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Addition of Some Simple Molecules to Transition Metal-Phosphine Complex and the Crystal and Molecular Structure of $Pd\{(C_6H_5)_3P\}_2(CS_2)$

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From the reaction of $M\{(C_6H_5)_3P\}_4$ (M=Pd or Pt) with CS_2, $M\{(C_6H_5)_3P\}_2(CS_2)$ has been isolated. It has been found that $M\{(C_6H_5)_3P\}_2$ also reacts with sulfur dioxide to form a novel complex, $[M\{(C_6H_5)_3P\}_4(SO_2)_n]$. The structure of one of these compounds, $Pd\{(C_6H_5)_3 \cdot P\}_2(CS_2)$, was determined by means of X-rays. $Pd\{(C_6H_5)_3P\}_2(CS_2)$ crystallizes in the monoclinic system, space group $P2_1/c$, with four molecules in a unit cell of dimensions: $a=11.55$, $b=19.52$, $c=18.38$ Å and $\beta=128°53'$. The most remarkable feature of the whole structure is the coordination of CS_2 to the Pd: only one of the S atoms, S(2), coordinates to the Pd, while the CS_2 ligand is bent at an angle of 140°. The Pd, two P's, S(2) and C(1) in CS_2 lie approximately on the same plane. The Pd–C(1) distance of 2.00 Å is slightly shorter than the sum of the covalent radii, 2.06 Å. But the S(2)–Pd–C(1) angle of 44° is very small.

Recently, the relationship between the catalytic activities of transition metal complexes and their structure has been widely discussed. Vaska and Diluzio[1] treated the catalyst, $IrCl(CO)\{(C_6H_5)_3P\}_2$, with molecular oxygen, or hydrogen, and obtained a complex in which O_2, or H_2 coordinates to the iridium atom. They considered those complexes to be intermediates in the oxygenation or hydrogenation, and discussed the relation between the catalytic mechanism and the structure of $IrCl(CO)\{(C_6H_5)_3P\}_2$. Successively, the structural studies of

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[1] L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

the complexes with simple molecules have been made by X-ray diffraction. LaPlaca and Ibers determined the structures of $IrO_2Cl(CO)\{(C_6H_5)_3P\}_2$[2a] and $IrSO_2Cl(CO)\{(C_6H_5)_3P\}_2$,[2b] and they gave some information about the catalytic activities of $IrCl(CO)\{(C_6H_5)_3P\}_2$.

Hagihara and his co-workers[3] recognized that the $M\{(C_6H_5)_3P\}_4$ (M=Pd or Pt) molecule catalyzes the following reactions.

$$2(C_6H_5)_3P + O_2 = 2(C_6H_5)_3PO$$

$$2(n\text{-}C_4H_9)_3P + O_2 = 2(n\text{-}C_4H_9)_3PO$$

$$2C_6H_{11}NC + O_2 = 2C_6H_{11}NCO$$

They obtained $M\{C_6H_5)_3P\}_nO_2$ as a reaction product of $M\{(C_6H_5)_3P\}_4$ and molecular oxygen.[4,5] $M\{(C_6H_5)_3P\}_nO_2$ is considered to be an active intermediate in the oxygenation.

The addition of the simple molecules, carbon disulfide or sulfur dioxide, to triphenylphosphine-palladium or -platinum complex is described in this paper.

The crystal and molecular structure of one of these compounds, $Pd\{(C_6H_5)_3P\}_2(CS_2)$, was determined to examine the coordination of CS_2 to $Pd\{(C_6H_5)_3P\}_2$ and to get some information about the catalytic mechanism.

Experimental

Materials. Tetrakis(triphenylphosphine)palladium, $Pd\{(C_6H_5)_3P\}_4$, and -platinum, $Pt\{(C_6H_5)_3P\}_4$, were prepared according to a modified method of Malatesta.[3,6,7]

All the procedures mentioned below were performed under a nitrogen atmosphere.

Reaction of $M\{(C_6H_5)_3P\}_4$ with Carbon Disulfide. At room temperature 578 mg of $Pd\{(C_6H_5)_3P\}_4$ was dissolved in 20 m*l* of carbon disulfide. A small amount of orange crystalline solid separated. After 30 min carbon disulfide was gradually removed under reduced pressure and the orange residue was recrystallized from hot carbon disulfide to give 220 mg (62% yield) of $Pd\{(C_6H_5)_3P\}_2(CS_2)$ (Ia): mp 130—133°C (decomp.).

Found: C, 63.00; H, 4.26; S, 9.33%. Calcd for $C_{37}H_{30}P_2S_2Pd$: C, 62.84; H, 4.28; S, 9.07%.

The platinum-carbon disulfide complex was prepared in a similar manner. In 15 m*l* carbon disulfide 622 mg of $Pt\{(C_6H_5)_3P\}_4$ was dissolved with stirring. After a few minutes the crystals of platinum-carbon disulfide complex began to separate. The crystals were filtered, washed with carbon disulfide, and dried. Pink crystals (350 mg, 88% yield) of $Pt\{(C_6H_5)_3P\}_2\cdot(CS_2)$ (Ib) were isolated, but further purification could not be attained because of its insolubility. Mp 151—154°C (decomp.)

Found: C, 55.65; H, 3.82; S, 8.15%. Calcd for $C_{37}H_{30}P_2S_2Pt$: C, 55.84; H, 3.80; S, 8.06%.

Preparation of $Pd\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}(CS_2)$. A solution of 200 mg (0.5 mmol) of 1,2-bis-(diphenylphosphino)-ethane in 10 m*l* carbon disulfide was added dropwise with stirring to a suspension of $Pd\{(C_6H_5)_3P\}_2(CS_2)$ in 20 m*l* carbon disulfide prepared from 578 mg of $Pd\{(C_6H_5)_3P\}_4$ and carbon disulfide. The crystals of $Pd\{(C_6H_5)_3P\}_2(CS_2)$ then dissolved, and the solution gradually became orange red. After 1 hr the solvent was removed and the residue, on recrystallization from hot carbon disulfide (15 m*l*), afforded 190 mg (67% yield) of red brown crystals, $Pd\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}(CS_2)$ (II): mp 115—124°C (decomp.) in a sealed capillary filled with nitrogen.

Found: C, 55.80; H, 4.23; S, 11.28%; mol wt (cryoscopic in nitrobenzene), 596. Calcd for $C_{27}H_{24}P_2S_2Pd$: C, 55.82; H, 4.16; S, 11.04%; mol wt, 580.9.

Reaction of $M\{(C_6H_5)_3P\}_4$ with Sulfur Dioxide.[*1] Sulfur dioxide was bubbled through a solution of 578 mg (0.5 mmol) of $Pd\{(C_6H_5)_3P\}_4$ in 30 m*l* benzene at room temperature. The reaction mixture became dark red. After 1.5 hr the solvent was gradually removed in a water-aspirator vacuum, leaving a red purple solid. Recrystallization from hot benzene gave 285 mg (48% yield) of analytically pure red purple needles, $[Pd\{(C_6H_5)_3P\}_4(SO_2)]_n$ (IIIa). It decomposed at 84—85.5°C without melting in a sealed capillary filled with nitrogen.

Found: C, 70.76; H, 4.08; O, 2.88; S, 2.54; P, 10.07%. Calcd for $C_{72}H_{60}O_2P_4SPd$: C, 70.90; H, 4.96; O, 2.62; S, 2.63; P, 10.16%.

According to a similar procedure the reaction between 622 mg (0.5 mmol) of $Pd\{(C_6H_5)_3P\}_4$ and sulfur dioxide in 20 m*l* benzene gave 360 mg (55% yield) of red purple needles $[Pt\{(C_6H_5)_3P\}_4(SO_2)]_n$ (IIIb). They decomposed at 124—125°C without melting in a sealed capillary filled with nitrogen.

Found: C, 65.98; H, 4.74; O, 2.79; S, 2.69; P, 9.28%. Calcd for $C_{72}H_{60}O_2P_4SPt$: C, 66.10; H, 4.62; O, 2.45; S, 2.45; P, 9.47%.

Density Measurement of $Pd\{(C_6H_5)_3P\}_2(CS_2)$. The density, 1.457 g·cm^{-3}, was measured by the flotation method in carbon tetrachloride - dioxane solution at room temperature.

X-Ray Diffraction. $Pd\{(C_6H_5)_3P\}_2(CS_2)$ gives light orange needle-like (along the *c* axis) crystals, which were very stable in air during the X-ray work. The crystals belong to the monoclinic system and the unit cell dimensions are:

$a=11.55\pm0.03$, $b=19.52\pm0.02$, $c=18.38\pm0.03$ Å. and $\beta=128°53'\pm10'$. From the systematic absence of $0k0$ reflections for k odd and $h0l$ for l odd, the space

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[2a] S. J. LaPlaca and J. A. Ibers, *ibid.*, **87**, 2581 (1965). b) S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).

[3] S. Takahashi, K. Sonogashira and N. Hagihara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 610 (1966).

[4] G. Wilke, H. Schott and P. Heimbach, *Angew. Chem. Int. Ed. Engl.*, **6(1)**, 92 (1967).

[5] C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Letters*, **3**, 31 (1967).

[6] L. Malatesta and C. Cariello, *J. Chem. Soc.*, **1958**, 2323.

[7] L. Malatesta and M. Angoletta, *ibid.*, **1957**, 1186.

[*1] It was reported that Levison and Robinson obtained $Pt\{(C_6H_5)_3P\}_3(SO_2)\cdot xC_6H_6$ ($x \cong 1.5$) and $Pd\{(C_6H_5)_3P\}_3(SO_2)$ by the reaction of $M\{(C_6H_5)_3P\}_4$ (M=Pd or Pt) with sulfur dioxide (*Chem. Commn.*, **1967**, 198).

TABLE 1.

(a) The final atomic coordinates and their standard deviations, $\sigma(10^{-2}\text{Å})$ and the isotropic thermal parameters, B (Å^2)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
Pd	0.0866	0.2	0.1042	0.1	0.2757	0.2	*
S(1)	−0.2125	0.8	0.1108	0.7	0.2743	1.1	*
S(2)	0.0363	0.8	0.2051	0.6	0.3163	1.1	*
P(1)	−0.0114	0.7	−0.0025	0.5	0.2101	0.8	*
P(2)	0.3202	0.7	0.1172	0.5	0.3046	0.8	*
C(1)	−0.068	3	0.137	2	0.285	3	*
C(11)	0.094	2	−0.060	2	0.190	3	2.9
C(12)	0.135	3	−0.126	2	0.231	3	4.2
C(13)	0.215	3	−0.165	2	0.206	3	4.5
C(14)	0.245	3	−0.141	3	0.150	4	5.3
C(15)	0.201	3	−0.074	3	0.112	4	5.2
C(16)	0.127	3	−0.033	2	0.132	3	4.3
C(21)	−0.196	3	−0.000	2	0.091	3	3.6
C(22)	−0.247	3	−0.060	2	0.031	3	4.5
C(23)	−0.384	3	−0.058	2	−0.053	3	4.8
C(24)	−0.470	3	0.004	3	−0.089	4	4.9
C(25)	−0.410	3	0.062	2	−0.032	3	4.3
C(26)	−0.271	2	0.061	2	0.063	3	3.2
C(31)	−0.035	2	−0.052	2	0.286	3	3.1
C(32)	−0.140	3	−0.106	3	0.248	4	5.6
C(33)	−0.147	3	−0.143	2	0.313	3	4.5
C(34)	−0.063	4	−0.124	3	0.402	4	6.3
C(35)	0.043	4	−0.069	3	0.439	4	6.3
C(36)	0.055	3	−0.034	2	0.378	3	4.5
C(41)	0.456	2	0.170	2	0.407	2	1.9
C(42)	0.408	3	0.230	2	0.423	3	4.6
C(43)	0.507	3	0.270	2	0.505	4	4.9
C(44)	0.659	3	0.253	3	0.570	4	5.9
C(45)	0.708	3	0.197	3	0.546	4	5.8
C(46)	0.606	3	0.155	2	0.468	3	4.3
C(51)	0.431	2	0.043	2	0.331	3	2.3
C(52)	0.429	3	−0.009	2	0.383	3	3.8
C(53)	0.531	3	−0.064	3	0.415	4	5.1
C(54)	0.619	3	−0.071	3	0.386	4	5.5
C(55)	0.617	3	−0.020	2	0.332	3	4.4
C(56)	0.522	3	0.038	2	0.306	3	3.8
C(61)	0.298	3	0.166	2	0.212	3	3.6
C(62)	0.424	3	0.202	2	0.230	3	3.7
C(63)	0.399	3	0.237	2	0.157	3	4.1
C(64)	0.267	3	0.237	2	0.067	4	4.9
C(65)	0.145	3	0.199	2	0.051	3	4.2
C(66)	0.166	3	0.162	2	0.125	3	3.9

* Refinement was undertaken with anisotropic thermal parameters. These parameters are listed in (b).

(b) The anisotropic thermal parameters for Pd, S, P and C(1). The thermal parameters are of the form: $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.0080	0.0017	0.0045	−0.0002	0.0084	−0.0002
S(1)	0.0119	0.0040	0.0082	−0.0009	0.0152	−0.0013
S(2)	0.0122	0.0027	0.0107	−0.0033	0.0163	−0.0043
P(1)	0.0096	0.0016	0.0045	−0.0016	0.0099	−0.0011
P(2)	0.0093	0.0016	0.0035	−0.0000	0.0070	0.0001
C(1)	0.0139	0.0037	0.0049	0.0013	0.0153	−0.0009

group was determined to be $P2_1/c$. The observed density, 1.457 g·cm^{-3}, suggested four molecules in a unit cell, the calculated density being 1.456 g·cm^{-3}.

A set of three-dimensional intensity data was collected on multifilm equi-inclination Weissenberg photographs with nickel-filtered Cu$K\alpha$ radiation. Layers 0 to 11 were recorded around the c axis. Intensities of 4079 independent reflections were measured.

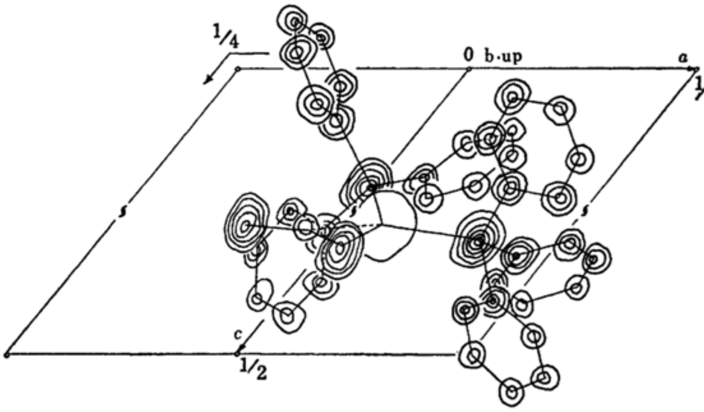

Fig. 1. A composite drawing of the final electron density map, viewed along the b axis. Contours are drawn at 3, 4 e.Å^{-3}··· for carbon, and at 5, 8 e.Å^{-3}··· for phosphorus and sulfur.

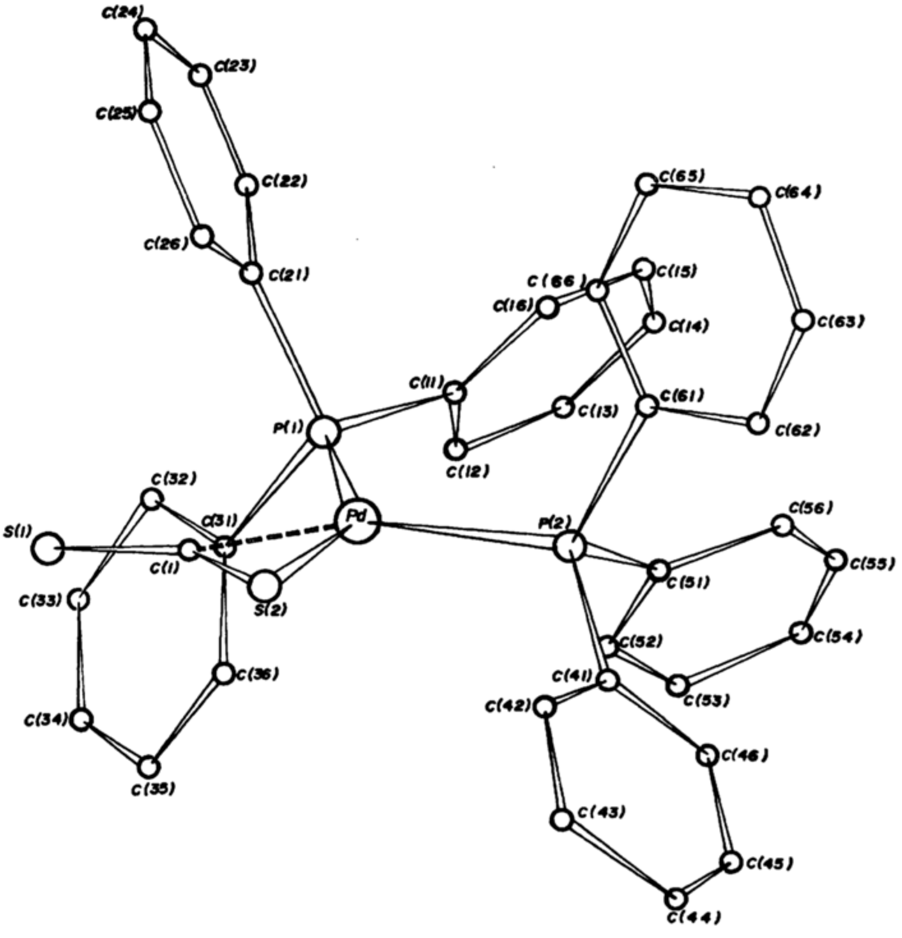

Fig. 2. View of molecule along the b axis.

visually. These intensities cover approximately 56% of possible reflections for Cu$K\alpha$. In order to get interlayer scale-factors, intensities around the *a* axis were also recorded. These intensities were corrected for the usual Lorentz and polarization factors, and spot-shape effects were also taken into account. As the dimensions of the crystal used in the experiment were about 0.09×0.10×0.27 mm, the absorption correction was ignored in spite of the large absorption coefficient for Cu$K\alpha$, $\mu=70.81\ \text{cm}^{-1}$.

Structure Determination and Refinement

The approximate position of Pd was deduced from the Patterson projections: $P(\text{U, V})$ and $P(\text{U,W})$. The Pd, S, P and twenty-seven C atoms were then obtained by inspection of the three-dimensional minimum function superposed by four equivalent positions of the Pd. The remaining ten C atoms were easily found in an electron density map based on the phases from the atoms which had already been determined. At this stage, the calculation of structure factors with a B of 3.0 Å^2 for all atoms gave a discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0.34.

The least-squares refinement was done on a HITAC 5020-E computer at the University of Tokyo with the program written by T. Ashida. The refinement of overall and interlayer scale-factors, and positional and thermal parameters was undertaken by the block-diagonal least-squares method. Because of the limited capacity of the computer memories, the number of reflections used for the refinement was reduced to 3432 ($\sin\theta/\lambda=0.56$), in which 461 non-observed reflections were included. In the refinement, the minimized function used was $\sum w(\Delta F)^2$, and the weight w was taken as unity for all reflections. The atomic scattering factors used were taken from those of Hanson *et al.*[8] After three cycles of the refinement, the R factor reduced to 0.176 for non-zero reflections. Another five cycles with anisotropic thermal parameters for Pd, S, P, and C(1) gave $R=0.133$ for non-zero reflections ($R=0.146$ for all reflections).

The final atomic coordinates with their standard deviations and thermal parameters are listed in Table 1. Tables of the observed and calculated structure factors are deposited by the Chemical Society of Japan.*2 The final electron density map, and molecular structure viewed along the *b* axis are shown in Figs. 1 and 2, respectively.

Discussion

Synthetic Aspect. It has been found that $M\{(C_6H_5)_3P\}_4$ reacts readily with carbon disulfide to form novel complexes Ia and Ib (Eq. (1)).

$$M\{(C_6H_5)_3P\}_4 + CS_2 \longrightarrow M\{(C_6H_5)_3P\}_2(CS_2) \quad (\text{Ia: M=Pd; Ib: M=Pt}) \tag{1}$$

Independently, Baird and Wilkinson[9] also obtained complex I in a manner similar to that indicated by Eq. (1). These complexes are air-stable in the solid state. Complex I was treated with triphenylstibine in benzene to form the substituted product with the simultaneous liberation of carbon disulfide.

$$M\{(C_6H_5)_3P\}_2(CS_2) + 2(C_6H_5)_3Sb \longrightarrow \{M(C_6H_5)_3P\}_2\{(C_6H_5)_3Sb\}_2{}^{3)} + CS_2 \tag{2}$$

The quantitative determination of the carbon disulfide liberated in the above reaction by gas chromatographic analysis indicated that about one mole of carbon disulfide per one mole of complex was generated. This fact suggests that the complex I involves carbon disulfide attached directly to metal atom. Attempts to prepare the diphosphine-metal-carbon disulfide complexes by the direct reaction of $M\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2$ with carbon disulfide were not successful. However, complex II was prepared from the reaction of the phosphine complex Ia with equivalent diphosphine in carbon disulfide solution as shown in Eq. (3).

$$Pd\{(C_6H_5)_3P\}_2(CS_2) + (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 \longrightarrow Pd\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}(CS_2) + 2(C_6H_5)_3P \tag{3}$$

The infrared spectra of the complexes exhibit characteristic CS_2 bands as shown in Table 2. The bands appearing at 1200–1100 cm^{-1} are probably to be assigned to the carbon-sulfur stretching vibration of the multiple bond of carbon disulfide. These absorption bands are shifted (*ca.* 300 cm^{-1}) toward lower frequencies by coordination to the metal atom in comparison with that of uncoordinated carbon disulfide.

Table 2. INFRARED FREQUENCIES (in cm^{-1}) OF COORDINATED CS_2 AND FREE CS_2 (in Nujol mulls)

Ia	$Pd(Ph_3P)_2(CS_2)$	1190	1177	1152	636
Ib	$Pt(Ph_3P)_2(CS_2)$	1179	1163	1145	653
II	$Pd(Ph_2PCH_2CH_2PPh_2)(CS_2)$	1178	1167	1152	632
	CS_2*,[10]		1510		656

* Liquid state

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[8] H. P. Hanson, F. Herman, J. D. Lea and S. S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

*2 The complete data of the F_o-F_c table are kept as Document No. 6801 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and remitting, in advance, ¥200 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

[9] M. C. Baird and G. Wilkinson, *Chem. Commn.*, **1966**, 514.

[10] T. Wentink, Jr., *J. Chem. Phys.*, **29**, 188 (1958).

TABLE 3. BOND LENGTHS AND ANGLES IN THE MOLECULE WITH THEIR ESTIMATED STANDARD DEVIATIONS (σ)

Bond		σ	Bond		σ
Pd-S(2)	2.305 Å	0.011 Å	Pd-P(1)	2.316 Å	0.008 Å
Pd-P(2)	2.415	0.008	Pd-C(1)	2.00	0.03
S(1)-C(1)	1.63	0.03	S(2)-C(1)	1.65	0.03
P(1)-C(11)	1.85	0.03	P(1)-C(21)	1.86	0.03
P(1)-C(31)	1.86	0.03	P(2)-C(41)	1.83	0.03
P(2)-C(51)	1.80	0.03	P(2)-C(61)	1.83	0.03
C-C(av.)[a]	1.41	0.05			

Angle		σ	Angle		σ
S(2)-Pd-P(2)	108.3°	0.4°	P(1)-Pd-P(2)	108.8°	0.3°
S(2)-Pd-C(1)	44	1	P(1)-Pd-C(1)	99	1
Pd-S(2)-C(1)	58	1	Pd-C(1)-S(2)	78	1
Pd-C(1)-S(1)	142	2	S(1)-C(1)-S(2)	140	2
Pd-P(1)-C(11)	119	1	Pd-P(1)-C(21)	114	1
Pd-P(1)-C(31)	110	1	Pd-P(2)-C(41)	114	1
Pd-P(2)-C(51)	119	1	Pd-P(2)-C(61)	112	1
C(11)-P(1)-C(21)	101	1	C(11)-P(1)-C(31)	105	1
C(21)-P(1)-C(31)	107	1	C(41)-P(2)-C(51)	100	1
C(41)-P(2)-C(61)	101	1	C(51)-P(2)-C(61)	109	1
C-C-C(av.)[a]	120	3			

a) The average value in benzene rings.

The complex $Pd\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}(CS_2)$ II was recognized to be mononuclear in nitrobenzene solution by means of molecular weight measurement. The similarity in the infrared absorption bands may imply that $M\{(C_6H_5)_3P\}_2(CS_2)$ has a structure analogous to that of II.

The sulfur dioxide complexes, IIIa and IIIb, are unstable in air, particulary in solution. When $[Pd\{(C_6H_5)_3P\}_4(SO_2)]_n$, IIIb was treated with triphenylstibine in benzene solution, bis(triphenylphosphine)bis(triphenylstibine)palladium, $Pd\{(C_6H_5)_3P\}_2\{(C_6H_5)_3Sb\}_2$, was quantitatively obtained and the simultaneous liberation of sulfur dioxide was verified by gas chromatographic analysis. Therefore it is evident that the complex (III) contains sulfur dioxide as a ligand (Eqs. (4) and (5)).

$$M\{(C_6H_5)_3P\}_4 + SO_2 \longrightarrow [M\{(C_6H_5)_3P\}_4(SO_2)]_n \quad (4)$$

(IIIa: M=Pd, IIIb: M=Pt)

$$[Pd\{(C_6H_5)_3P\}_4(SO_2)]_n + (C_6H_5)_3Sb \longrightarrow Pd\{(C_6H_5)_3P\}_2\{(C_6H_5)_3Sb\}_2 \quad (5)$$

The infrared spectra of the complex $[M\{(C_6H_5)_3P\}_4(SO_2)]_n$ exhibit characteristic strong bands near 1200 cm^{-1} and 1050 cm^{-1} (IIIa: 1206, 1051 cm^{-1}; IIIb: 1198, 1047 cm^{-1}; in Nujol mull) ascribed to the asymmetric, and symmetric stretching modes of the $-SO_2-$ group attached to the metal. Unfortunately, further detailed information about the structure was not obtained, because the molecular weight of the complex could not been measured owing to its low solubility. We have not, as yet, been able to comfirm whether complex III has a monomeric structure such as $IrCl(SO_2)(CO)\{(C_6H_5)_3P\}_2$,[11,2b] or a dimeric structure with a sulfur dioxide bridge such as the iron carbonyl-sulfur dioxide complex.[12]

Crystal and Molecular Structure of $Pd\{(C_6H_5)_3P\}_2(CS_2)$. Intramolecular distances and angles with their standard deviations are listed in Table 3.

The most remarkable feature of the whole structure is the coordination of CS_2 to the Pd atom. Figure 3 shows the geometry around the

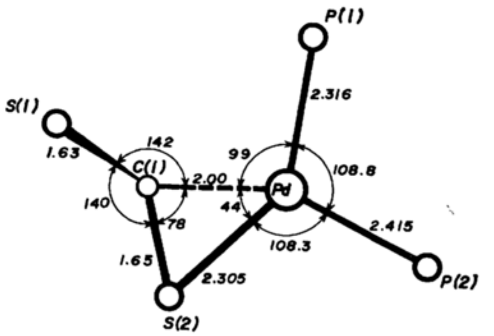

Fig. 3 Neighbors of the palladium atom in $Pd(Ph_3P)_2(CS_2)$, interatomic distances (Å) and bond angles (degree).

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[11] L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, **88**, 1333 (1966).

[12] E. H. Braye and W. Hübel, *Angew. Chem.*, **75**, 345 (1963).

Pd atom. With only one of the S atoms, S(2), coordinated to the Pd, the CS_2 ligand, which is linear in a free molecule, is bent, the $\angle$S–C–S being 140°. The Pd atom and its neighboring atoms, P(1), P(2), S(2), and C(1) lie approximately on the same plane. The following is the equation of the least-squares plane;

$$0.11X + 0.73Y - 0.92Z + 3.12 = 0.0$$

where $X = ax + cx \cdot \sin\beta$, $Y = by$, and $Z = cz \cdot \sin\beta$.

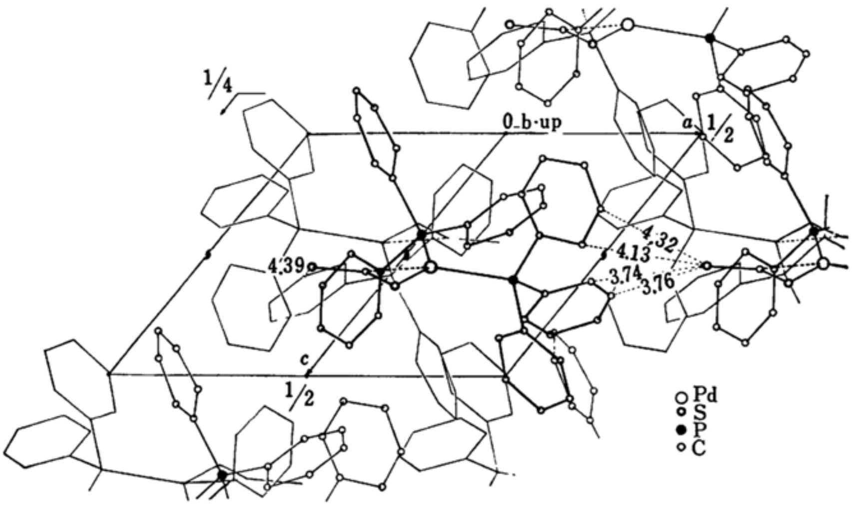

Fig. 4. The crystal structure viewed along the *b* axis.

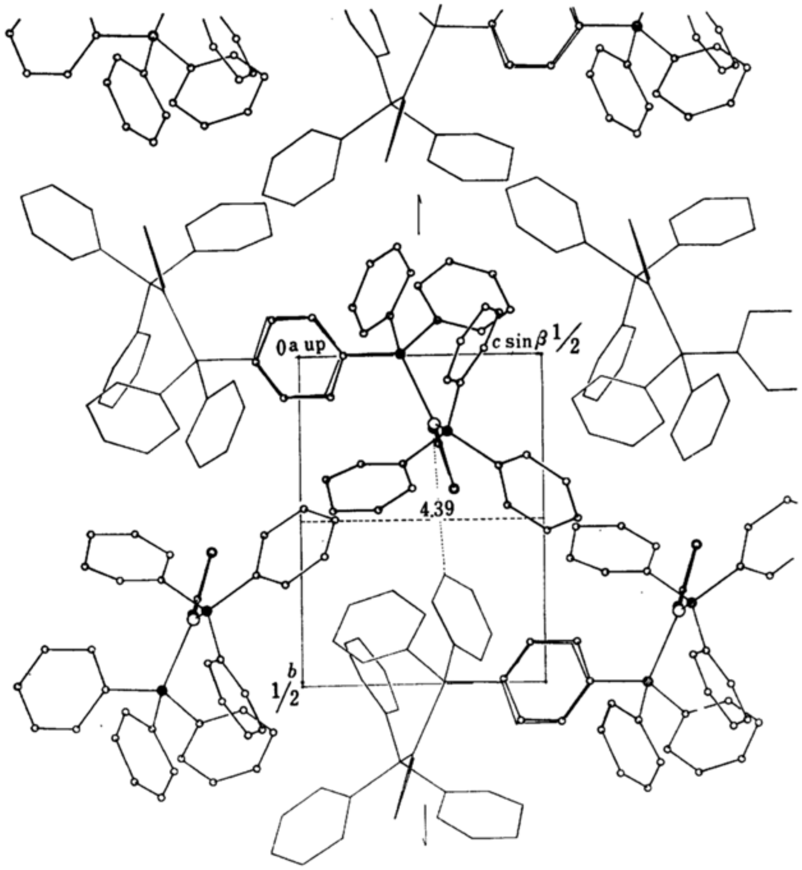

Fig. 5. The crystal structure viewed along the *a* axis.

TABLE 4. DEVIATIONS FROM THE LEAST-SQUARES PLANE

Atom	Deviation
Pd	0.00 Å
S(2)	0.08
P(1)	0.05
P(2)	−0.03
C(1)	−0.10
S(1)	−0.31

The angle between the S(1)–C(1) vector and this plane is 7°. The deviations of above-mentioned atoms from the best plane are listed in Table 4.

The Pd–S(2) distance is 2.305 Å, while Pd–S(1) is 3.441 Å (sum of the covalent radii, 2.36 Å). The S(1) atom is located far from any atoms of the surrounding molecules by over 3.74 Å as Figs. 4 and 5 show (sum of the van der Waals radii for S and benzenic C, 3.55 Å). The Pd–C(1) distance of 2.00 Å is slightly shorter than the sum of the covalent radii for Pd and trigonal hydridized C, 2.06 Å. But the ∠S(2)–Pd–C(1) of 44° is very small. One of the possible explanations for the C(1)–Pd bond is the bent-bond configuration. The two C–S distances in the CS_2 ligand are 1.63 Å and 1.65 Å (E. S. D., 0.034 Å), and they show no significant difference. However, these distances are longer than the ordinary C–S distance of 1.55 Å in a free molecule.[13] Recently, in Pt-$\{(C_6H_5)_3P\}_2(CS_2)$ a similar coordination of CS_2 to Pt (instead of Pd) as described above was found by Baird *et al.*[14] They also mentioned that $Pd\{(C_6H_5)_3P\}_2(CS_2)$ and $Pt\{(C_6H_5)_3P\}_2(CS_2)$ are isostructural. In this case, though, they reported preliminary results which indicated a big difference between the two C–S distances in the CS_2 ligand.

The Pd–P(1), and Pd–P(2) distances are 2.316, and 2.415 Å, respectively, and they differ significantly from each other. The longer Pd–P(2) distance may be interpreted as due to the trans-lengthening effect found in $(PdCl_2C_2H_4)_2$[15] and $(PdCl_2CH_2CHC_6H_5)_2$.[16] The Pd–P(1) distance of 2.316 Å is considerably shorter than the sum of the covalent radii (2.42 Å). This value corresponds to Pd–P=2.31 Å in $(C_4H_7)PdP(C_6H_5)_3$,[17] and also to Ir–P (av.)=2.34 Å in $IrO_2Cl(CO)$-$\{(C_6H_5)_3P\}_2$.[2a] Such a shortening of the Pd–P distance may be a result of the partial double bond character acquired through back donation[18] of electrons from the Pd atom into the two P's.

Since the average angles of ∠C–P–C's, and ∠Pd–P–C's are 104°, and 115°, respectively, the geometry around the P atom is a distorted tetrahedral arrangement.

In benzene rings of $P(C_6H_5)_3$ groups the average bond distance, and angle are normal, 1.41 Å, and 120°C, respectively. Like a three-bladed propeller, the three planes of the benzene rings bonded to the P(1) rotate in the same direction, the average dihedral angle between these planes being 108°. However, this is not so in the case of benzene rings bonded to P(2), because these are in contact with the S(1) of the next molecule. An ordinary contact, 3.54 Å, is found as the shortest intermolecular benzene-benzene distance.

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13) A. H. Guenther, *J. Chem. Phys.*, **31**, 1095 (1959).

14) M. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae and G. Wilkinson, *Chem. Commn.*, **1967**, 92.

15) J. N. Dempsy and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4984 (1955).

16) J. N. Dempsy and N. C. Baenziger, *ibid.*, **77**, 4987 (1955).

17) M. Mason and D. R. Russel, *Chem. Commn.*, **1966**, 26.

18) A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).