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Preparation and Characterization of [RhCl$_2$(edpp)$_2$]$^+$ (edpp=(2-aminoethyl)diphenylphosphine). Crystal Structures of *trans*(Cl,Cl), *cis*(P,P)-[RhCl$_2$(edpp)$_2$]Cl · 2C$_2$H$_5$OH and *cis*(Cl,Cl), *trans*(P,P)-[RhCl$_2$(edpp)$_2$]Cl · 4H$_2$O

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Two of the five possible geometrical isomers of [RhCl$_2$(edpp)$_2$]$^+$ were formed by reaction of RhCl$_3$ · 2H$_2$O with edpp (edpp=(2-aminoethyl)diphenylphosphine) in 1 : 2 molar ratio in ethanol. The chlorides of the isomers were separated by fractional crystallization from ethanol. The structures of the more soluble (main product) and the less soluble (minor product) complexes were determined by X-ray analyses to have the trans(Cl,Cl), cis(P,P) and cis(Cl,Cl), trans(P,P) configurations, respectively. Crystal data are: for *trans*(Cl,Cl), *cis*(P,P)-[RhCl$_2$(edpp)$_2$]Cl · 2C$_2$H$_5$OH, triclinic, space group $P\bar{1}$, with a=10.024(3), b=18.865(3), c=9.833(2) Å, α=97.66(1), β=103.92(2), γ=82.30(2)°, and Z=2, and for *cis*(Cl,Cl), *trans*(P,P)-[RhCl$_2$(edpp)$_2$]Cl · 4H$_2$O, triclinic, space group $P\bar{1}$, with a=11.341(4), b=17.780(6), c=8.712(3) Å, α=95.60(4), β=112.31(3), γ=82.56(4)°, and Z=2. The trans influence of the P atom on the Rh–N and Rh–P bond lengths is observed. The mean Rh–N and Rh–P bond lengths (2.125(4) and 2.300(1)Å) in the trans(Cl,Cl), cis(P,P) isomer are respectively longer and shorter than those of the cis(Cl,Cl), trans(P,P) isomer (2.078(12) and 2.336(3)Å). ^{13}C NMR and absorption spectra of the isomers were recorded and are discussed.

In a previous paper,[1)] we reported the preparation of [CoCl$_2$(edpp)$_2$]$^+$, where edpp denotes (2-aminoethyl)diphenylphosphine. Although five geometrical isomers are possible for the [MCl$_2$(edpp)$_2$]-type complex (Fig. 1), the cobalt(III) complex formed only one isomer and the structure was determined to have the trans(Cl,Cl),cis(P,P) configuration by X-ray analysis.[2)] Of the two trans(Cl,Cl) isomers, the formation of the sterically less favorable trans(Cl,Cl),cis(P,P) isomer might be attributable to the strong trans effect of the phosphorus donor atoms.[2)] For the rhodium(III) complex, [RhCl$_2$(edpp)$_2$]$^+$ the magnitudes of the steric and trans effects should be different from those of the cobalt(III) complex, and other isomers than trans(Cl,Cl),cis(P,P) might be expected to be formed.

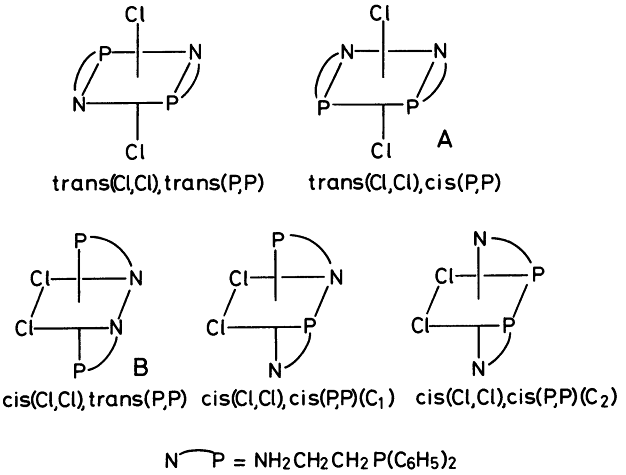

Fig. 1. The five possible geometrical isomers of [M$^{\mathrm{III}}$Cl$_2$(edpp)$_2$]$^+$.

This paper describes the preparation and X-ray structure analyses of the trans(Cl,Cl),cis(P,P) and the cis(Cl,Cl),trans(P,P) isomers of [RhCl$_2$(edpp)$_2$]$^+$. Also, the absorption and ^{13}C NMR spectra of the isomers are compared with each other and with those of related complexes.

Experimental

The edpp ligand was prepared according to a literature method,[3)] and handled under an atmosphere of nitrogen until it formed air-stable rhodium(III) complexes. Absorption and ^{13}C NMR spectra were recorded on a Hitachi 323 spectrophotometer and a JEOL JNM-GX 400 spectrometer, respectively.

Preparation of *trans*(Cl,Cl),*cis*(P,P)-[RhCl$_2$(edpp)$_2$]Cl · 2C$_2$H$_5$OH (isomer A) and *cis*(Cl,Cl),*trans*(P,P)-[RhCl$_2$(edpp)$_2$]Cl · H$_2$O (isomer B). A deaerated ethanol solution (8 cm^3) of RhCl$_3$·2H$_2$O (0.587 g, 2.39 mmol) was added to a stirred solution of edpp (1.098 g, 4.79 mmol) in deaerated ethanol (3 cm^3) over a period of 15 min. The mixture was heated at 70 °C for 7 h and gave a yellow solution together with a small amount of pale yellow precipitate. The mixture was evaporated to dryness in vacuo and the residue washed with diethyl ether to remove excess edpp before it was exposed to the air. The washed residue was shaken repeatedly with hot ethanol (ca. 175 cm^3) to extract the products until the extracts were colorless. The combined extracts were heated (ca. 70 °C) and filtered while hot, and the filtrate on evaporation to a volume of ca. 75 cm^3 gave a pale yellow precipitate. This was collected by filtration (The mother liquor was treated as described below.) and recrystallized from ethanol to yield a yellow powder of isomer B. Yield: 0.032 g. Found: C, 48.75; H, 5.22; N, 4.07%. Calcd for C$_{28}$H$_{34}$N$_2$Cl$_3$OP$_2$Rh=[RhCl$_2$(edpp)$_2$]Cl·H$_2$O: C, 49.04; H,5.00; N, 4.08%. UV-

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Table 1. Crystal Data and Experimental Details

	(A)	(B)
Chemical formula	$[RhCl_2(C_{14}H_{16}NP)_2]Cl\cdot 2C_2H_5OH$	$[RhCl_2(C_{14}H_{16}NP)_2]Cl\cdot 4H_2O$
Formula weight	759.9	739.8
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.024(3)	11.341(4)
b/Å	18.865(3)	17.780(6)
c/Å	9.833(2)	8.712(3)
α/°	97.66(1)	95.0(4)
β/°	103.92(2)	112.31(3)
γ/°	82.30(2)	82.56(4)
V/Å^3	1778.6(6)	1591.2(10)
Z	2	2
D_x/g cm^{-3}	1.42	1.54
D_m/g cm^{-3}	1.41(1)	1.56(1)
μ(Mo $K\alpha$)/mm^{-1}	8.18	9.10
Color and Habit of crystals	Yellow prisms	Yellow prisms
Solvent used to recrystallize	Ethanol	Acetonitrile
Size of specimen/mm^3	0.27×0.55×0.55	0.5×0.2×0.15
Number of standard reflections, n and variation of their $\lvert F_o\rvert$ amplitudes, $(\lvert F_o\rvert/\lvert F_o\rvert_{\mathrm{initial}})/n$	5 0.99—1.01	5 0.93—1.01
Number of reflections measured	8624	7771
Number of reflections observed with $\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$	7064	4575
Transmission factor	0.42—0.62	0.65—0.75
R	0.074	0.088
wR	0.089	0.116
Weight $w^{-1}=\sigma^2(\lvert F_o\rvert)+(c\lvert F_o\rvert)^2$	c=0.025	c=0.02
$S=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/(m-n)]^{1/2}$	2.8	2.9
Number of observed unique reflections, m	6650	4353
Number of parameters, n	477	331
$(\Delta/\sigma)_{\max}$ for non-hydrogen atoms	0.5	0.3
Peak height in the final difference synthesis/e Å^{-3}	−2.4—2.2	−1.6—2.8

(CH_3CN) 28000 (sh, log ε=3.41), 33000 (sh, 4.21), 35400 (4.28), 36100 (sh, 4.28), and 45000 cm^{-1} (sh, 4.51). Single crystals of isomer B, $[RhCl_2(edpp)_2]Cl\cdot 4H_2O$ suitable for X-ray crystallography were obtained by slow evaporation of an acetonitrile solution of the chloride at room temperature. The presence of four molecules of water of crystallization was suggested by the density and microanalytical data of the crystals. Found: C, 45.33; H, 4.72; N, 3.76%. Calcd for $C_{28}H_{40}N_2Cl_3O_4P_2Rh$: C, 45.41; H, 5.44; N, 3.79%.

By evaporating the mother liquor to a small volume isomer A was obtained as yellow-orange crystals. They were collected by filtration, washed with ethanol, and air dried. Yield: 0.25 g. Found: C, 50.88; H, 5.51; N, 3.84%. Calcd for $C_{32}H_{44}N_2Cl_3O_2P_2Rh=[RhCl_2(edpp)_2]Cl\cdot 2C_2H_5OH$: C, 50.58; H, 5.84; N, 3.69%. UV(C_2H_5OH) 24450 (log ε=2.24), 29000 (sh, 2.2), 34500 (sh, 3.97), 38900 (4.40), and 45700 cm^{-1} (sh, 4.67). The crystals effloresce in the air giving off the ethanol of crystallization.

Crystal Structure Determination. Crystal data and experimental details are given in Table 1. Crystals of both (A) and (B) were sealed into capillary tubes together with their mother liquors and mounted on an automated four-circle diffractometer, Rigaku AFC-5. Intensities were measured up to 2θ=55° by θ—2θ scan technique with scan speed 6° min^{-1} in θ, graphite monochromatized Mo $K\alpha$ radiation being used. Lattice constants were determined from 25 2θ values ($20°<2\theta<30°$) with (Mo $K\alpha$)=0.71073 Å. After absorption correction, the structures were solved by the Patterson-Fourier method. Two ethanol molecules in (A) could be found from Fourier synthesis. From the difference synthesis 30 of the 32 hydrogen atoms except those of the ethanol molecules were found and others were calculated. One of the phenyl groups bonded to the P(2) atom in (B) exhibited orientational disorder. The two sets of positions for the C(24)—C(28) atoms were included with 50% population. The dihedral angle between the least squares planes in two possible orientations for the disordered phenyl group is 77.8°. The water molecules as well as the Cl^- ion could not be found from Fourier synthesis. The difference synthesis gave five positions with peak heights 3.7—4.7 e Å^{-3}, the distances between them being longer than 2.65(2) Å. We were unable to distinguish the disordered water molecules from the disordered Cl^- ions on the basis of the difference synthesis. In the present study we have tentatively assumed that the five positions are all occupied by Cl^- ions and we have estimated their population parameters by the trial and error method with the restriction that the isotropic thermal parameters of the Cl^- ions remain almost equal. Positional parameters of all the hydrogen atoms in (B) were calculated and not refined, although eight hydrogen atoms were found from difference synthesis. By introducing these calculated hydrogen atoms, the R factor reduced from 0.092 to 0.088. Anisotropic thermal parameters

Table 2. Positional Parameters (×10^4; for Rh×10^5) and Equivalent Isotropic Temperature Factors

(A)	*X*	*Y*	*Z*	B_{eq}(Å^2)	(B)	*X*	*Y*	*Z*	B_{eq}(Å^2)
Rh	18897(4)	24027(2)	4348(3)	3.0	Rh	33210(8)	28037(5)	320(12)	2.8
Cl(1)	1923(1)	1153(1)	23(1)	4.1	Cl(1)	3463(3)	4103(2)	−130(4)	4.3
Cl(2)	2102(2)	3625(1)	1121(1)	4.8	Cl(2)	2160(3)	3003(2)	1810(4)	5.0
Cl(0)	6525(2)	2564(1)	−6344(2)	6.6	P(1)	5273(3)	2648(2)	2270(4)	3.3
P(1)	−429(1)	2475(1)	403(1)	3.2	P(2)	1477(3)	2900(2)	−2381(4)	3.7
P(2)	1987(1)	2556(1)	−1817(1)	3.1	N(1)	3295(10)	1654(5)	250(13)	4.4
N(1)	2153(4)	2302(2)	2619(4)	4.1	N(2)	4249(9)	2594(6)	−1639(12)	4.0
N(2)	4071(4)	2243(3)	768(5)	4.4	C(1)	5408(14)	1638(7)	2543(19)	5.8
C(1)	−292(6)	2185(3)	2148(6)	4.5	C(2)	4189(23)	1341(11)	1708(31)	13.7
C(2)	877(6)	2520(3)	3138(5)	4.9	C(3)	2227(13)	2930(8)	−3859(17)	5.6
C(3)	3797(5)	2728(3)	−1461(6)	4.1	C(4)	3426(13)	2434(8)	−3366(15)	5.1
C(4)	4618(5)	2165(4)	−511(6)	4.9	C(5)	5449(10)	3117(6)	4258(13)	3.3
C(5)	−1471(5)	3339(3)	379(5)	3.6	C(6)	6363(12)	2803(8)	5766(16)	5.0
C(6)	−1265(6)	3856(3)	−410(6)	4.5	C(7)	6478(15)	3194(9)	7238(15)	6.1
C(7)	−2140(7)	4495(3)	−513(7)	5.2	C(8)	5779(13)	3881(8)	7330(15)	4.9
C(8)	−3188(6)	4623(3)	155(8)	5.5	C(9)	4913(13)	4159(7)	5953(16)	4.7
C(9)	−3397(6)	4120(4)	952(8)	5.9	C(10)	4704(11)	3805(7)	4335(15)	4.1
C(10)	−2547(5)	3474(3)	1086(6)	4.5	C(11)	6684(10)	2853(7)	1962(14)	3.8
C(11)	−1544(5)	1885(3)	−870(5)	3.4	C(12)	6811(13)	3618(9)	1950(21)	6.4
C(12)	−2382(5)	2153(3)	−2084(5)	4.0	C(13)	7931(13)	3835(11)	1707(22)	7.7
C(13)	−3209(6)	1717(4)	−3078(6)	5.0	C(14)	8860(12)	3287(11)	1641(18)	6.8
C(14)	−3219(7)	1004(4)	−2872(7)	5.5	C(15)	8741(13)	2558(11)	1704(18)	7.0
C(15)	−2402(7)	739(3)	−1670(8)	5.4	C(16)	7645(13)	2313(9)	1846(17)	5.5
C(16)	−1569(6)	1178(3)	−677(6)	4.5	C(17)	520(10)	2096(6)	−2993(14)	3.3
C(17)	955(5)	3299(3)	−2716(5)	3.5	C(18)	389(16)	1671(7)	−4416(18)	5.8
C(18)	−252(5)	3208(3)	−3725(5)	3.9	C(19)	−413(21)	1090(10)	−4813(22)	9.0
C(19)	−1044(6)	3785(4)	−4322(6)	5.2	C(20)	−988(17)	934(9)	−3747(23)	8.0
C(20)	−670(7)	4462(4)	−3925(7)	5.7	C(21)	−795(15)	1361(8)	−2335(19)	6.0
C(21)	530(8)	4571(3)	−2927(7)	5.8	C(22)	−46(12)	1924(7)	−1925(17)	4.9
C(22)	1328(6)	3996(3)	−2318(6)	4.6	C(23)	296(11)	3722(7)	−2717(19)	5.8
C(23)	1794(5)	1793(3)	−3160(5)	3.4	C(24A)	−835(24)	3722(13)	−3943(30)	4.1
C(24)	2773(5)	1572(3)	−3983(6)	4.1	C(25A)	−1699(26)	4377(14)	−4098(33)	4.7
C(25)	2547(7)	1030(3)	−5070(6)	5.1	C(26A)	−1635(25)	4913(14)	−3036(31)	4.4
C(26)	1328(8)	705(3)	−5394(7)	5.6	C(27A)	−729(30)	4794(16)	−1450(38)	5.8
C(27)	339(7)	922(4)	−4585(8)	5.7	C(28A)	306(26)	4215(14)	−1173(33)	4.6
C(28)	614(6)	1445(3)	−3451(6)	4.4	C(24B)	−580(31)	3828(16)	−2411(38)	5.9
O(01)1	5029(5)	1215(3)	−6878(6)	6.7	C(25B)	−1544(28)	4557(15)	−2639(35)	5.3
C(01)1	5785(13)	532(7)	−7127(15)	11.3	C(26B)	−1240(28)	5042(15)	−3607(35)	5.1
C(01)2	6680(17)	514(10)	−8036(20)	15.0	C(27B)	−336(30)	4990(16)	−3951(38)	6.1
O(02)1	4078(5)	3084(3)	5023(6)	7.2	C(28B)	470(31)	4319(16)	−3814(38)	6.0
C(02)1	3760(10)	3863(6)	5125(12)	9.0	Cl(01)[a)]	8254(15)	295(8)	584(19)	5.6
C(02)2	4792(13)	4191(7)	6251(15)	11.7	Cl(02)	1254(16)	841(9)	1837(20)	5.3
					Cl(03)	5915(16)	1060(9)	−1879(20)	5.2
					Cl(04)	3237(20)	331(11)	−2251(26)	5.1
					Cl(05)	3783(25)	287(13)	−4965(32)	4.6

a) Population parameters of disordered Cl^- ion: Cl(01), 0.25; Cl(02), 0.23; Cl(03), 0.22; Cl(04), 0.17; and Cl(05), 0.13.

were introduced for all the non-hydrogen atoms except for the ethanol molecules in (A) and for the disordered Cl^- ion and a phenyl group in (B). The function, $\sum w\|F_o|-|F_c\|^2$ was minimized by block-diagonal least squares. Complex neutral-atom scattering factors were used.[4] The calculations were carried out on a FACOM M380-R computer at Keio University with the UNICS III computation program system.[5] The final atomic parameters and bond lengths and bond angles are listed in Tables 2 and 3.[6]

Results and Discussion

Preparation, Absorption and ^{13}C NMR Spectra of the Two Isomers of $[RhCl_2(edpp)_2]^+$. Rhodium(III) chloride was reacted with edpp in a 1:2 molar ratio in ethanol to form a mixture of two isomers of $[RhCl_2(edpp)_2]Cl$. The mixture was separated into the isomers A and B by fractional crystallization from ethanol. Isomer B is much less soluble in ethanol than isomer A. The relative abundance of isomer B to isomer A was ca. 1:10. No isomerization of the isomers took place on refluxing in ethanol.

Figure 2 shows the absorption spectra of isomers A and B together with that of *trans*(Cl,Cl),*cis*(P,P)-$[CoCl_2(edpp)_2]^+$.[1,2] The spectral pattern of isomer A is quite similar to that of *trans*(Cl,Cl),*cis*(P,P)-$[CoCl_2(edpp)_2]^+$, although all the bands of isomer A are shifted by 7000—10000 cm^{-1} toward higher energy compared to the corresponding bands of the cobalt(III) complex. Thus isomer A is suggested to have the trans(Cl,Cl),cis(P,P) configuration. The same structure was

Table 3. Bond Lengths (l/Å) and Bond Angles (ϕ/°)

	(A)	(B)		(A)	(B)
Rh - Cl(1)	2.335(2)	2.358(4)	P(2) - Rh - N(2)	83.7(1)	83.5(3)
Rh - Cl(2)	2.338(2)	2.362(4)	N(1) - Rh - N(2)	87.3(2)	92.6(4)
Rh - P(1)	2.303(1)	2.334(3)	Rh - P(1) - C(1)	98.9(2)	101.1(4)
Rh - P(2)	2.297(1)	2.337(3)	Rh - P(1) - C(5)	120.3(2)	120.1(4)
Rh - N(1)	2.131(4)	2.076(9)	Rh - P(1) - C(11)	120.2(2)	117.2(5)
Rh - N(2)	2.118(4)	2.079(12)	C(1) - P(1) - C(5)	105.9(3)	106.4(6)
P(1) - C(1)	1.838(6)	1.814(13)	C(1) - P(1) - C(11)	106.7(3)	108.2(6)
P(1) - C(5)	1.814(5)	1.798(12)	C(5) - P(1) - C(11)	103.2(2)	103.0(6)
P(1) - C(11)	1.829(5)	1.806(14)	Rh - P(2) - C(3)	98.4(2)	98.6(6)
P(2) - C(3)	1.828(5)	1.800(18)	Rh - P(2) - C(17)	121.0(2)	117.0(4)
P(2) - C(17)	1.822(5)	1.822(12)	Rh - P(2) - C(23)	118.9(2)	121.9(4)
P(2) - C(23)	1.816(5)	1.815(12)	C(3) - P(2) - C(17)	107.3(2)	108.0(7)
N(1) - C(2)	1.477(7)	1.402(23)	C(3) - P(2) - C(23)	106.1(2)	106.1(7)
N(2) - C(4)	1.471(8)	1.461(14)	C(17) - P(2) - C(23)	103.6(2)	103.9(5)
C(1) - C(2)	1.485(8)	1.439(27)	Rh - N(1) - C(2)	113.4(3)	116.3(10)
C(3) - C(4)	1.529(8)	1.460(19)	Rh - N(2) - C(4)	115.5(3)	115.6(8)
C(5) - C(6)	1.389(9)	1.439(15)	P(1) - C(1) - C(2)	107.5(4)	110.8(12)
C(5) - C(10)	1.397(8)	1.405(16)	N(1) - C(2) - C(1)	109.3(4)	120.7(19)
C(6) - C(7)	1.393(8)	1.367(19)	P(2) - C(3) - C)4)	106.3(4)	109.6(10)
C(7) - C(8)	1.347(11)	1.380(21)	N(2) - C(4) - C(3)	108.0(5)	111.9(11)
C(8) - C(9)	1.374(11)	1.320(16)	P(1) - C(5) - C(6)	120.5(4)	120.7(8)
C(9) - C(10)	1.392(8)	1.432(18)	P(1) - C(5) - C(10)	120.1(4)	119.6(8)
C(11) - C(12)	1.397(7)	1.388(21)	C(6) - C(5) - C(10)	119.2(5)	119.8(10)
C(11) - C(16)	1.376(8)	1.383(19)	C(5) - C(6) - C(7)	120.1(6)	118.1(12)
C(12) - C(13)	1.378(8)	1.468(26)	C(6) - C(7) - C(8)	120.7(6)	122.8(12)
C(13) - C(14)	1.388(11)	1.353(23)	C(7) - C(8) - C(9)	119.8(6)	119.2(12)
C(14) - C(15)	1.378(9)	1.329(28)	C(8) - C(9) - C(10)	121.4(6)	123.3(12)
C(15) - C(16)	1.383(8)	1.420(25)	C(5) - C(10) - C(9)	118.6(6)	116.8(10)
C(17) - C(18)	1.382(6)	1.355(18)	P(1) - C(11) - C(12)	119.4(4)	115.4(10)
C(17) - C(22)	1.395(8)	1.390(22)	P(1) - C(11) - C(16)	121.8(4)	124.8(11)
C(18) - C(19)	1.369(8)	1.396(26)	C(12) - C(11) - C(16)	118.8(5)	119.7(13)
C(19) - C(20)	1.360(11)	1.386(34)	C(11) - C(12) - C(13)	120.7(5)	119.0(14)
C(20) - C(21)	1.377(9)	1.339(24)	C(12) - C(13) - C(14)	119.9(6)	118.9(17)
C(21) - C(22)	1.373(8)	1.331(21)	C(13) - C(14) - C(15)	119.6(6)	121.2(17)
C(23) - C(24)	1.405(8)		C(14) - C(15) - C(16)	120.4(6)	122.2(16)
C(23) - C(28)	1.381(8)		C(11) - C(16) - C(15)	120.7(5)	118.8(14)
C(24) - C(25)	1.376(8)		P(2) - C(17) - C(18)	122.3(4)	121.3(11)
C(25) - C(26)	1.390(10)		P(2) - C(17) - C(22)	119.6(4)	117.4(10)
C(26) - C(27)	1.403(11)		C(18) - C(17) - C(22)	117.9(5)	121.2(12)
C(27) - C(28)	1.387(9)		C(17) - C(18) - C(19)	120.8(5)	116.9(17)
Cl(1) - Rh - Cl(2)	172.1(1)	95.2(1)	C(18) - C(19) - C(20)	120.8(5)	121.0(17)
Cl(1) - Rh - P(1)	88.7(1)	93.6(1)	C(19) - C(20) - C(21)	119.9(7)	119.3(18)
Cl(1) - Rh - P(2)	95.0(1)	87.6(1)	C(20) - C(21) - C(22)	119.7(6)	121.2(18)
Cl(1) - Rh - N(1)	88.0(1)	177.1(3)	C(17) - C(22) - C(21)	120.9(5)	120.2(13)
Cl(1) - Rh - N(2)	87.0(1)	86.6(3)	P(2) - C(23) - C(24)	121.8(4)	
Cl(2) - Rh - P(1)	95.7(1)	92.0(1)	P(2) - C(23) - C(28)	119.6(4)	
Cl(2) - Rh - P(2)	90.2(1)	93.5(1)	C(24) - C(23) - C(28)	118.5(5)	
Cl(2) - Rh - N(1)	86.0(1)	85.7(3)	C(23) - C(24) - C(25)	120.7(5)	
Cl(2) - Rh - N(2)	87.5(1)	176.4(3)	C(24) - C(25) - C(26)	120.4(6)	
P(1) - Rh - P(2)	105.4(1)	174.1(1)	C(25) - C(26) - C(27)	119.6(6)	
P(1) - Rh - N(1)	83.9(1)	83.6(3)	C(26) - C(27) - C(28)	119.2(7)	
P(1) - Rh - N(2)	170.3(1)	90.9(3)	C(23) - C(28) - C(27)	121.5(6)	
P(2) - Rh - N(1)	170.3(1)	95.1(3)			

suggested by the ^{13}C NMR spectrum, and the assignment was confirmed by the X-ray structure determination (vide infra). The lowest-energy absorption band at 24450 cm^{-1} of isomer A can be assigned to the split component (I_a) of the first absorption band, ${}^1A_{1g}\rightarrow{}^1T_{1g}$ (O_h). The band is at higher energy by 8550 cm^{-1} than the I_a band of the cobalt(III) complex. A similar energy difference (8550 cm^{-1}) is observed between the I_a bands of *trans*-$[RhCl_2(en)_2]^+$[7] and *trans*-$[CoCl_2(en)_2]^+$[8] (en=ethylenediamine). The *trans*-dichloro rhodium(III) complexes of dppe[9] (dppe=1,2-bis(diphenylphosphino)ethane) and en[7] show the I_a band at 23700 and 24600 cm^{-1}, respectively. Thus the spectrochemical series for the ligands can be determined as en≧edpp> dppe. The same order, en≧edpp has been reported for the *trans*-dichloro cobalt(III) complexes.[1,2] The spectral data of *trans*-$[CoCl_2(dppe)_2]^+$ is not available; the complex is reported to be extremely unstable.[10] However, dppe forms a stable cobalt(III) complex with two acac ligands (acac=2,4-pentanedionate ion). The

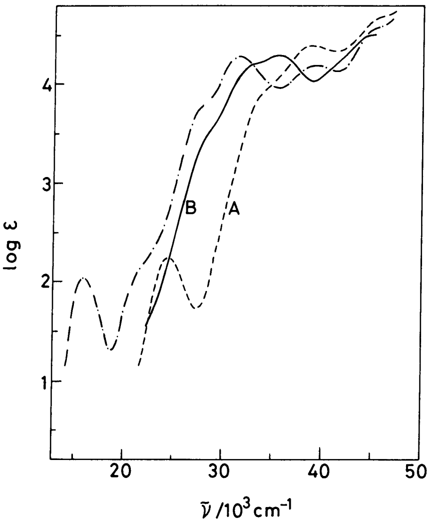

Fig. 2. Absorption spectra of *trans*(Cl,Cl), *cis*(P,P)-$[RhCl_2(edpp)_2]Cl \cdot 2C_2H_5OH$ (isomer A) in ethanol (---), *cis*(Cl,Cl), *trans*(P,P)-$[RhCl_2(edpp)_2]Cl \cdot H_2O$ (isomer B) in acetonitrile (——), and *trans*(Cl,Cl), *cis* (P,P)-$[CoCl_2(edpp)_2]Cl \cdot 2H_2O$ in methanol (—·—).

energy of the first absorption band of $[Co(acac)_2L]^+$ (L=dppe, edpp, en) decreases in the order dppe> edpp≧en.[11] This order is reversed to that for the *trans*-dichloro complexes. The apparent disagreement in the order may be ascribed to the difference in steric repulsion among the complexes. Examination of molecular models indicates that severe steric repulsions occur in *trans*-$[MCl_2(dppe)_2]^+$ (M=Co, Rh), whereas $[Co(acac)_2(dppe)]^+$ has no particular steric repulsions. In the absence of severe steric repulsions, therefore, it is apparent that the ranking of dppe in the spectrochemical series is higher than that of en. The I_b band of isomer A is observed as a shoulder (ca. 29000 cm^{-1}) and the second absorption band is hidden by the strong charge-transfer (CT) bands.

The first d-d absorption band of isomer B is almost hidden by strong bands in the higher energy region. However, the shoulder at ca. 28000 cm^{-1} can be assigned to a part of the first absorption band, since *cis*-$[RhCl_2(en)_2]^+$ shows the first d-d band maximum at nearly the same wavenumber (28400 cm^{-1}).[7] The shoulder of isomer B is at higher energy than that of the I_a band of isomer A. These positions correspond well to those of the lowest energy d-d transition bands of the cis (28800 cm^{-1}) and trans (24500 cm^{-1}) isomers of $[RhCl_2(dmpe)_2]^+$ [9] (dmpe=1,2-bis(dimethylphosphino)ethane). From these results isomer B is suggested to have a cis(Cl,Cl) configuration. The first absorption band of isomer B is more intense than that of isomer A. Similar trends where cis-isomers exhibit more intense absorption bands than the corresponding trans-isomers were observed between the cis- and trans-isomers of $[RhX_2(en)_2]^+$ [7] (X=Cl, Br, I, etc.) and $[RhCl_2(dmpe)_2]^+$.[9] The bands around 33000 cm^{-1} in the absorption spectrum of isomer B may be assigned to a CT transition Rh^{III}–P.[10] Since the bands are at lower energy than the corresponding band of isomer A, isomer B would be assigned to have a trans(P,P) configuration. The trans(P,P) isomer of a bis(phosphine) cobalt(III) complex is reported to exhibit the Co^{III}–P CT band at lower energy than the corresponding cis(P,P) isomer.[12,13] Similar absorption spectral characteristics to those of isomers B and A have been observed for *cis*(NCS,NCS),*trans*(P,P)- and *trans*(NCS,NCS),*cis*(P,P)-$[Co(NCS)_2(edpp)_2]^+$.[14]

Figure 3 shows the ^{13}C NMR spectra of isomers A and B in dimethyl-d_6 sulfoxide. The spectral assignment was made according to previous work on bis(acac) cobalt(III) complexes of edpp and related ligands.[11] The mutual arrangement of the two chlorine donor atoms can be assigned on the basis of the number of the resonances. Isomer A exhibits six kinds of signals and can be assigned to either of the two trans(Cl,Cl) isomers (Figs. 1 and 3). This assignment is in accord with that given on the basis of the absorption spectrum. The spectrum of isomer B shows one kind of signal for each carbon of the two methylenes of the edpp ligands, while the two phenyl groups on each phosphorus atom are observed diastereotopically. Thus isomer B is suggested to have either cis(Cl,Cl),trans-(P,P)(C_2) or cis(Cl,Cl),cis(P,P)(C_2) configuration from symmetry argument. One of the most noticeable aspects in the two spectra is the difference in line shape of the P–CH_2 and P–C_1 signals; the signals for isomer B appear as a 1:2:1 triplet, while those for isomer A as a five-line multiplet. Such differences can be explained on the basis of the difference in magnitude of the phosphorus-phosphorus coupling constant, $^2J_{PP}$ between the two isomers. The appearance of the phosphine α-carbon multiplet in the ^{13}C NMR spectrum of a bis(phosphine) complex has been shown to be a function of $^2J_{PP}$.[15,16] In a trans(P,P) complex $^2J_{PP}$ is usually large so that the signal appears as a 1:2:1 triplet (so-called virtually coupled triplet). On the other hand, a five-line multiplet is expected to appear only for a cis(P,P) complex. Hence isomers B and A can be assigned to cis(Cl,Cl),trans(P,P), and trans(Cl,Cl),cis-(P,P), respectively. These assignments are confirmed by the X-ray analyses.

Structures of (A) and (B). Figure 4 shows perspective drawings of the complex cations (A) and (B). The main product, (A) is the trans(Cl,Cl),cis(P,P) isomer. The lesser product, (B) is the cis(Cl,Cl),trans(P,P) isomer. The structures agree with the assignments based on the ^{13}C NMR and absorption spectra. Both complex cations have a pseudo twofold axis running through the Rh atom and the midpoint of the N(1) and N(2) atoms. The trans influence of the P atom on the Rh–N and Rh–P bond lengths is seen from Table 3. The mean Rh–N bond length, 2.125(4) Å, in (A) is longer than that in (B) by 0.047(12) Å. The mean Rh–P bond length, 2.336(3) Å, in (B) is longer than that in (A) by 0.036(3) Å. It is noted that the mean Co–P

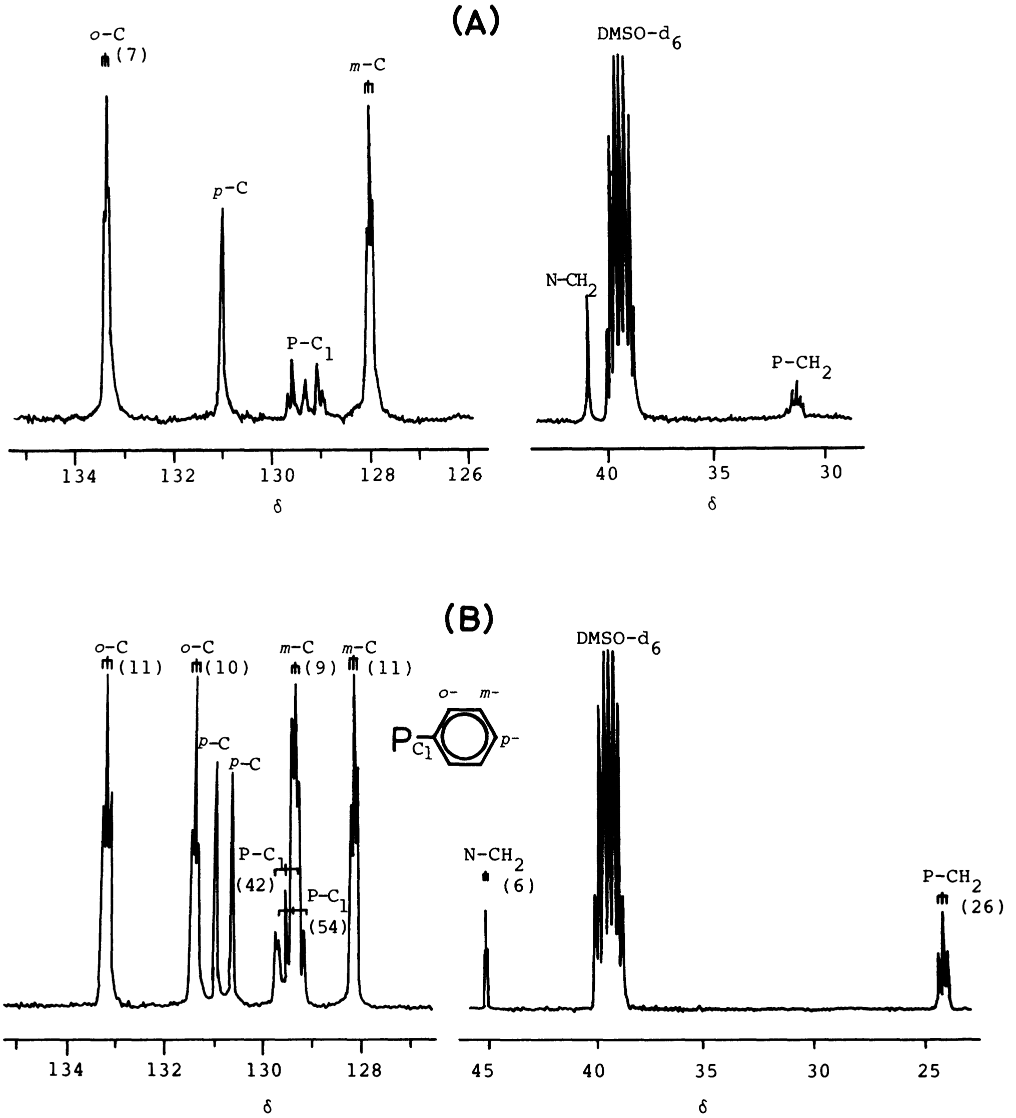

Fig. 3. ^{13}C NMR spectra of (A) *trans*(Cl,Cl), *cis*(P,P) (isomer A)- and (B) *cis*(Cl,Cl), *trans*(P,P) (isomer B)- $[RhCl_2(edpp)_2]^+$ in dimethyl-d_6 sulfoxide. The numbers in parentheses are the coupling constants in Hz of the triplet signals.

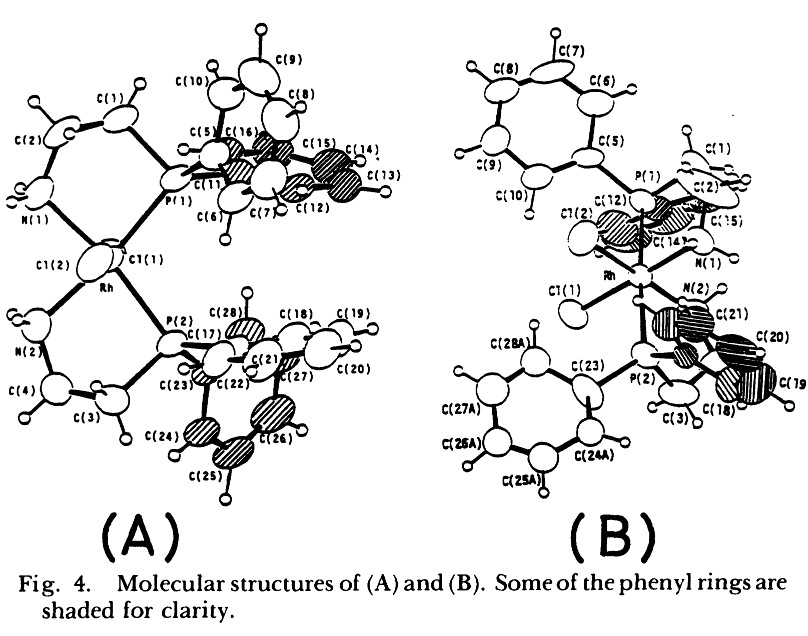

Fig. 4. Molecular structures of (A) and (B). Some of the phenyl rings are shaded for clarity.

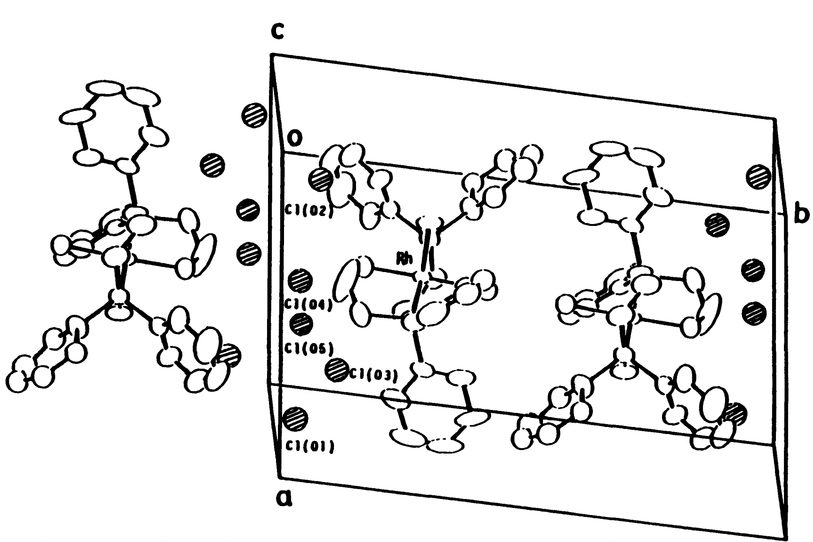

Fig. 5. A view of the crystal structure of (B) perpendicular to *ab*. The shaded circles represent the disordered Cl^- ion.

bond length in the trans(NCS,NCS),cis(P,P) isomer of $[Co(NCS)_2(edpp)_2]^+$ is almost the same as that in the cis(NCS,NCS),trans(P,P) isomer, although the mean $Co-NH_2$ bond length in the former is longer than that in the latter by 0.031(4) Å.[14] The molecular structure of (A) is essentially the same as that of the corresponding cobalt(III) complex.[2] The mean M–Cl and M–N bond lengths in (A) are longer than those in the cobalt(III) complex by ca. 0.10 Å.[2] On the other hand, the mean M–P bond length in (A) is longer than that in the cobalt(III) complex only by 0.045(3) Å. These results may indicate a stronger affinity of Rh^{3+} for P than Co^{3+} for P.

The close contact between the phenyl groups in (A) is avoided by the large P(1)–Rh–P(2) angle, 105.4(1)° and the appropriate orientations of the phenyl groups. The shortest non-bonded C···C distance is 3.516(8) Å for C(6)···C(17). The angle between the two coordination planes through Rh, N(1) and P(1), and through Rh, N(2) and P(2) atoms is 5.1°. The large thermal parameter of C(2) in (B) may be due to the puckering motion of the five-membered chelate ring. The crystal structure of (B) is shown in Fig. 5. The Cl^- ions are distributed over five sets of general positions with different population parameters and are between the layers of complex cations parallel to the *ac* plane; the shortest interatomic distance involving them is 3.04(2) Å for Cl(04)···N(1). Water molecules, which were not included in the structure refinement, might also be accommodated randomly in the hollow. The positional disorder of counter ions was also reported for $[Co\{(NH_2CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2NH_2)_2\}]Br_3\cdot H_2O$.[17]

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References

1) M. Atoh, I. Kinoshita, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **55**, 3179 (1982).

2) I. Kinoshita, Y. Yokota, K. Matsumoto, S. Ooi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1067 (1983).

3) K. Issleib and D. Haferburg, *Z. Naturforsch., B*, **20**, 916 (1965).

4) International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present Distributor D. Reidel, Dordrecht.)

5) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

6) Tables of the coordinates of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, bond lengths and bond angles in the disordered phenyl group, and observed and calculated structure factors are kept as Document No. 8629 at the Chemical Society of Japan.

7) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).

8) M. Linhard and M. Weigel, *Z. Anorg. Chem.*, **271**, 101 (1952); Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **28**, 572 (1955); M. Nakahara and M. Mitsuya, *ibid.*, **45**, 2209 (1972).

9) S. A. Butter and J. Chatt, *J. Chem. Soc. (A)*, **1970**, 1411.

10) V. M. Miskowski, J. L. Robbins, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **98**, 2477 (1978).

11) K. Kashiwabara, I. Kinoshita, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **54**, 725 (1981).

12) K. Kashiwabara, K. Katoh, T. Ohishi, J. Fujita, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **55**, 149 (1982).

13) K. Katoh, H. Sugiura, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 3580 (1984).

14) M. Atoh, K. Kashiwabara, H. Ito, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 3139 (1984).

15) D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, **14**, 50 (1975).

16) P. S. Pregosin and R. W. Kunz," ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes," Springer-Verlag, New York (1979), p. 65.

17) T. Ishii, S. Ohba, M. Ito, S. Fukushi, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **58**, 826 (1985).