Preparation and Circular Dichroism of Dichloro-(*S*)-2-(butylphenylphosphinomethyl)pyrrolidine-palladium(II)([$PdCl_2L$]) and Its Related Complexes, and the Absolute Configuration of [$PdCl_2L$] Determined by X-Ray Analysis

Isamu KINOSHITA, Kazuo KASHIWABARA, Junnosuke FUJITA,* Takashi YAMANE,**
Hitoshi UKAI,** and Tamaichi ASHIDA**

*Department of Chemistry, Faculty of Science, and **Department of Applied Chemistry,
Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464*

(Received November 29, 1978)

(*S*)-2-(Butylphenylphosphinomethyl)pyrrolidine(L) was prepared from (*S*)-proline *via* four main reaction steps. A pair of diastereomers of the $PdCl_2L$ complex, the isomerism of which comes from chiral configuration of the phosphorus atom, crystallized in different forms (needle and block), which were separated by hand picking. The molecular structure and absolute configuration of one(block) of the dichloro complexes was determined by X-ray analysis. Crystallographic data are: $P2_12_12_1$, $Z=4$, $a=13.576(4)$, $b=16.351(3)$, $c=8.041(2)$ Å, and $R=7.8\%$ for 1659 reflections. The Pd atom has a distorted square planar coordination of four donor atoms. The Pd–Cl bond distance *trans* to Pd–P, 2.367 Å, is longer than that *trans* to Pd–N, 2.296 Å. The absolute configuration of the coordinated phosphorus atom was determined to be *R* by assuming *S* configuration for the asymmetric carbon atom of the aminophosphine. The corresponding diastereomers of the dibromo complex were also prepared from each diastereomer of the chloro complex. The circular dichroism spectra of these diastereomers were compared with one another and with those of other related complexes, and the vicinal effects due to the chiral phosphorus atoms in these complexes were examined.

There has been much interest in asymmetric syntheses catalized by transition metal complexes, especially by rhodium(I) complexes containing chiral phosphines. These studies have extensively developed preparations[1–5)] and optical resolutions[6)] for a variety of chiral phosphines. Recently, some of optically active natural products have been used for precursors of chiral phosphines.[7–9)] However, tedious procedures are often required for preparing optically active phosphines with a chiral phosphorus atom. The importance of a chiral center at a phosphorus atom has been pointed out for high efficiency of asymmetric hydrogenation.[10)]

This paper reports the preparation of (*S*)-2-(butylphenylphosphinomethyl)pyrrolidine, which has three chiral centers at the carbon, nitrogen, and phosphorus atoms, and the isolation of a pair of diastereomers of its dichloro palladium(II) complex caused by a pair of the chiral phosphorus atoms. The chiral carbon atom has *S* configuration and the nitrogen one should yield the same *S* configuration stereoselectively upon coordination as seen in bis(*S*-prolinato)palladium(II).[11)] The paper also describes the molecular structure and absolute configuration of one of the diastereomers determined by X-ray analysis.

So far little work has been reported concerning circular dichroism(CD) spectra of metal complexes containing chiral phosphines. The accumulation of CD data of chiral phosphine complexes will be necessary for investigating the stereochemistry of phosphine complexes catalyzing asymmetric syntheses. In this paper the CD spectra of diastereomers of the dichloro complex are compared with those of the related complexes and the vicinal effects due to the coordinated chiral phosphorus atoms are examined. A part of this study has been reported briefly.[12)]

Experimental

All the preparations and handlings of the aminophosphines were carried out under an atmosphere of nitrogen or *in vacuo*. The palladium(II) complexes containing the aminophosphines can be handled in air. Absorption, CD, ^{1}H-NMR, and IR spectra were recorded on a HITACHI 323 spectrometer, a JASCO J-20 or J-40 spectropolarimeter, a JEOL PMX-60 spectrometer, and a HITACHI EPI-L 2 spectrometer, respectively.

Preparations. The following compounds were prepared according to the methods previously reported; (*S*)-2-(diphenylphosphinomethyl)pyrrolidine[8)] and (*S*)-2-(aminomethyl)pyrrolidine.[13)]

(S)-2-(Phenylphosphinomethyl)pyrrolidine. To liquid ammonia (150 cm^3) in a 500 cm^3 round-bottom, three neck flask with a mechanical stirrer, a dropping funnel, and nitrogen inlet was added sodium metal(3.3 g) and then phenylphosphine(15 g) dropwise with vigorous stirring over 40 min at −78 °C (Dry Ice-methanol). After stirring for further 20 min, (*S*)-2-(bromomethyl)pyrrolidine hydrobromide[14)] (17 g) was added in small portions and then the solution was stirred for 2 h at −78 °C. The liquid ammonia was evaporated off at room temperature and oxygen-free tetrahydrofuran(THF) was added on the residue. The undissolved material (sodium bromide) was filtered off and the filtrate was evaporated to remove THF. The oily residue was distilled under reduced pressure to yield colorless liquid. Yield: 7.4 g, bp 140.5—141 °C/933 Pa.

(S)-2-(Butylphenylphosphinomethyl)pyrrolidine. To a mixture of liquid ammonia (150 cm^3) and sodium metal (0.52 g) was added dropwise (*S*)-2-(phenylphosphinomethyl)pyrrolidine(4.38 g) with vigorous stirring over 20 min at −78 °C. The solution changed from blue green to green. After stirring for 1 h, butylchloride (6 cm^3) was added dropwise to the solution. The color of the solution changed to deep red instantly and the stirring was continued until the color became light yellow. The liquid ammonia was evaporated off at room temperature and oxygen-free THF was added on the residue to extract the object. The undissolved material (sodium chloride) was filtered off and the filtrate was evaporated to give oily residue. It was distilled in vacuo to yield colorless liquid. Yield: 3.6 g, bp 135—136 °C/13.3 Pa.

*{(S)-2-(Butylphenylphosphinomethyl)pyrrolidine}dichloropalladium(II) (**1a** and **1b**).* To an acetonitrile solution (50 cm^3) of $PdCl_2(CH_3CN)_2$[15] (198 mg) was added (*S*)-2-(butylphenylphosphinomethyl)pyrrolidine(190 mg). After stirring for 3 h at 50 °C, appropriate amounts of diethyl ether and then hexane were added to the resultant solution to yield yellow precipitate, which was filtered(250 mg). The product was dissolved in a small amount of chloroform and the solution was poured into a column (ϕ 1.2×10 cm) of acidic activated alumina. The adsorbed yellow band was eluted with a mixture of chloroform and ethanol(20 : 1). The yellow eluate was concentrated to a small volume(10 cm^3) and mixed with ethanol(50 cm^3). The ethanol solution was slowly concentrated at room temperature in air to yield two different crystal forms (total yield 77%), needle (**1a**) and block(**1b**), which were separated by hand picking. The crystals of each form were separately recrystallized from a mixture of chloroform and ethanol. Yield: *ca.* 15% for each isomer. Found for **1a**: C, 42.41; H, 5.66; N, 3.21%. Found for **1b**: C, 42.43; H, 5.68; N, 3.26%. Calcd for $PdCl_2(C_{15}H_{24}NP)$: C, 42.22; H, 5.68; N, 3.28%.

*{(S)-2-(Butylphenylphosphinomethyl)pyrrolidine}dibromopalladium(II) (**2a** and **2b**).* To the complex **1a** or **1b** (60 mg) in a mixture(30 cm^3) of chloroform and ethanol (1 : 1) was added an ethanol solution (10 cm^3) saturated with sodium bromide. After stirring for 3 h at room temperature, the solution was evaporated to dryness under reduced pressure and dichloromethane was added to the residue to extract the dibromo complex. To the extract was added diethyl ether to yield yellow precipitate, **2a** or **2b** from **1a** or **1b**, respectively. Yield: 50 mg. Found for **2a**: C, 34.65; H, 4.70; N, 2.32%. Found for **2b**: C, 34.77; H, 4.69; N, 2.50%. Calcd for $PdBr_2(C_{15}H_{24}NP)$: C, 34.94; H, 4.70; N, 2.32%.

*{(S)-2-(Diphenylphosphinomethyl)pyrrolidine}dichloropalladium(II) (**3**).* To a suspension of $PdCl_2(CH_3CN)_2$(328 mg) in chloroform(30 cm^3) was added a chloroform solution (10 cm^3) of (*S*)-2-(diphenylphosphinomethyl)pyrrolidine (341 mg). After stirring overnight, the solution was poured into a column (ϕ 1.5×10 cm) of acidic activated alumina and the adsorbed band was eluted with a mixture of chloroform and ethanol(5 : 1). Diethyl ether was added to the eluate to yield yellow crystals (**3**). Yield: *ca.* 30%. Found: C, 45.38; H, 4.50; N, 3.03%. Calcd for $PdCl_2(C_{17}H_{20}NP)$: C, 45.71; H, 4.52; N, 3.14%.

*{(S)-2-(Aminomethyl)pyrrolidine}dichloropalladium(II) (**4**).* To a chloroform solution(150 cm^3) of $PdCl_2(CH_3CN)_2$ (1.1 g) was added a chloroform solution(70 cm^3) of (*S*)-2-(aminomethyl)pyrrolidine (0.43 g) and the solution was stirred for 3 h at room temperature to give a precipitate gradually. The precipitate was filtered and dissolved in hot water containing a few drops of concd hydrochloric acid. The solution was concentrated and then potassium chloride was added to the concentrate to yield yellow crystals (**4**). Yield: 0.7 g. Found: C, 21.64; H, 4.37; N, 10.10%. Calcd for $PdCl_2(C_5H_{12}N_2)$: C, 21.39; H, 4.49; N, 10.09%.

*(2-N,N-Dimethylaminoethyldiphenylphosphine)dichloropalladium(II) (**5**).* This complex was prepared according to the method of Meek *et al.*[16]

*Structure Determination of **1b**.* The crystal data of **1b** are as follows: orthorhombic, $P2_12_12_1$, $a=13.576(4)$, $b=16.351(3)$, $c=8.041(2)$Å, $D_m=1.60$, $D_x=1.588$ g cm^{-3}, $Z=4$, and μ(Mo $K\alpha$)=14.1 cm^{-1}. The intensity data were collected on a Hilger & Watts automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation. The crystal used for the data collections had the dimensions of 0.45×0.40×0.25 mm. Independent 1840 reflections with $2\theta \leq 50°$ were measured by the θ-2θ step scan technique, of which nonzero reflections were 1659. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was also carried out by the Furnas's method.[17]

The structure was solved by the heavy atom method. The refinement was carried out by the block-diagonal least-squares method.[18] In the refinement, the weights $w=1/(\sigma^2(F)+a|F_o|+b|F_o|^2)$ for $|F_o|>0$, and $w=c$ for $|F_o|=0$ were assigned ,where $\sigma(F)$ is the standard deviation

TABLE 1. THE ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS (×10^4) OF **1b**
Thermal parameters are in the form: $\exp(-\beta_{11}h^2-\beta_{22}k^2-B_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	1983 (1)	880 (1)	690 (1)	45 (1)	31 (1)	171 (1)	1 (1)	5 (2)	−10 (1)
Cl (1)	483 (2)	1186 (2)	−472 (5)	59 (2)	48 (1)	288 (9)	21 (3)	−60 (8)	−51 (6)
Cl (2)	1551 (3)	−498 (2)	1207 (5)	77 (2)	35 (1)	279 (9)	−23 (3)	−9 (7)	31 (5)
P	2575 (3)	2101 (2)	72 (5)	53 (2)	30 (1)	236 (7)	8 (3)	51 (6)	−20 (5)
N	3349 (7)	673 (5)	1803 (14)	64 (6)	35 (4)	203 (20)	−5 (8)	31 (20)	14 (15)
C (1)	3948 (10)	1426 (8)	2064 (22)	67 (9)	50 (6)	308 (38)	−27 (13)	−31 (33)	−52 (27)
C (2)	4998 (11)	1097 (9)	2347 (22)	50 (7)	78 (8)	326 (39)	14 (14)	−101 (30)	−42 (32)
C (3)	5058 (11)	335 (9)	1310 (21)	72 (9)	71 (7)	313 (43)	−2 (16)	16 (33)	157 (30)
C (4)	3972 (9)	91 (7)	882 (18)	53 (7)	47 (6)	219 (27)	30 (10)	−46 (28)	−1 (23)
C (5)	3874 (9)	1975 (7)	515 (23)	54 (8)	40 (5)	408 (43)	5 (10)	107 (35)	−21 (29)
C (6)	2140 (9)	2961 (6)	1289 (15)	77 (9)	27 (4)	188 (24)	16 (10)	−37 (26)	7 (16)
C (7)	1226 (8)	2913 (7)	2055 (16)	41 (6)	45 (5)	194 (25)	7 (10)	27 (23)	−50 (20)
C (8)	886 (9)	3599 (9)	2987 (23)	70 (9)	56 (6)	288 (35)	−3 (13)	−101 (32)	−48 (27)
C (9)	1394 (10)	4320 (8)	3074 (19)	92 (10)	58 (7)	207 (27)	20 (14)	19 (31)	−63 (24)
C (10)	2316 (10)	4351 (6)	2266 (19)	105 (11)	40 (6)	250 (30)	5 (13)	−81 (33)	−20 (21)
C (11)	2676 (9)	3683 (6)	1363 (17)	77 (9)	28 (4)	254 (31)	−11 (10)	1 (27)	−41 (20)
C (12)	2418 (10)	2414 (7)	−2116 (18)	41 (13)	47 (6)	226 (30)	46 (16)	151 (36)	8 (24)
C (13)	2920 (20)	3207 (11)	−2622 (32)	309 (31)	81 (10)	583 (77)	−31 (35)	581 (91)	177 (46)
C (14)	3721 (28)	2894 (16)	−3672 (87)	126 (30)	24 (10)	1177 (99)	−29 (29)	292 (99)	34 (90)
C (14′)	3427 (29)	3456 (23)	−3761 (75)	135 (33)	85 (21)	983 (98)	29 (45)	566 (99)	245 (99)
C (15)	4237 (16)	3325 (18)	−4692 (35)	153 (22)	173 (22)	448 (73)	−13 (35)	102 (71)	83 (66)

Table 2. The positional($\times 10^3$) and thermal(Å^2) parameters of the hydrogen atoms of **1b**

The standard deviations are given in parentheses.

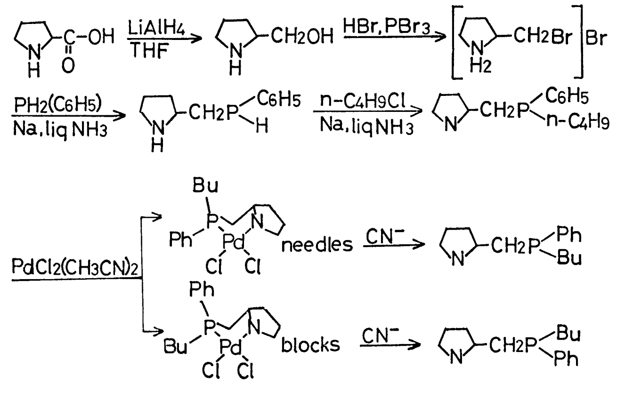
	Bonded to	x	y	z	B
H (1)	N	307 (10)	41 (8)	284 (23)	8 (4)
H (2)	C (1)	378 (8)	167 (6)	281 (15)	3 (3)
H (3)	C (2)	503 (11)	106 (7)	346 (17)	6 (4)
H (4)	C (2)	569 (8)	145 (8)	240 (19)	6 (4)
H (5)	C (3)	515 (11)	6 (7)	211 (26)	8 (5)
H (6)	C (3)	532 (10)	60 (9)	13 (22)	7 (5)
H (7)	C (4)	373 (7)	12 (5)	−11 (13)	1 (2)
H (8)	C (4)	373 (8)	−32 (7)	113 (15)	4 (3)
H (9)	C (5)	414 (9)	258 (8)	87 (16)	6 (4)
H (10)	C (5)	426 (8)	178 (7)	−20 (17)	4 (3)
H (11)	C (7)	82 (10)	225 (9)	186 (23)	8 (4)
H (12)	C (8)	33 (8)	333 (8)	390 (16)	5 (4)
H (13)	C (9)	114 (11)	494 (8)	366 (19)	7 (4)
H (14)	C (10)	265 (11)	500 (8)	222 (23)	8 (4)
H (15)	C (11)	344 (9)	361 (7)	69 (17)	5 (3)
H (16)	C (12)	145 (10)	269 (7)	−234 (16)	7 (4)
H (17)	C (12)	267 (10)	222 (8)	−259 (20)	8 (4)

based on counting statistics. A disorder occurs at the butyl group. Both the C^β and C^γ atoms of the butyl group were located at two sites with occupancies of 0.5 each from the D-map. Finally the C^β atom converged into the resultant position, though its temperature factors are significantly larger than those of the other atoms. The H atoms were found on the D-map. However, those bonded to the C^β, C^γ, C^δ atoms of the butyl group were not found, and not included in the further refinement. The final R value is 9.9% ($a=-0.1777$, $b=0.0082$, and $c=0.2184$), while it is 7.8% for non-zero reflections.

The atomic scattering factors for the Pd^{2+}, Cl^-, P, N, C, and H were taken from International Tables for X-Ray Crystallography, Vol. IV.[19] Calculations were carried out on the FACOM 230-75 computers at Nagoya University. The final atomic parameters are listed in Tables 1 and 2.[20]

Results and Discussion

Preparation and Properties. Mislow[21] and Horner[22] prepared a number of chiral phosphines and phosphine oxides containing asymmetric phosphorus atoms. However, their methods are somewhat tedious. In the present study, a pair of diastereomers of (*S*)-2-(butylphenylphosphinomethyl)pyrrolidine was easily obtained by the following scheme:



The aminophosphine was prepared from (*S*)-proline by a method similar to those for 2-aminoethylphenylphosphine derivatives reported by Issleib.[23] The dichloro palladium(II) complex of the aminophosphine yields only two diastereomers arising from a pair of chiral phosphorus atoms. The nitrogen atom will have *S* configuration stereoselectively upon coordination as confirmed by X-ray analysis on [Pd(*S*-prol)$_2$].[11] The diastereomers (**1a** and **1b**) crystallize in different forms, needle and block, by slow evaporation of an ethanol solution, and can be separated by hand picking. They are stable in air and do not isomerize in boiling ethanol. The free chiral phosphines are easily liberated from the diastereomers by treating with sodium cyanide in water. The corresponding chiral dibromo complexes (**2a** and **2b**) were derived from each diastereomer of the dichloro complex.

Table 3. NMR spectral data of palladium complexes in $CDCl_3$

(δ/ppm from TMS)

Complex	$-CH_3$	$-CH_2-$	N-H	$-C_6H_5$
1a	0.83	1—4.2	7.0	7.5—8.3
1a[a]	0.93	1—4.0	6.6	7.5—8.3
1b	0.97	1—4.2	6.1	7.4—8.3
1b[a]	0.88	1—4.0	6.2	7.5—8.5
2a	0.85	1—3.9	6.5	7.5—8.3
2b	0.91	1—4.1	5.7	7.5—8.3
3	—	1—4.0	6.9	7.3—8.3

a) solvent: DMSO-d_6.

Table 3 shows the data of ^{1}H-NMR spectra of the aminophosphine complexes prepared. The peaks in the region 5.7—7.0 ppm can be assigned to the N–H protons, since these peaks disappear on deuteration. The N–H protons of **1b** and **2b** resonate at a considerably higher magnetic field than do those of **1a** and **2a** respectively. The chiral phosphorus atoms of **1a**, and **1b** have *S* and *R* configurations, respectively (*vide post*). In the *R* configuration(**1b**), the N–H proton and the phenyl group face each other on the same side of the complex plane. Therefore, the up-field shifts of the N–H protons of **1b** and **2b** indicate that the phenyl group causes the shielding effect to the N–H proton. In a previous paper,[12] such a phenyl group was considered to give the deshielding effect to the N–H proton, hence the absolute configuration of **1b** was assigned reversely. The chemical shifts of these N–H protons seem to be sensitive to environment such as the kinds of ligating halide ions and solvents (Table 3). The complex **3**, which has the phenyl group in the same arrangement as **1b** shows the N–H resonance at nearly the same field, 6.9 ppm as that of **1a**.

In the far IR spectra, all the dichloro-aminophosphine complexes show absorption bands around 280 and 330 cm^{-1}. These bands can be assigned to the ν(Pd–Cl), since the corresponding dibromo complexes show no band in this region. The dichloro-diamine complex (**4**) exhibits two strong bands at 301 and 337 cm^{-1} which may be correspond to the ν(Pd–Cl) of 306 and

327 cm^{-1} observed for *cis*-$[\mathrm{PdCl_2(NH_3)_2}]$.[24] The IR spectra of the present complexes are too complicated to be assigned.

*Molecular Structure of **1b*** The stereoscopic view of **1b** (block crystal) drawn by ORTEP II[25] is shown in Fig. 1. The absolute configuration of the phosphorus atom in **1b** becomes *R*, when the asymmetric carbon atom of the pyrrolidine ring is assumed to be *S* configuration. Therefore the phosphorus atom of **1a** (needle crystal) has *S* configuration. The bond lengths and angles concerning non-hydrogen atoms are shown in Fig. 2. The e.s.d.'s are; 0.02—0.03 Å for bond lengths except for Pd–X(0.005—0.014 Å) and C(14)–X(0.05 Å), and 0.7—1.6° for bond angles except for X–Pd–X(0.2—0.4°) and C(13)–C(14)–C(15) (5°). The equations of the best planes and the related data are given in Table 4.

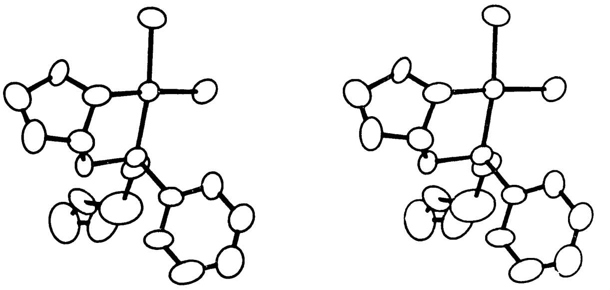


Fig. 1. The stereoscopic view of **1b**.

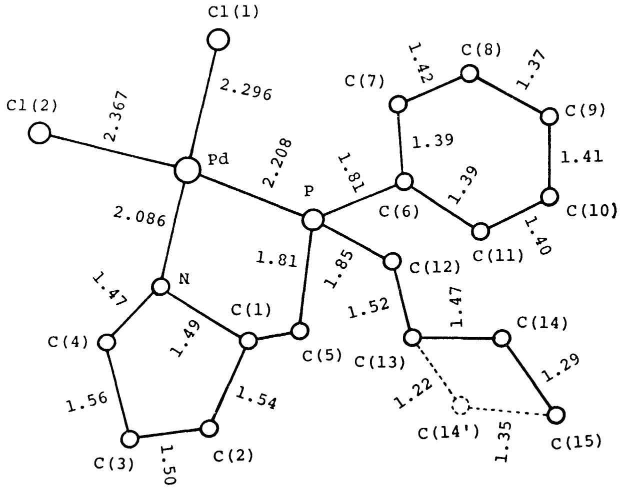


Fig. 2.(a) The bond lengths(Å) of **1b**.

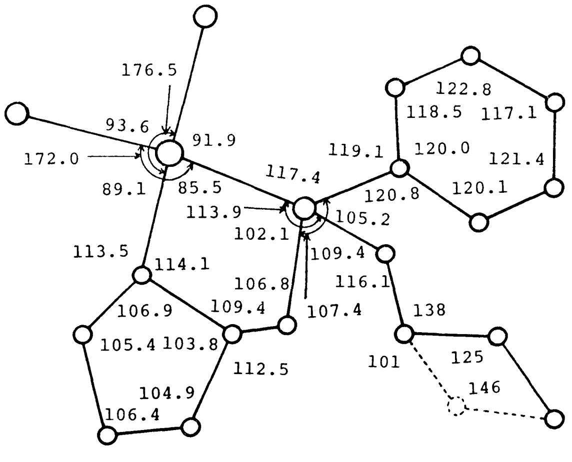


Fig. 2(b). The bond angles (°) of **1b**.

The Pd(II) ion forms a distorted square plane with four donor atoms. The dihedral angle between the plane of Pd, Cl(1), and Cl(2), and that of Pd, P, and N is 174.0°. The P atom deviates by 0.27 Å from the best plane formed with Pd, Cl(1), Cl(2), and N. However, the planarity is rather better than that in $[\mathrm{PdCl_2}\{N,N$-dimethyl-α-methyl-*o*-(butylphenylphosphino)benzylamine$\}]$ (BENZYL),[26] in which the N

Table 4. The best planes of **1b**

(a) Equations of the best planes

$X=ax,\ Y=by,\ Z=cz$

Plane I: Pd, Cl(1), Cl(2), P, N
$0.3384X-0.3067Y-0.8896Z+0.0011=0$

Plane II: Pd, Cl(1), Cl(2), N
$-0.3693X+0.2483Y+0.8955Z+0.1180=0$

Plane III: Pd, P, N
$0.3515X-0.3562Y-0.8658Z+0.0475=0$

Plane IV: Pd, Cl(1), Cl(2)
$-0.3523X+0.2565Y+0.9001Z+0.0790=0$

Plane V: N, C(2), C(3), C(4)
$-0.0139X+0.5767Y-0.8169Z+0.5990=0$

Plane VI: P, C(6), C(7), C(8), C(9), C(10), C(11)
$-0.4532X+0.3437Y-0.8225Z+0.4784=0$

(b) Dihedral angles (°) between the planes

	I	II	III	IV	V
II	176.2				
III	176.8	173.5			
IV	177.0	178.9	174.0		
V	123.0	125.7	119.8	125.6	
VI	118.2	118.9	115.5	119.5	151.2

(c) Displacements ($\times 10^2$ Å) of atoms from the planes

The atoms with asterisks are not included in the best plane calculations.

I		II		III	
Pd	−2	Pd	2	Pd	0
Cl(1)	−3	Cl(1)	−1	P	0
Cl(2)	10	Cl(2)	0	N	0
P	7	N	−1	Cl(1)*	−8
N	−9	P*	27	Cl(2)*	24
C(1)*	−36	C(1)*	−19	C(1)*	−32
C(2)*	8	C(2)*	26	C(2)*	17
C(3)*	123	C(3)*	134	C(3)*	136
C(4)*	115	C(4)*	120	C(4)*	128
C(5)*	40	C(5)*	63	C(5)*	37
C(6)*	−143	C(6)*	−118	C(6)*	−156
C(12)*	140	C(12)*	162	C(12)*	126
IV		V		VI	
Pd	0	N	−1	P	3
Cl(1)	0	C(2)	1	C(6)	−3
Cl(2)	0	C(3)	−3	C(7)	1
P*	22	C(4)	3	C(8)	−1
N*	−6	C(1)*	52	C(9)	2
		C(5)*	204	C(10)	0
		Pd*	94	C(11)	−2

atom deviates by 0.423 Å from the best plane of Pd, Cl(1), Cl(2), and P. The Pd–Cl(2) (*trans* to Pd–P) length of 2.367 Å is longer than the Pd–Cl(1) (*trans* to Pd–N) length of 2.296 Å. The same trend in the Pd–Cl lengths is seen in BENZYL (2.386 and 2.285 Å). The elongation of Pd–Cl(2) bond may be attributed to the stronger *trans* effect of P than that of N. The Pd–P length of 2.208 Å is significantly short as compared with those of 2.241 Å in BENZYL and of 2.286 Å in [PdCl{(S)-isopropyl-t-butylphenylphosphine}{(R)-N,N-dimethyl-α-(2-naphthyl)ethylamine-3C,N}] (NAPHTHYL).[6] The Pd–N length of 2.086 Å is also shorter than those in BENZYL (2.134 Å) and NAPHTHYL (2.167 Å).

The five-membered chelate ring is fairly puckered to form a δ conformation. The torsion angles concerning the ring are: Pd–N–C(1)–C(5), −40.9°; N–C(1)–C(5)–P, 49.7°; C(1)–C(5)–P–Pd, −35.7°; C(5)–P–Pd–N, 11.9°; P–Pd–N–C(1), 13.7°. The deviations of C(1) and C(5) from the plane of Pd, P, and N are 0.32 Å (to the direction to C(6) (phenyl group)) and 0.37 Å(to the direction to C(12) (butyl group)), respectively. The N–Pd–P angle is 85.5°, while that of the six-membered chelate ring in BENZYL is 94.0°. On the contrary, the Cl–Pd–Cl angle (93.6°) is larger than that in BENZYL (88.12°).

The coordinated N atom of the pyrrolidine ring has S configuration. The torsion angles of the pyrrolidine ring are; $\chi_1=32.2$, $\chi_2=-16.8$, $\chi_3=-4.7$, and $\chi_4=25.1$°. The C^α ($=$C(1)) atom is puckered out by 0.52 Å in the pyrrolidine ring, while C^δ puckering is observed for [Pd(S-prol)$_2$].[11]

The disorder occurs at the location of C(14). Therefore the abnormal bond lengths and angles concerning this atom are observed. However, the distance between C(13) and C(15), 2.49 Å is rather normal.

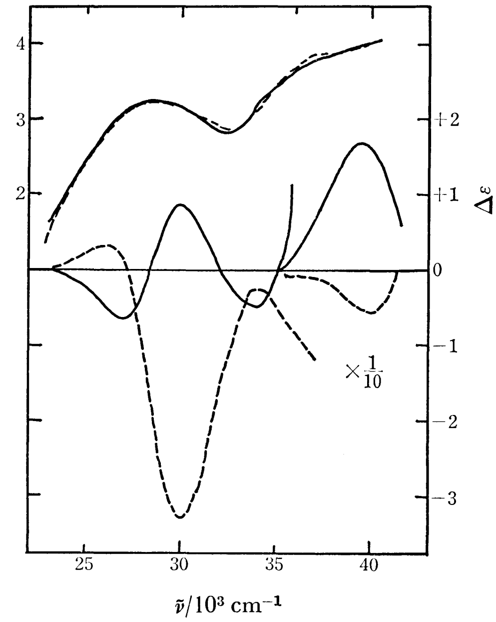


Fig. 3. Absorption and CD spectra of [(S)-2-(butylphenylphosphinomethyl)pyrrolidine]dichloropalladium(II), **1a**(——) and **1b**(----).

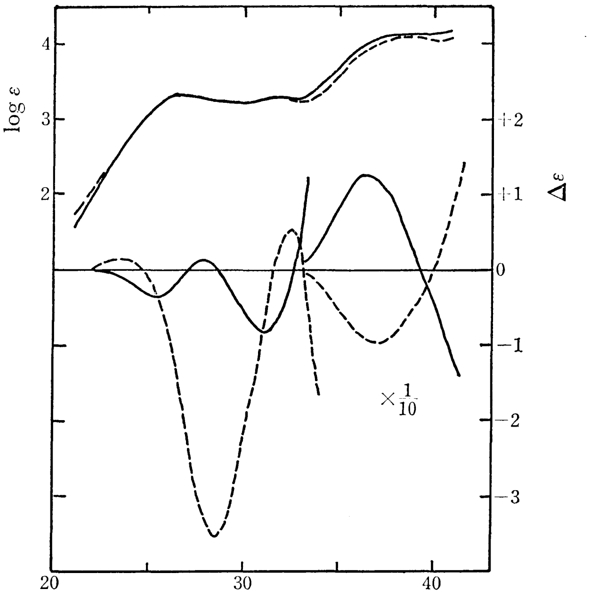


Fig. 4. Absorption and CD spectra of [(S)-2-(butylphenylphosphinomethyl)pyrrolidine]dibromopalladium(II), **2a**(——) and **2b**(----).

Absorption and CD Spectra. The absorption and CD spectra of the dichloro (**1a** and **1b**) and the dibromo (**2a** and **2b**) complexes are shown in Figs. 3 and 4, respectively. The numerical data are given in Table 5 together with those of the other related complexes. The absorption spectra of a pair of diastereomers quite resemble each other, while the CD spectra are nearly enantiomeric to each other. The diastereoisomerism arises from a pair of enantiomeric configurations of the phosphorus atom, the other chiral centers at the carbon and nitrogen atoms being all S configurations. If it is assumed that the vicinal effects due to these three chiral atoms contribute additively to the CD, the vicinal effects of the chiral phosphorus atoms (S configuration) in the dichloro and dibromo complexes can be estimated by the following equations, respectively; $[\Delta\varepsilon(\mathbf{1a})-\Delta\varepsilon(\mathbf{1b})]/2$ and $[\Delta\varepsilon(\mathbf{2a})-\Delta\varepsilon(\mathbf{2b})]/2$. (Fig. 5) The calculated curves are very similar in the pattern between the dichloro and dibromo complexes, although the curve of the latter complex shifts to the smaller wavenumber side according to the spectrochemical series. From these curves, it is concluded that the coordinated (S)-phosphorus atom shows a positive main CD band in the region of the absorption band of the smallest wavenumbers. On the other hand, the curve of the combined vicinal effect due to both chiral atoms of the carbon and nitrogen can be derived by the equation, $[\Delta\varepsilon(\mathbf{1a})+\Delta\varepsilon(\mathbf{1b})]/2$. The derived curve is shown in Fig. 6 together with the absorption and CD spectra of the related complexes. The curve closely resemble the CD spectrum of **3** in the region of the smallest wavenumber absorption band. The complex **3** has two chiral centers at the carbon and nitrogen atoms with the same S chirality as **1a** and **1b**. The curve of the same vicinal effect calculated from **2a** and **2b** also show a pattern similar to that of the dichloro complex. These results indicate that the vicinal effects of the three different chiral atoms are additive in the CD spectra

TABLE 5. ABSORPTION AND CD SPECTRAL DATA

Complex	Absorption maxima $\tilde{\nu}/10^3$ cm^{-1} (ε/mol^{-1} dm^3 cm^{-1})	CD extrema $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
1a	28.75 (1800)	26.75 (−0.67)
	36.5 (5560 sh[a])	30.0 (+0.86)
		34.0 (−0.49)
		39.6 (+17.0)
1b	28.75 (1790)	26.00 (+0.33)
	37.0 (7270 sh)	30.0 (−3.29)
		40.0 (−5.6)
2a	27.00 (2220)	25.40 (−0.36)
	31.5 (1940)	27.9 (+0.11)
	38.5 (13300)	31.0 (−0.84)
		36.5 (+12.5)
2b	26.75 (2150)	23.50 (+0.16)
	31.4 (1900)	28.6 (−3.52)
	38.5 (12100)	32.7 (+0.54)
		37.0 (−9.57)
3	28.25 (2080)	25.25 (+0.13)
	37.5 (12900)	29.7 (−2.41)
		36.5 (+3.43)
4	26.75 (406)	25.75 (+0.50)
	37.0 (996 sh)	29.0 (−0.28)
		38.3 (+0.41)
5	28.17 (2050)	
	37.2 (13400)	

a) sh: shoulder.

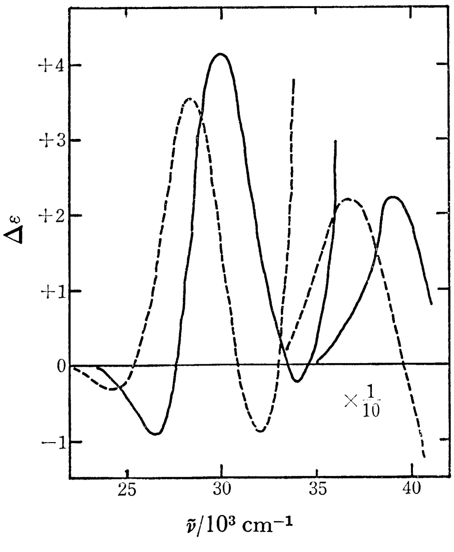


Fig. 5. CD curves calculated from (1/2)[Δε(**1a**)−Δε(**1b**)](——) and (1/2)[Δε(**2a**)−Δε(**2b**)](----).

of the present complexes. The diamine complex (**4**) which has the same chiral atoms as **3** also gives a CD pattern similar to that of **3** in the same region, although the CD intensity of the negative band is very weak.

Meek *et al.*[16] reported that the complex **5** gives absorption bands due to the d-d transitions at *ca.* 21000 cm^{-1}. However, all of the aminophosphine complexes prepared here shows neither absorptions nor CD in this region. Therefore, the fairly strong bands at 28000 cm^{-1} of the aminophosphine complexes may be assigned to those associated with the d-d transitions. This assignment will be supported by the fact that the dichloro(diamine)Pd(II) complexes[27] including **4** exhibit similar absorption bands at nearly the same wavenumbers. The nitrogen and phosphorus atoms are known to stand at nearly the same position in the spectrochemical series.[28]

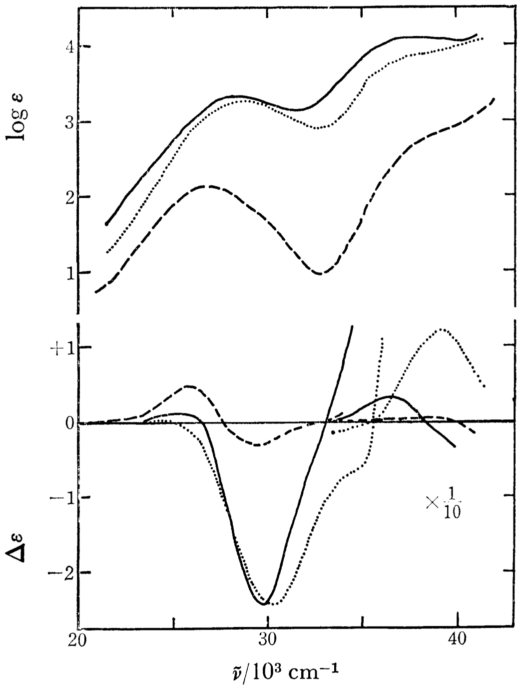


Fig. 6. Absoprtion and CD spectra of [(*S*)-2-(diphenylphosphinomethyl)pyrrolidine]dichloropalladium(II), **3** (——) and [(*S*)-2-(aminomethyl)pyrrolidine]dichloropalladium(II), **4** (----), and CD curve calculated from (1/2)[Δε(**1a**)+Δε(**1b**)] (……).

The authors express their thanks to Professor J. Tanaka of Nagoya University, who kindly allowed them to use the diffractometer in his laboratory. The authors also wish to thank the Ministry of Education for Scientific Research Grant-in-Aid No. 243013.

References

1) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **99**, 5946 (1977).

2) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977).

3) T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto, and M. Kumada, *Tetrahedron Lett.*, **1976**, 1133.

4) K. Yamamoto, A. Tomita, and J. Tsuji, *Chem. Lett.*, **1978**, 3.

5) H. B. Kagan, *Pure Appl. Chem.*, **43**, 401 (1975).

6) K. Tani, L. D. Brown, J. Ahmed, J. A. Ibers, M. Yokota, A. Nakamura, and S. Otsuka, *J. Am. Chem. Soc.*, **99**, 7876 (1977).

7) H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972).

8) I. Ogata, F. Mizukami, Y. Ikeda, and M. Tanaka, Japan Patent, Kokai, **76**, 43754 (1976); *Chem. Abstr.*, **85**,

124144z(1976).

9) K. Achiwa, *J. Am. Chem. Soc.*, **98**, 8265(1976).

10) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J. Chem. Soc., Chem. Commun.*, **1972**, 10.

11) T. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **27**, 1062 (1971).

12) I. Kinoshita, K. Kashiwabara, and J. Fujita, *Chem. Lett.*, **1977**, 831.

13) S. Schnell and P. Karrer, *Helv. Chim. Acta*, **38**, 2036 (1955).

14) S. Seanles, Jr., G. E. Roelofs, M. Tamres, and R. N. McDonald, *J. Org. Chem.*, **30**, 3445 (1965).

15) R. A. Walton, *Spectrochim. Acta*, *Part A*, **21**, 1795 (1965).

16) D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Am. Chem. Soc.*, **92**, 5351 (1970).

17) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee (1956).

18) All the programs used are in the "UNICS-Osaka" system, The Computation Center, Osaka University (1973).

19) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72—84.

20) The observed and calculated structure factors are available at the Office of the Editor of the Bulletin of the Chemical Society of Japan as Document No. 7919.

21) O. Kospium, R. A. Lewis, J. Chickos, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4842(1968); K. Naumann, G. Aon, and K. Mislow, *ibid.*, **91**, 7012 (1969).

22) L. Horner, *Pure Appl. Chem.*, **9**, 225(1964).

23) K. Issleib and H. Oehme, *Chem. Ber.*, **100**, 2685(1967).

24) C. H. Perry, D. P. Athus, E. F. Young, J. R. Durig, and B. R. Mitchell, *Spectrochim. Acta*, *Part A*, **23**, 1137 (1967).

25) C. K. Johnson, "ORTEP-II," Report ORNL-3794, Oak Ridge National Laboratory, Tennessee (1971).

26) A. Takenaka, Y. Sasada, K. Yamamoto, and J. Tsuji, *Bull. Chem. Soc. Jpn.*, **50**, 3177 (1977).

27) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 2863 (1969).

28) K. Kashiwabara, I. Kinoshita, and J. Fujita, *Chem. Lett.*, **1978**, 673.