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The Crystal and Molecular Structures of Dichloro-1,2-bis(di-*t*-butylphosphino)ethaneplatinum(II) and its Chlorobenzene Solvate

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X-Ray crystal structure analyses of $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}]$ (I) and $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}, C_6H_5Cl]$ (II) have been carried out. Crystals of I belong to monoclinic system: $a=20.595(3)$, $b=7.917(3)$, $c=14.885(2)$ Å, $\beta=109.03(1)°$, space group $P2_1/c$ with $Z=4$. II forms monoclinic crystals, $P2_1/c$: $a=14.873(2)$, $b=13.193(2)$, $c=15.314(2)$ Å, $\beta=98.75(1)°$, $Z=4$. Both structures, solved by the heavy-atom method, have been refined anisotropically by least-squares procedure to $R=0.067$ and 0.078 for I and II respectively. There is no essential difference between the structures of $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}]$ molecules in I and II. The coordination around the platinum atom is square-planar; Pt–P=2.262(3) and 2.265(3) Å and Pt–Cl=2.374(4) and 2.365(4) Å. The molecule has a pseudo-C_2 symmetry: the platinum atom and the center of the C–C bond in the P–C–C–P lie on this pseudo-C_2 axis.

Recently, Otsuka and his co-workers have made studies of a series of bis(di-substituted phosphino)alkaneplatinum complexes. In co-operation with them we have carried out the molecular structure determination of these complexes by means of X-ray diffraction. This paper describes the crystal structure analyses of dichloro-1,2-bis(di-*t*-butylphosphino)ethaneplatinum(II) $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}]$ and its chlorobenzene solvate.

Experimental

Crystals of $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}$ (I) were kindly provided by Professor Sei Otsuka and co-workers. Depending upon the recrystallization conditions two kinds of crystals were obtained. Preliminary Weissenberg photographs (Cu-$K\alpha$) showed that both crystals belong to the monoclinic system, and their corresponding space groups are both $P2_1/c$ (No. 14; absent reflections, $h0l$, $l=2n+1$ and $0k0$, $k=2n+1$). Crystals with approximate dimensions of (I) $0.15\times0.17\times0.25$ and (II) $0.27\times0.45\times0.60$ mm were carefully centered on a Rigaku automated, four-circle single-crystal diffractometer. It was necessary to seal the latter crystal in a thin-walled glass capillary tube with a small amount of chlorobenzene in order to prevent decomposition during the experiment.

The unit-cell parameters of both crystals were determined at 20 °C by least-squares fits using 23 and 45 high-angle reflections, respectively. The crystal data are given in Table 1.

Intensity data of both crystals were collected at 20 °C on the Rigaku diffractometer. Graphite-monochromatized Mo$K\alpha$ radiation was used. All data within a 2θ sphere of 54° were measured using the θ-2θ scan technique. The asymmetric scan width $\Delta(2\theta)$ of each reflection was calculated by the equation: $\Delta(2\theta)=(A+B\tan\theta_c)°$, where θ_c is the calculated value of the Bragg angle using $\lambda(\text{Mo}K\alpha_1)$ (=0.70926 Å) and $A=2.0$, $B=0.69$ for I and $A=2.4$, $B=0.69$ for II. The starting angle of the scan was $(2\theta_c-A/2)°$, and the scanning speed was 4.0° min^{-1}. The background count was obtained by averaging the two values measured, for 6 and 5 s respectively for I and II, at both ends of a scan. Corrections for background scattering and the usual Lorentz and polarization effects were applied. No absorption correction was employed. For weak reflections of $|F|<3\sigma(F)$ the peak scan was repeated twice. Four standard reflections (10,0,0, 006, 440, $42\bar{9}$) were measured after every 60 reflections; these remained constant within the error limits, throughout the data collections. Totals of 5035 (4350 non-zero ($|F|\geqq3\sigma(F)$)) and 6504 (5437 non-zero) reflections were collected for I and II, respectively.

TABLE 1. CRYSTAL DATA OF $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}]$ (I) AND ITS C_6H_5Cl SOLVATE (II)

	I	II
$F.W.$	584.46	697.02
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a[Å]	20.595(3)	14.873(2)
b[Å]	7.917(3)	13.193(2)
c[Å]	14.885(2)	15.314(2)
β[°]	109.03(1)	98.75(1)
U[Å^3]	2294.4(11)	2970.0(8)
D_m[g cm^{-3}]	1.70$^{a)}$	
Z	4	4
D_c[g cm^{-3}]	1.692	1.559
μ(Mo$K\alpha$)[cm^{-1}]	68.0	53.5

a) Flotation in tribromomethane-carbon tetrachloride solution at 20 °C.

Solution and Refinement of Structures

Each of the structures of I and II was solved by the heavy atom method. The platinum atom was located from a three-dimensional Patterson map. All the non-hydrogen atoms were revealed from the subsequent Fourier syntheses. Refinement of the atomic positional and thermal parameters was carried out by the block-diagonal least-squares procedure. The HBLS V program[1] was used.

Final reliability factors are: I, $R=0.088$ (0.067 for non-zero reflections); II, $R=0.105$ (0.078). The weighting scheme used was $w=\{\sigma(F)^2+a|F_o|+b|F_o|^2\}^{-1}$ for $|F_o|>0$ and $w=FWT$ for $|F_o|=0$, where $a=0.10071$, $b=0.00007$, and $FWT=0.05613$ for I and $a=0.0365$, $b=0.0039$, and $FWT=0.04715$ for II. A difference synthesis, based on the final atomic parameters, did not reveal the positions of hydrogen atoms nor any other significant features. The final positional and thermal parameters are given in Table 2.*

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* The Tables of structure factors are kept as Document No. 7636 and 7637 at the Chemical Society of Japan.

Table 2a. Atomic fractional coordinates along with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
	$[PtCl_2\{(t\text{-Bu})_2P(CH_2)_2P(t\text{-Bu})_2\}]$		
Pt	0.25246 (2)	0.10719 (6)	0.15184 (3)
Cl (1)	0.1767 (2)	0.0411 (5)	−0.0014 (2)
Cl (2)	0.3294 (2)	−0.0888 (5)	0.1198 (3)
P (1)	0.17675 (14)	0.2917 (4)	0.1782 (2)
P (2)	0.32715 (14)	0.1669 (4)	0.2978 (2)
C (1)	0.2249 (6)	0.406 (2)	0.2890 (8)
C (2)	0.2793 (6)	0.298 (2)	0.3591 (7)
C (10)	0.1473 (7)	0.470 (2)	0.0899 (8)
C (11)	0.1263 (8)	0.630 (2)	0.1333 (11)
C (12)	0.2088 (8)	0.520 (2)	0.0559 (10)
C (13)	0.0859 (7)	0.419 (2)	0.0015 (11)
C (20)	0.1004 (5)	0.187 (2)	0.1991 (7)
C (21)	0.0543 (6)	0.315 (2)	0.2289 (10)
C (22)	0.1304 (8)	0.061 (2)	0.2818 (10)
C (23)	0.0552 (7)	0.085 (2)	0.1142 (11)
C (30)	0.3562 (6)	−0.019 (2)	0.3808 (8)
C (31)	0.3747 (7)	0.035 (2)	0.4877 (10)
C (32)	0.2966 (7)	−0.144 (2)	0.3622 (11)
C (33)	0.4186 (6)	−0.113 (2)	0.3674 (10)
C (40)	0.4041 (6)	0.297 (2)	0.2970 (9)
C (41)	0.4518 (8)	0.337 (3)	0.3956 (11)
C (42)	0.3751 (7)	0.468 (2)	0.2461 (11)
C (43)	0.4436 (8)	0.214 (2)	0.2381 (13)
	$[PtCl_2\{(t\text{-Bu})_2P(CH_2)_2P(t\text{-Bu})_2\}, C_6H_5Cl]$		
Pt	0.25144 (3)	0.20667 (3)	0.21163 (2)
Cl (1)	0.1546 (3)	0.1512 (3)	0.3111 (2)
Cl (2)	0.3692 (2)	0.1178 (3)	0.3013 (2)
P (1)	0.1363 (2)	0.2914 (2)	0.1297 (2)
P (2)	0.3454 (2)	0.2561 (2)	0.1165 (2)
C (1)	0.1874 (9)	0.3640 (9)	0.0486 (7)
C (2)	0.2727 (7)	0.3108 (9)	0.0217 (8)
C (10)	0.0803 (10)	0.3919 (10)	0.1914 (9)
C (11)	0.0435 (15)	0.4799 (14)	0.1283 (13)
C (12)	0.1518 (11)	0.4353 (11)	0.2632 (9)
C (13)	0.0002 (10)	0.3477 (14)	0.2369 (11)
C (20)	0.0485 (11)	0.2092 (11)	0.0620 (9)
C (21)	−0.0290 (11)	0.2736 (15)	0.0073 (13)
C (22)	0.0988 (12)	0.1432 (13)	−0.0017 (10)
C (23)	0.0031 (12)	0.1343 (14)	0.1185 (10)
C (30)	0.4014 (11)	0.1471 (11)	0.0626 (9)
C (31)	0.4247 (14)	0.179 (2)	−0.0293 (12)
C (32)	0.335 (2)	0.0568 (13)	0.0544 (13)
C (33)	0.4939 (13)	0.1149 (15)	0.1234 (12)
C (40)	0.4295 (9)	0.3566 (11)	0.1594 (9)
C (41)	0.4890 (13)	0.3861 (14)	0.0853 (12)
C (42)	0.3777 (12)	0.4491 (6)	0.1804 (14)
C (43)	0.4956 (11)	0.325 (2)	0.2432 (11)
Cl (5)	0.7707 (11)	0.239 (2)	0.2898 (10)
C (51)	0.749 (2)	0.261 (3)	0.179 (2)
C (52)	0.7345 (15)	0.197 (2)	0.115 (2)
C (53)	0.716 (2)	0.236 (2)	0.020 (2)
C (54)	0.714 (2)	0.327 (2)	0.005 (2)
C (55)	0.735 (2)	0.400 (2)	0.073 (4)
C (56)	0.7510 (15)	0.376 (2)	0.174 (3)

TABLE 2b. TEMPERATURE FACTORS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES ($\times 10^3$)
Anisotropic temperature factors are expressed in 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}
$[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}]$						
Pt	1.655(10)	14.65(7)	2.83(2)	1.25(5)	1.50(2)	−0.45(6)
Cl(1)	2.68(9)	25.0(7)	2.81(13)	1.7(4)	1.0(2)	−2.8(5)
Cl(2)	2.84(10)	24.0(8)	5.8(2)	5.9(5)	2.1(2)	−5.9(6)
P(1)	1.70(7)	14.5(5)	2.90(13)	1.3(3)	1.5(2)	0.5(4)
P(2)	1.50(7)	15.1(5)	3.40(14)	0.4(3)	1.0(2)	−1.3(5)
C(1)	2.0(3)	17(2)	4.2(6)	0.8(13)	1.9(7)	−11(2)
C(2)	1.7(3)	21(3)	2.9(5)	0.3(14)	0.2(6)	−6(2)
C(10)	2.8(4)	18(2)	3.8(6)	7(2)	2.0(6)	5(2)
C(11)	3.9(5)	19(3)	6.8(10)	5(2)	3.3(12)	4(3)
C(12)	3.6(5)	28(4)	5.7(8)	1(2)	4.7(11)	11(3)
C(13)	1.9(4)	35(4)	5.8(9)	2(2)	−0.3(9)	1(3)
C(20)	1.7(3)	16(2)	3.3(5)	−0.6(13)	1.3(6)	1(2)
C(21)	2.0(3)	27(3)	6.6(9)	3(2)	3.7(9)	−4(3)
C(22)	3.2(5)	29(4)	5.3(8)	−1(2)	3.6(10)	8(3)
C(23)	2.8(4)	24(3)	5.8(8)	−3(2)	2.0(10)	−5(3)
C(30)	1.6(3)	18(2)	4.2(6)	0.8(14)	0.0(7)	1(2)
C(31)	2.9(4)	26(3)	4.5(7)	2(2)	0.4(9)	2(3)
C(32)	2.6(4)	20(3)	7.1(9)	−2(2)	1.8(10)	5(3)
C(33)	1.9(3)	25(3)	5.3(7)	4(2)	1.3(8)	3(2)
C(40)	1.6(3)	16(2)	5.2(7)	−4.0(13)	2.4(7)	−0(2)
C(41)	2.7(4)	34(4)	5.9(9)	−4(2)	−0.7(10)	−6(3)
C(42)	2.9(4)	17(3)	7.2(9)	0(2)	3.5(10)	5(3)
C(43)	2.9(4)	28(4)	9.9(12)	−0(2)	7.4(13)	−1(4)
$[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}, C_6H_5Cl]$						
Pt	3.90(2)	4.76(2)	2.09(2)	0.43(4)	1.50(3)	0.47(3)
Cl(1)	5.5(2)	9.1(3)	3.02(12)	−0.8(3)	3.2(2)	3.0(3)
Cl(2)	5.7(2)	9.0(3)	4.1(1)	3.7(4)	1.1(3)	4.2(3)
P(1)	3.72(13)	5.4(2)	2.25(11)	−0.3(2)	1.3(2)	0.1(2)
P(2)	3.98(14)	5.3(2)	2.68(12)	0.4(3)	2.2(2)	−0.5(2)
C(1)	6.0(7)	5.1(7)	2.8(5)	1.3(11)	3.2(9)	1.8(10)
C(2)	3.3(5)	5.0(7)	3.2(5)	0.2(13)	3.4(8)	2.0(10)
C(10)	5.6(7)	5.8(8)	5.0(7)	2.7(13)	2.9(11)	−0.9(12)
C(11)	10.9(14)	8.0(12)	7.7(11)	9(2)	6(2)	1(2)
C(12)	7.1(9)	6.5(9)	4.3(7)	−0.7(14)	2.1(12)	−0.3(13)
C(13)	5.3(8)	10.4(13)	6.3(9)	2(2)	5.0(13)	−1(2)
C(20)	6.1(8)	8.2(11)	3.2(6)	−5.5(14)	0.7(11)	−1.0(12)
C(21)	5.2(8)	12(2)	6.6(10)	1(2)	−5(2)	2(2)
C(22)	8.8(11)	10.0(13)	4.2(7)	−6(2)	3.2(14)	−9(2)
C(23)	7.7(10)	10.2(13)	4.7(7)	−7(2)	1.4(14)	3(2)
C(30)	7.7(9)	7.4(10)	4.0(6)	2(2)	5.4(13)	0.7(13)
C(31)	10.1(13)	13(2)	5.4(9)	8(2)	10(2)	2(2)
C(32)	15(2)	7.9(12)	7.3(11)	−9(2)	12(2)	−9(2)
C(33)	8.1(11)	12(2)	7(2)	11(2)	3(2)	−3(2)
C(40)	4.2(6)	8.7(11)	4.2(6)	−2.5(13)	1.0(10)	1.4(13)
C(41)	8.9(12)	10.7(14)	6.6(9)	−9(2)	7(2)	3(2)
C(42)	6.8(10)	7.8(12)	10.4(14)	−0(2)	0(2)	−5(2)
C(43)	5.5(8)	13(2)	4.8(8)	−3(2)	−0.8(13)	−0(2)
Cl(5)	19.4(13)	61(3)	16.7(14)	2(3)	3(2)	18(3)
C(51)	6.0(14)	24(3)	12(2)	2(3)	3(2)	4(5)
C(52)	5.5(11)	15(2)	20(3)	−1(2)	5(3)	−12(4)
C(53)	10(2)	15(2)	15(2)	−3(3)	13(3)	−3(4)
C(54)	9(2)	12(2)	20(3)	−4(3)	13(4)	12(4)
C(55)	12(2)	5.2(13)	64(9)	6(3)	20(7)	30(6)
C(56)	6.6(12)	10(2)	33(4)	5(2)	13(4)	11(5)

Throughout the calculation the atomic scattering factors used were those of neutral atoms given in International Tables for X-ray Crystallography, Vol. IV.[2] For I, the effects of the anomalous dispersion of Pt, Cl, P, and C atoms were included in the calculation; the values of $\Delta f'$ and $\Delta f''$ were also taken from the International Tables for X-Ray Crystallography.[3]

Results and Discussion

Molecular Structure. Figure 1 gives a stereoscopic drawing of the molecule in I. Bond lengths and bond angles are listed in Table 3. Selected bond lengths and bond angles of the molecule in II are given in Fig. 2 with the numbering scheme of the atoms. Figure 3 shows a comparison of selected bond lengths and bond angles between I and II, in which chemically equivalent bond lengths and bond angles have been averaged. This result clearly shows that there is no essential difference between the molecular structures in I and II, in spite of the different molecular packings. Therefore, from now on we will discuss only the molecular structure of I, the more accurate one of the two, except for the case of crystalline chlorobenzene.

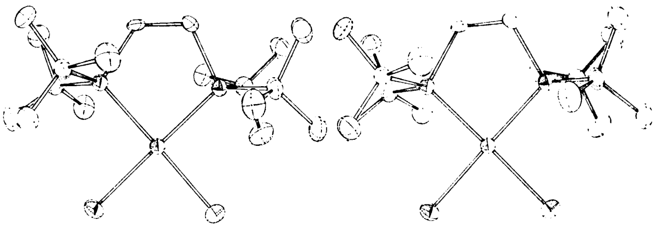

Fig. 1. A stereoscopic drawing of [$PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2\text{-}P(t\text{-}Bu)_2\}$] molecule in I. Thermal ellipsoids are drawn at 30% probability level.

The co-ordination around the platinum atom is square-planar: Pt, P, and two Cl atoms are coplanar within 0.004 Å. The molecule has a pseudo C_2 symmetry. The platinum atom lies on the pseudo C_2 axis, which also passes through the center of the C(1)–C(2) bond in $\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}$ ligand. The P–C–C–P moiety, as a bidentate chelating ligand,

Table 3. Bond lengths and bond angles in [$PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}$]

Bond lengths (l/Å)			
Pt-P(1)	2.262(3)	C(10)-C(11)	1.55(2)
Pt-P(2)	2.265(3)	C(10)-C(12)	1.56(2)
Pt-Cl(1)	2.365(4)	C(10)-C(13)	1.55(2)
Pt-Cl(2)	2.374(4)	C(20)-C(21)	1.55(2)
		C(20)-C(22)	1.55(2)
P(1)-C(1)	1.859(13)	C(20)-C(23)	1.53(2)
P(2)-C(2)	1.864(14)	C(30)-C(31)	1.57(2)
P(1)-C(10)	1.886(14)	C(30)-C(32)	1.53(2)
P(1)-C(20)	1.892(13)	C(30)-C(33)	1.55(2)
P(2)-C(30)	1.889(14)	C(40)-C(41)	1.51(2)
P(2)-C(40)	1.893(13)	C(40)-C(42)	1.57(2)
		C(40)-C(43)	1.53(2)
C(1)-C(2)	1.52(2)		
Bond angles (ϕ/°)			
P(1)-Pt-P(2)	89.42(12)	Pt-P(1)-C(1)	105.7(4)
P(1)-Pt-Cl(1)	91.98(12)	Pt-P(2)-C(2)	106.5(5)
P(2)-Pt-Cl(2)	92.30(13)	Pt-P(1)-C(10)	116.4(4)
P(1)-Pt-Cl(2)	178.27(13)	Pt-P(1)-C(20)	113.7(4)
P(2)-Pt-Cl(1)	178.57(13)	Pt-P(2)-C(30)	115.8(4)
Cl(1)-Pt-Cl(2)	86.29(13)	Pt-P(2)-C(40)	114.5(4)
C(1)-P(1)-C(10)	102.3(6)	C(2)-P(2)-C(30)	102.7(6)
C(1)-P(1)-C(20)	107.3(6)	C(2)-P(2)-C(40)	106.1(6)
C(10)-P(1)-C(20)	110.3(6)	C(30)-P(2)-C(40)	109.9(6)
P(1)-C(1)-C(2)	113.4(9)	P(2)-C(2)-C(1)	111.5(9)
P(1)-C(10)-C(11)	113.1(10)	P(2)-C(30)-C(31)	111.8(10)
P(1)-C(10)-C(12)	107.8(10)	P(2)-C(30)-C(32)	108.8(10)
P(1)-C(10)-C(13)	112.8(10)	P(2)-C(30)-C(33)	113.0(10)
P(1)-C(20)-C(21)	112.4(10)	P(2)-C(40)-C(41)	112.8(11)
P(1)-C(20)-C(22)	106.0(10)	P(2)-C(40)-C(42)	106.5(9)
P(1)-C(20)-C(23)	114.1(9)	P(2)-C(40)-C(43)	111.9(10)
C(11)-C(10)-C(12)	107.1(12)	C(31)-C(30)-C(32)	106.0(12)
C(11)-C(10)-C(13)	107.7(12)	C(31)-C(30)-C(33)	108.8(12)
C(12)-C(10)-C(13)	108.3(12)	C(32)-C(30)-C(33)	108.3(12)
C(21)-C(20)-C(22)	108.5(12)	C(41)-C(40)-C(42)	108.2(12)
C(21)-C(20)-C(23)	108.4(12)	C(41)-C(40)-C(43)	110.5(13)
C(22)-C(20)-C(23)	107.1(12)	C(42)-C(40)-C(43)	106.6(12)

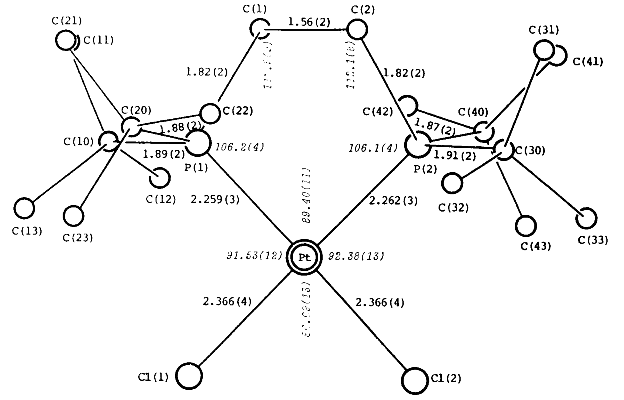

Fig. 2. Selected bond lengths (l/Å) and bond angles (ϕ/°) of the molecule in II.

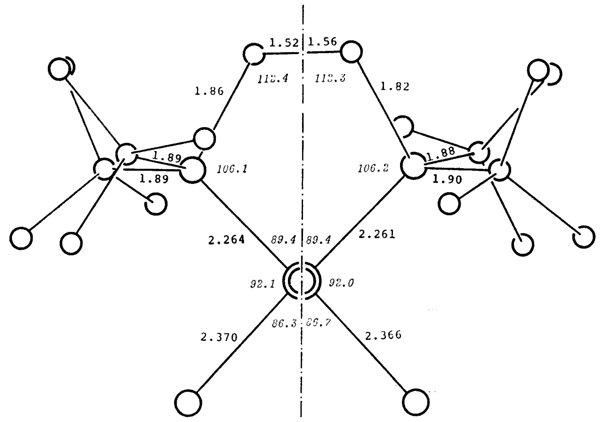

Fig. 3. Comparison of the selected bond lengths (l/Å) and bond angles (ϕ/°) of the molecule in I(left) and II(right).

is puckered in a manner similar to that observed in co-ordinated ethylenediamine rings. The methylene carbon atoms are displaced, by 0.30 and 0.28 Å, to the opposite sides of the co-ordination plane.

The Pt–P bond lengths [2.262(3) and 2.265(3) Å] are as much as 0.14 Å shorter than the sum of the covalent radii [2.41 Å].[4] On the other hand, the Pt–Cl bond lengths [2.374(4), 2.365(4) Å] are significantly longer than the sum of the covalent radii [2.30 Å].

The P–C(bridge) bond lengths [both 1.86(2) Å] are close to the sum of the covalent radii [1.87 Å], and are slightly shorter than the P–C(t-Bu) bonds [all 1.89(2) Å]. The two t-butyl groups attached to the same phosphorus atom are in a staggered position.

Solvated Chlorobenzene Molecule. Crystals of II contain solvated chlorobenzene molecules. The electron-density map calculated on the mean plane of chlorobenzene does not show a normal distribution with respect to magnitude and anisotropy. The rather low peak heights suggest that the occupancy of chlorobenzene is less than unity and/or that their positional fluctuations in the crystal are fairly large. Consequently, the bond lengths and bond angles are not satisfactory ones.

Crystal Structure. A stereoscopic drawing of the molecular packings of I and II are given in Figs. 4 and 5. Figure 6 illustrates the crystal structure of II projected along the c axis. The $[PtCl_2\{(t\text{-Bu})_2P(CH_2)_2P(t\text{-Bu})_2\}]$ molecules are piled up in columns along the c axis, and the chlorobenzene molecules are packed in voids between these columns with rather loose molecular contacts.

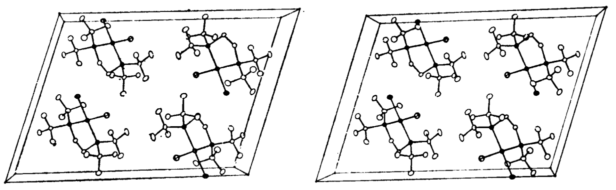

Fig. 4. A stereoscopic drawing of the molecular packing in I.

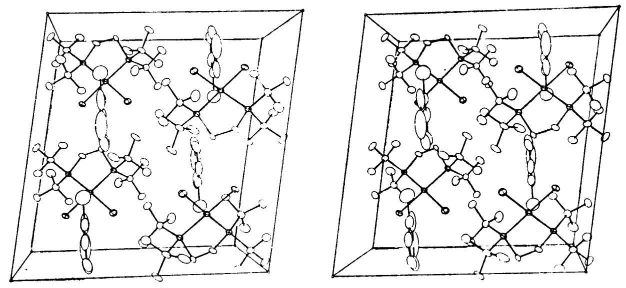

Fig. 5. A stereoscopic drawing of the molecular packing in II.

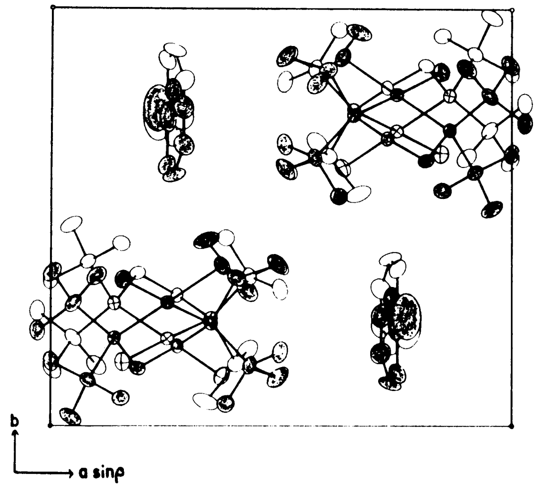

Fig. 6. Crystal structure of II projected along the c axis.

All intermolecular atomic contacts in I and II are considered to be at the usual van der Waals distances.

Computations throughout the present study were carried out on a NEAC 2200-700 computer at Osaka University. Figures 1, 4, and 6 were drawn on the NUMERICON 7000 system at Osaka University with a local version of ORTEP.[5]

The authors wish to express their thanks to Professor Sei Otsuka and his co-workers for the crystals and their helpful discussions.

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