4.6(8)
C(1A)	0.573(1)	0.614(2)	0.3895(6)	3.3(6)
C(1B)	0.240(1)	0.491(2)	0.3812(7)	3.5(6)
C(1C)	0.235(1)	0.094(2)	0.5249(6)	2.7(5)
C(2)	0.188(2)	0.088(2)	0.3981(8)	6(1)
C(2A)	0.520(2)	0.695(2)	0.3379(7)	5.2(9)
C(2B)	0.266(2)	0.422(2)	0.3272(7)	4.8(8)
C(2C)	0.174(2)	0.118(2)	0.5762(7)	3.4(6)
C(3A)	0.581(2)	0.684(3)	0.2871(9)	7(1)
C(3B)	0.199(2)	0.475(3)	0.2723(9)	6(1)
C(3C)	0.208(2)	0.022(2)	0.6251(9)	4.4(8)
C(4A)	0.698(2)	0.587(3)	0.2885(9)	7(1)
C(4B)	0.111(2)	0.597(3)	0.2709(9)	7(1)
C(4C)	0.302(2)	-0.094(2)	0.6233(8)	4.5(7)
C(5A)	0.753(2)	0.511(3)	0.338(1)	6(1)
C(5B)	0.087(2)	0.671(3)	0.322(1)	6(1)
C(5C)	0.364(2)	-0.120(2)	0.576(1)	4.7(8)
C(6A)	0.694(2)	0.517(2)	0.3908(9)	5.2(9)
C(6B)	0.152(2)	0.618(2)	0.3803(8)	4.3(8)
C(6C)	0.329(2)	-0.029(2)	0.5243(8)	4.0(7)

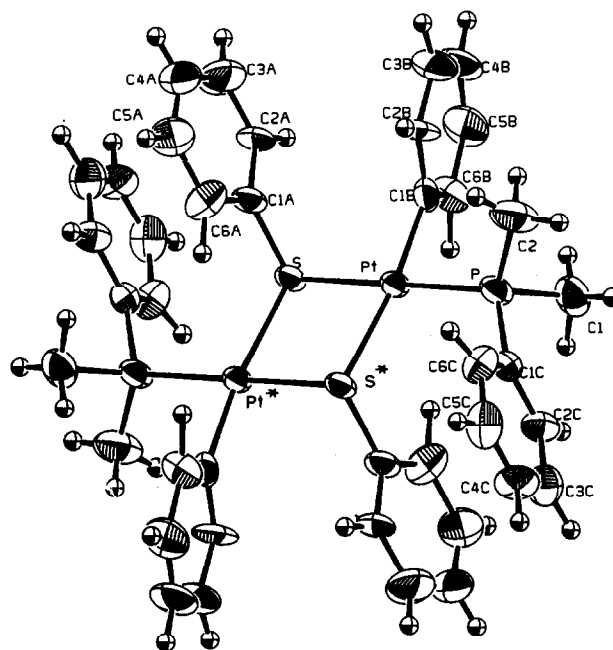
3.3. Crystallography

Intensity data were collected from transparent prismatic crystal of $\text{C}_{40}\text{H}_{42}\text{S}_2\text{P}_2\text{Pt}$ at RT on a Rigaku AFC6S diffractometer fitted with graphite-monochromated Mo K α radiation using an ω scan technique to a maximum 2θ value of 50.0°. Crystal data and refinement details are given in Table 4, and fractional atomic coordinates are listed in Table 5.

Three representative reflections were monitored after every 150 reflections and were unchanged throughout. Thus no decay correction was applied. Based on azimuthal scans of several reflections an empirical absorption correction was applied, resulting in transmission factors ranging from 0.30 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods [17]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement converged with unweighted and weighted agreement factors of R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) = 0.065 and R_w ($= [\sum_w (|F_o| - |F_c|)^2 / \sum_w (F_o)^2]^{1/2}$) = 0.071.

Neutral atom scattering factors were taken from the work of Cromer and Waber [18]. Anomalous dispersion effects were included in F_c [19]; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer [20]. All calculations were performed using the TEXSAN [21] crystallographic software package of the Molecular Structure Corporation. An ORTEP [22] plot of the molecule is shown in Fig. 1. Tables of thermal parameters, and hydrogen atom co-

Fig. 1. ORTEP plot of $[\text{Pt}_2\text{Ph}_2(\mu\text{-SPh})_2(\text{PMe}_2\text{Ph})_2]$ with numbering scheme for non-hydrogen atoms.

ordinates have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgments

The authors thank Dr. J.P. Mittal and Dr. D.D. Sood for their interest throughout this investigation. We are grateful to the Head of the Analytical Chemistry Division for providing microanalyses of the compounds. The facilities provided by the 500 MHz NMR National Facility supported by DST and located at TIFR are gratefully acknowledged. J.P.J. thanks the National Science Foundation–RUI program for providing funds to set up the New England Molecular Structure Centre.

References

- 1 V.K. Jain, *Curr. Sci.*, 59 (1990) 143.
- 2 H.J. Gysling, *Coord. Chem. Rev.*, 42 (1982) 133; I.G. Dance, *Polyhedron*, 5 (1986) 1037; P.J. Blower and J.R. Dilworth, *Coord. Chem. Rev.*, 76 (1987) 121.
- 3 M.C. Hall, J.A.J. Jarvis, B.T. Kilbourn and P.G. Owston, *J. Chem. Soc., Dalton Trans.*, (1972) 1544.
- 4 E.M. Padilla, J.A. Golen, P.N. Richman and C.M. Jensen, *Polyhedron*, 10 (1991) 1343.
- 5 V.K. Jain, R.P. Patel and K. Venkatasubramanian, *Polyhedron*, 10 (1991) 851.
- 6 V.K. Jain and G.S. Rao, *Inorg. Chim. Acta*, 127 (1986) 161.
- 7 K.R. Dixon, K.C. Moss and M.A.R. Smith, *J. Chem. Soc., Dalton Trans.*, (1974) 971.
- 8 P.H. Bird, U. Siriwardane, R.D. Lai and A. Shaver, *Can. J. Chem.*, 60 (1982) 2075.
- 9 C.E. Briant, C.J. Gardner, T.S.A. Hor, N.D. Howells and D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.*, (1984) 2645.
- 10 T.G. Appleton, H.C. Clark and L.E. Manzer, *Coord. Chem. Rev.*, 10 (1973) 335.
- 11 V.K. Jain, V.S. Jakkal and R. Bohra, *J. Organomet. Chem.*, 389 (1990) 417; C. Panattoni, G. Bombieri, E. Forsellini, B. Crociani and U. Belluco, *Chem. Commun.*, (1969) 187.
- 12 A.C. Smithies, M. Rycheck and M. Orchin, *J. Organomet. Chem.*, 12 (1968) 199.
- 13 J. Chatt, N.P. Johnson and B.L. Shaw, *J. Chem. Soc.*, (1964) 1662.
- 14 C. Eaborn, K.J. Odell and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, (1978) 1288.
- 15 C. Eaborn, H.L. Hornfeld and D.R.M. Walton, *J. Organomet. Chem.*, 10 (1967) 529.
- 16 V.K. Jain and S. Kannan, *Polyhedron*, 11 (1992) 27.
- 17 C.J. Gilmore, *J. Appl. Crystallogr.*, 17 (1984) 42; P.T. Beurskens, *Tech. Rep. 1984/1*, (1984) (Crystallography Laboratory, Toer-nooiveld, Nijmegen).
- 18 D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, 1974, Table 2.2A.
- 19 J.A. Ibers and W.C. Hamilton, *Acta Crystallogr.*, 17 (1964) 781.
- 20 D.T. Cromer, *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, 1974, Table 2.3.1.
- 21 *TEXSAN – TEXRAY Structure Analysis Package*, Molecular Structure Corporation, The Woodlands, TX, 1985.
- 22 C.K. Johnson, *ORTEP II*, *Rep. ORNL-5138*, 1976, (Oak Ridge National Laboratory, Oak Ridge, TN).