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Reaction of *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ with Carbon Disulphide. Kinetic Study of the Insertion Reaction and X-Ray Structure of *trans*-$\{PtH(S_2CH)[P(C_6H_{11})_3]_2$

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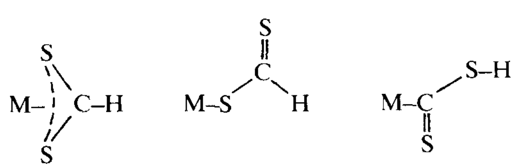
Carbon disulphide inserts into the Pt–H bond of trans-$\{PtH_2[P(C_6H_{11})_3]_2\}$ to give trans-$\{PtH(S_2CH)[P(C_6H_{11})_3]_2\}$. The X-ray structure shows that the $-S_2CH$ group is bonded to the metal through a sulfur atom as a monodentate thioformate anion. The kinetics of the carbon disulfide insertion have been investigated. The results account for a mechanism involving CS_2 addition to trans-$\{PtH_2[P(C_6H_{11})_3]_2\}$ to give a five-coordinate intermediate, which collapses to trans-$\{PtH(S_2CH)[P(C_6H_{11})_3]_2\}$.

Introduction

The insertion reaction of carbon disulphide with hydrido and alkyl metal complexes to give dithio compounds has been reported by several authors[1–6].

An X-ray structural determination on $\{Re(CO)_2[P(C_6H_5)_3]_2(S_2CH)\}$ has shown that the $-S_2CH$ group is bonded to the metal through both sulfur atoms as a bidentate dithioformate anion (**Ia**)[7].



Ia **Ib** **Ic**

Moreover spectroscopic evidence (IR and Raman) suggests that the $-S_2CH$ group is bonded to the metal in $\{M(CO)_3(DPE)(S_2CH)\}$ (M = Mn, Re; DPE = diphenylphosphinoethane) as a monodentate dithioformate anion (**Ib**)[3]. Both structures **Ib** and **Ic** have been proposed for $\{Ir(CO)(S_2CH)[P(C_6H_5)_3]_2\}$ and $\{PtCl(S_2CH)[P(C_6H_5)_3]_2\}$[1,2]. Palazzi *et al.* favour structure (**Ib**) for the Pt complex on the basis of chemical evidence. In the light of the X-ray structure of $\{Pt(S_2CF)[P(C_6H_5)_3]_2\}HF_2$ where the $-S_2CF$ group is a fluorodithioformate anion bonded through both sulfur atoms to platinum, it as been proposed that $\{PtCl(S_2CH)[P(C_6H_5)_3]_2\}$ could have an analogous structure with the $-S_2CH$ group bound to the metal as a bidentate ligand[8].

In the course of our studies on the reactivity of *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$[9,10] we have found that carbon disulphide reacts smoothly with the dihydrido complex to give *trans*-$\{PtH(S_2CH)[P(C_6H_{11})_3]_2\}$. We considered it worthwhile to perform a spectroscopic investigation and an X-ray structural determination on this complex in order to elucidate the mode of bonding of the $-S_2CH$ group to platinum. A kinetic study of the reaction of carbon disulphide with *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ is also reported.

Results and Discussion

Spectroscopic Data

The white complex *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ readily reacts with carbon disulphide under mild conditions to give an orange–yellow product identified from analytical and spectroscopic data as *trans*-$\{PtH(S_2CH)[P(C_6H_{11})_3]_2\}$. The IR spectrum of this compound (nujol mull) shows a medium absorption at 2130 cm^{-1} for the Pt–H stretching and two strong and sharp bands at 1240 and 1005 cm^{-1} which may be attributable to the $-S_2CH$ moiety[3]. The 1005 cm^{-1} band overlaps with a weaker band present in the starting complex.

The p.m.r. spectrum recorded in $CDCl_3$ displays the hydride resonance at 22.58τ as a triplet with $^2J_{P-H}$ 13 Hz in agreement with a *trans* phosphine configuration. ^{195}Pt satellites are observed with J_{Pt-H} 1280 Hz. The low field region shows at –2.12τ the proton resonance of the $-S_2CH$ group. The signal appears as a triplet (J 48 Hz) owing to the ^{195}Pt coupling. Besides, both the resonances at –2.12τ and 22.58τ show a further splitting (J 4–5 Hz) assignable to a long range coupling between the hydrido and the $-S_2CH$ protons.

These p.m.r. data do not appear to establish conclusively the coordination mode of the $-S_2CH$ group.

Structural Determination

Crystal data: $PtP_2S_2C_{37}H_{68}$,M.W. = 833.52, D_{calc} = 1.23, D_{obs} = 1.21(2), Triclinic, a = 13.794(10) Å, b = 14.194(12) Å, c = 11.942(10) Å, α = 103.87(5)°, β = 96.03(6)°, γ = 78.42(4)°. Space group P$\bar{1}$, Z = 2.

A crystal of prismatic habit of approximate dimensions 0.15 × 0.18 × 0.32 mm was chosen for collecting the data. The intensities were collected on a Philips PW1100 single crystal diffractometer using graphite monochromatized MoKα radiation up to a $\sin\vartheta/\lambda$ value of 0.48 Å^{-1}. An $\omega/2\vartheta$ scan mode was used with a scan width of 1.00° and a scan speed of 0.05° sec^{-1}. The background was counted for half the total scanning time on each side of the peak. Of the 4074 independent reflections collected, 3271 having a net intensity I ≧ 3σ(I) were used in the refinement. The set of data was corrected for Lorentz and polarization factors but not for absorption. During the data collection the

TABLE I. Final Positional (x10^4) and Thermal Parameters.[a]

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	3607(.8)	2195(.8)	2637(.9)	2.45(3)	3.17(3)	3.75(3)	−0.34(5)	0.37(5)	0.30(5)
P1	1993(3)	3052(3)	2647(4)	2.99(21)	3.34(21)	4.33(23)	−0.96(34)	0.43(35)	−0.17(36)
P2	5315(3)	1856(3)	2815(4)	3.02(20)	3.87(22)	3.55(22)	−0.53(34)	0.11(34)	−0.22(35)
S1	3344(4)	592(4)	1577(5)	4.24(24)	4.34(30)	6.34(30)	−0.25(39)	−0.71(42)	−0.71(43)
S2	2772(5)	385(5)	3870(6)	7.67(38)	7.13(36)	9.07(42)	−1.45(59)	3.25(64)	5.10(63)
C1	2919(14)	5(16)	2442(20)	4.17(96)	6.43(116)	7.79(133)	0.50(170)	2.64(180)	4.77(203)
	x/a	y/b	z/c	B(A^2)					
C2	964(13)	2341(13)	2121(15)	4.3(4)					
C3	972(14)	1956(14)	732(16)	5.0(4)					
C4	261(16)	1174(16)	387(19)	6.3(5)					
C5	−836(19)	1699(19)	772(22)	7.3(6)					
C6	−816(18)	2074(17)	2047(20)	7.1(5)					
C7	−94(15)	2876(15)	2515(17)	5.3(4)					
C8	1618(13)	3764(13)	4125(16)	4.6(4)					
C9	8341(16)	6945(16)	5086(18)	5.9(5)					
C10	8691(18)	6328(18)	3832(21)	7.3(6)					
C11	8084(19)	5539(19)	3316(22)	8.3(6)					
C12	8097(18)	4845(18)	4125(21)	7.3(6)					
C13	7712(16)	5449(16)	5327(19)	6.3(5)					
C14	1955(13)	4005(13)	1825(15)	4.5(4)					
C15	949(15)	4742(15)	1731(17)	5.5(4)					
C16	1118(16)	5605(15)	1247(18)	6.0(5)					
C17	1614(17)	5244(17)	71(20)	6.9(5)					
C18	2596(17)	4479(17)	144(20)	6.8(5)					
C19	2422(14)	3613(14)	638(17)	5.0(4)					
C20	5869(13)	2428(13)	1854(15)	4.1(4)					
C21	5700(17)	3573(17)	12(20)	6.9(5)					
C22	3970(15)	7562(15)	252(18)	5.8(5)					
C23	6021(17)	4042(17)	1298(20)	6.8(5)					
C24	5520(15)	3612(15)	2141(17)	5.3(4)					
C25	5575(13)	1982(13)	570(16)	4.5(4)					
C26	5913(13)	530(13)	2430(15)	4.4(4)					
C27	7367(17)	9152(17)	1744(20)	6.9(5)					
C28	7123(17)	8560(16)	2574(19)	6.5(5)					
C29	6000(19)	8821(18)	2842(21)	7.2(6)					
C30	5682(15)	−20(14)	3335(17)	5.3(4)					
C31	7058(16)	312(15)	2184(18)	5.9(5)					
C32	4280(14)	7519(14)	5659(16)	4.9(4)					
C33	3113(17)	7652(17)	5400(19)	6.5(5)					
C34	4833(17)	7697(17)	4753(20)	6.9(5)					
C35	4614(18)	6932(18)	3559(21)	7.3(6)					
C36	3482(21)	7050(21)	3279(25)	7.6(7)					
C37	2899(19)	6932(19)	4219(23)	8.2(8)					

[a] The anisotropic temperature factors are expressed as $T = \exp[-1/4(B_{11}a^{*2}h^2+B_{22}b^{*2}k^2+B_{33}c^{*2}l^2+2B_{12}a^*b^*hk+2B_{13}a^*c^*hl+2B_{23}b^*c^*kl)]$. The e.s.d.'s are given in parentheses and refer to the last significant figure.

stability of the crystal and of the diffractometer was checked measuring three standard reflections every 90 minutes and no significant variations were detected in the intensities.

The structure was solved by conventional Patterson and Fourier methods using a fast Fourier program[11] and refined by block diagonal least squares[12] with weights chosen after Cruickshank[13]. The scattering factors used were those of Cromer and Mann[14] and the corrections for the real part of the anomalous dispersion were obtained from those listed by Cromer[15]. After four cycles of block diagonal least squares with isotropic thermal parameters the agreement factor R was 0.125 and after four other cycles with anisotropic thermal parameters for the Pt, the two P and S atoms and the carbon atom of the $-S_2CH$ group, the agreement factor R ($R = \Sigma(K|F_o|-|F_c|/\Sigma K|F_o|)$) reached the final value of 0.067.

No attempt was made to locate the hydrogen atoms or to put them in calculated positions; the final Fourier difference map showed no residual peaks greater than 0.8 e/Å^3. The final positional and thermal factors are listed in Table I; a list of observed and calculated structure factors is available from the authors.

The structure as determined definitively shows the $-S_2CH$ group bonded to the platinum as a monodentate thioformate anion (Figure 1). The hydrogen atom has not been located, however it can be safely assumed that it is bonded to the carbon. The more relevant distances and angles and their standard deviations are given in Table II.

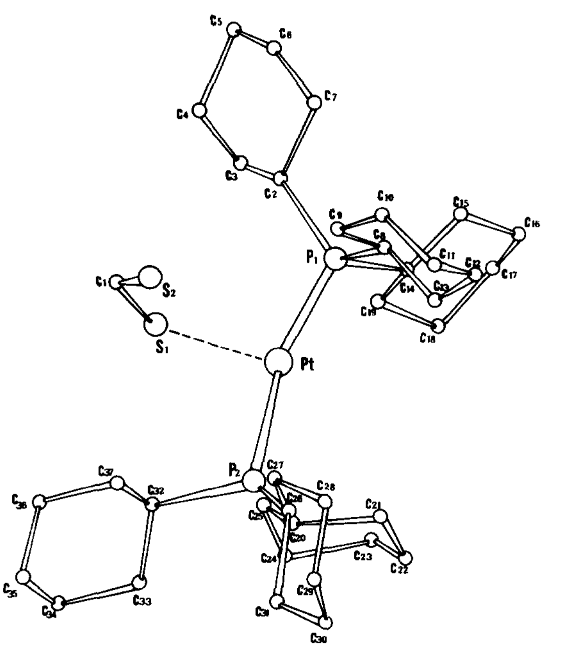


Figure 1. Molecular structure of *trans*-$PtH(S_2CH)[P(C_6H_{11})_3]_2$.

TABLE II. Selected Interatomic Distances and Angles (Numbers in parentheses are the e.s.d. 's on the last significant figure).

Bond Distances (Å)		Bond Angles (°)	
Pt–P1	2.274(5)	Pt–P1–C2	118.6(5)
Pt–P2	2.278(5)	Pt–P1–C8	114.8(5)
Pt–S1	2.368(6)	Pt–P1–C14	103.6(4)
Pt–S2	3.749(7)	Pt–P2–C20	106.3(5)
Pt–C1	3.379(9)	Pt–P2–C26	113.6(5)
S1–C1	1.73(2)	Pt–P2–C32	115.7(5)
S2–C1	1.68(3)	Pt–S1–C1	111.2(6)
P1–C2	1.86(2)	P1–Pt–P2	161.1(4)
P1–C8	1.87(2)	P1–Pt–S1	99.9(1)
P1–C14	1.86(2)	P2–Pt–S1	98.4(1)
P2–C20	1.86(2)	S1–C1–S2	129.0(5)
P2–C26	1.91(2)	C2–P1–C14	113.5(5)
P2–C32	1.83(2)	C2–P1–C8	100.1(5)
C–C[a]	1.56(3)	C8–P1–C14	105.9(5)
		C20–P2–C32	112.3(4)
		C20–P2–C26	105.4(5)
		C26–P2–C32	103.5(4)

Internal Rotation Angles (°)	
Pt–S1–S2–C1	175.4(4)
Pt–S1–C1–S2	4.9(2)
P1–Pt–S1–S2	78.5(3)
P1–Pt–S1–C1	76.4(2)
P2–Pt–S1–C1	108.2(2)
P2–Pt–S1–S2	106.1(2)
S1–Pt–P1–C2	9.6(1)
S1–Pt–P2–C32	12.3(2)
P1–Pt–P2–C32	178.1(2)
P2–Pt–P1–C2	175.4(1)

[a] Average distance.

The two C–S bond distances are equal within the standard deviations which implies a certain degree of electron delocalization along the S–C–S group. The observed C–S distances compare with those observed for $\{Re(S_2CH)(CO)_2[P(C_6H_5)_3]_2\}$ [1.64(2); 1.68 (1) Å][7], $\{Pt(S_2CF)[P(C_6H_5)_3]_2\}HF_2$ [1.67(2); 1.82 (2) Å][8], $[Re(S_2CC_6H_5)(CO)_4]$ (1.68 Å)[16], $\{Ni[S_2CCH_2C_6H_5]_2\}$ [1.73(3); 1.66(3) Å][17]. Thus it appears that this distance is unaffected by the coordination mode of the $-S_2CH$ group, whether as a mono or bidentate ligand. The conformation of the phosphine ligands shows no particular features, with all the cyclohexane rings in their chair conformations.

The P–Pt–P moiety has a bent geometry as for $\{M[P(C_6H_{11})_3]_2\}$ (M = Pd, Pt)[18,19] and *trans*-$\{PtHCl[P(C_6H_5)_2C_2H_5]_2\}$[20].

Kinetics

The insertion of CS_2 into *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ has been investigated kinetically. During the reaction the U.V. spectrum of the mixture changes as shown in Figure 2.

Spectrum **I** refers to a solution of the starting compound in heptane while spectrum **II** to the final CS_2

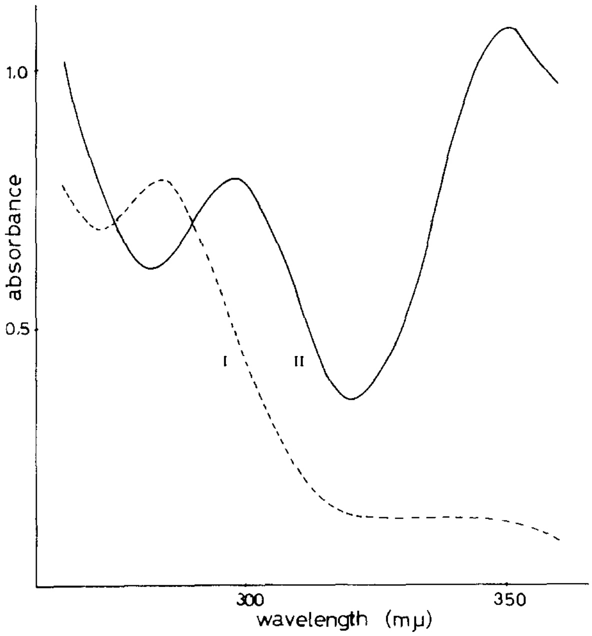


Figure 2. Spectral changes for the reaction of *trans*-$PtH_2[P(C_6H_{11})_3]_2$ with CS_2. Initial complex concentration = 2.04×10^{-4} *M*.

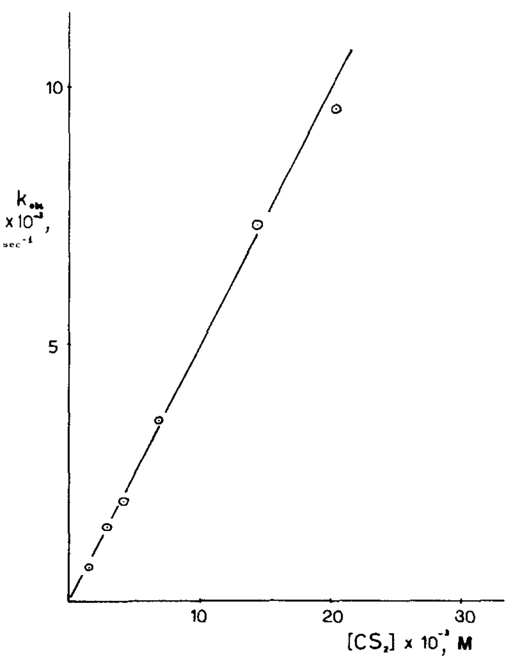


Figure 3. Plot of k_{obs} *vs.* $[CS_2]$ in heptane solution at 25° C.

TABLE III. Second Order Rate Constants, k_2, for CS_2 Insertion at 25° C.

Solvent	10 k_2, M^{-1} sec^{-1}
Heptane	4.50 ± 0.85
Benzene	3.04 ± 0.60
Ethyl ether	4.90 ± 1.20

adduct. On plotting the measured k_{obs} values *vs.* the CS_2 concentration a straightline is obtained as shown in Figure 3. The values of the slopes obtained using different solvents are reported in Table III. The extrapolated intercept values were quite negligible and not reliable. Thus the calculated value for the plot in Figure 3 is $[-2.2 \pm 5.1] \times 10^{-4}$ sec^{-1}.

Therefore the results indicate a rate law of the form:

$$k_{obs} = k_2[CS_2].$$

A reasonable mechanism accounting for this rate law involves the addition of CS_2 to the starting *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ to give a five-coordinate labile intermediate, which rapidly collapses to the final *trans*-$\{PtH(S_2CH)[P(C_6H_{11})_3]_2\}$.

In contrast to the insertion of CS_2 into *trans*-$\{PtHCl[P(C_6H_5)_3]_2\}$[2], the final rearrangement of the five-coordinate intermediate was not detected. This may account for a higher insertion rate into the Pt–H bond in the intermediate of the type $\{PtH_2(CS_2)[P(C_6H_{11})_3]_2\}$ than in the $\{PtHCl(CS_2)[P(C_6H_5)_3]_2\}$.

No CS_2 insertion was observed with *trans*-$\{PtHCl[P(C_6H_{11})_3]_2\}$ and with *trans*-$\{PtH(S_2CH)[P(C_6H_{11})_3]_2\}$ even under severe experimental conditions. The solvent certainly plays an important role in the intermediate formation, and no reaction was observed on using coordinative solvents such as THF and CH_3CN. It is noteworthy that the THF U.V. spectrum of *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ is different from that in heptane and the compound does not react with CS_2 in that solvent. This fact could be interpreted assuming the formation of a complex of the type $\{PtH_2[P(C_6H_{11})_3]_2(THF)\}$ owing to the unlikely hydride displacement by the solvent. On the other hand, the almost similar values of k_2 observed in ether, benzene and heptane are in agreement with the low coordinative character of these solvents.

Experimental

Analytical grade solvents and chemicals were employed throughout. IR spectra were recorded on a Perkin–Elmer 457 spectrophotometer, and ^1H n.m.r. data were obtained using a Varian NV 14 spectrometer in $CDCl_3$ solution using TMS as internal reference.

Trans-$\{PtH_2[P(C_6H_{11})_3]_2\}$[9] and $[Pt(\pi\text{-allyl})Cl]_4$[21] were prepared according to the literature methods.

The progress of the reaction was followed with an Optica CF4 recording spectrophotometer equipped with a thermostatted cell compartment where the temperature was controlled within $\pm 1°$ C. In each kinetic run initial and final spectra of the reaction mixture were identical to those of authenthic samples of the initial and final compounds respectively. Details of the procedure were described elsewhere[22]. All kinetics runs were carried out under pseudo-first order conditions by use of an excess of CS_2. Spectral changes were monitored in the range 360–260 mμ.

Preparation of trans-{$PtHCl[P(C_6H_{11})_3]_2$}

Tricyclohexylphosphine (2.24 g, 8 mmol) was added to a CH_2Cl_2 suspension of $[Pt(\pi\text{-allyl})Cl]_4$ (1.09 g, 1 mmol) at room temperature with vigorous stirring under nitrogen. In 1 hour a colourless solution was obtained which was evaporated to dryness leaving a white solid. This was diluted with 30 ml of anhydrous methanol and 5 ml of a 1.56*M* sodium methoxide solution in methanol was added under nitrogen with stirring. After 30 minutes 212 mg of LiCl (5 mmol) were added and the suspension was allowed to react for 24 hours. The white compound was filtered off, washed with 5 ml of methanol and recrystallized from benzene–ether. The obtained white product (2.23 g; 70% yield) was identified as *trans*-{$PtHCl[P(C_6H_{11})_3]_2$} from its spectroscopic properties[23]. From a CS_2 solution of this compound after 7 days at 90° C in sealed tube the unaltered complex was precipitated with hexane.

Preparation of trans-{$PtH(S_2CH)[P(C_6H_{11})_3]_2$}.

The complex *trans*-$PtH_2[P(C_6H_{11})_3]_2$ (379 mg; 0.5 mmol) was treated with 5 ml of CS_2 under nitrogen. The solution immediately turned orange and was left for 2 hours at room temperature. It was concentrated to low volume, then ether and hexane were added to give the orange–yellow crystalline adduct *trans*-{$PtH(S_2CH)[P(C_6H_{11})_3]_2$} in almost quantitative yield. *Anal.* Found: C, 54.83; H, 8.21; S, 7.60%. $C_{37}H_{68}P_2PtS$, calcd.: C, 54.71; H, 8.32; S, 7.69%.

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