July, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 2051—2057 (1990) 2051

Preparation and Characterization of Cobalt(III) Complexes Containing 3,7-Diphenyl-3,7-diphosphanonane-1,9-diamine, $NH_2CH_2CH_2P(C_6H_5)CH_2CH_2CH_2P(C_6H_5)CH_2CH_2NH_2$

Minho Jung, Masamichi Atoh,[†] Kazuo Kashiwabara, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University,
Chikusa-ku, Nagoya 464-01

(Received February 17, 1990)

New cobalt(III) complexes with the titled ligand and its analog, *cisα*-[Co(L)(*rac*(*P*)-232NPPN)]$^{n+}$ (L=2,4-pentanedionate (acac) and oxalate(ox) ions, and ethylenediamine(en)), *cisβ*-[Co(L)(*rac*(*P*)-or *meso*(*P*)-232NPPN)]$^{n+}$ (L=acac and ox) and *cisα*-[Co(acac)(*rac*(*P*)-222NPPN)]$^{2+}$ and *cisβ*-[Co(acac) (*meso*(*P*)-222NPPN)]$^{2+}$ were prepared and characterized by ^{1}H and ^{13}C NMR,. and absorption spectra, where *rac*(*P*)-and *meso*(*P*)-232NPPN and -222NPPN denote recemic(P)-and meso(P)-$NH_2CH_2CH_2P(C_6H_5)(CH_2)_nP(C_6H_5)CH_2CH_2NH_2$ with n=3 and 2, respectively. All the cisα isomers except the en complex react with concd hydrochloric acid at room temperature to yield the corresponding cisα-dichloro complexes. For the cisβ isomers, the acac complexes dissociate one amino group of NPPN reversibly depending on the acidity of solution, yielding [Co(acac)(H_2O)-(NPPNH$^+$)]$^{3+}$, while the ox complexes of *rac*(*P*)-and *meso*(*P*)-232NPPN yield the cisα and trans-dichloro complexes, respectively in hydrochloric acid. All the cisβ isomers except [Co(ox)(*rac*(*P*)-232NPPN)]$^+$ decompose slowly in concd hydrochloric acid to give Co(II) species.

In a previous paper,[1)] we reported the preparation and characterization of cobalt(III) complexes containing quadridentate ligands having two chiral phosphorus donor atoms, $NH_2CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2NH_2$(222NPPN) and *SS*(*C*)-$NH_2CH(CH_3)CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH(CH_3)NH_2$ (*SS*(*C*)-222NPPN). The racemic(P) ligands formed selectively either the trans or cisα isomer, while no stable complex was obtained with the *meso*(*P*) ligands except *cisβ*-[Co(acac)(*meso*(*P*)-*SS*(*C*)-222NPPN)]$^{2+}$ which slowly decomposed in water. The selectivity in complex formation is quite different from that of tetramine analogs such as $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$(trien).[2)] In order to explore such features of quadridentate phosphine ligands, we have studied cobalt(III) complexes with 3,7-diphenyl-3,7-diphosphanonane-1,9-diamine, $NH_2CH_2CH_2P(C_6H_5)CH_2CH_2CH_2P(C_6H_5)CH_2CH_2NH_2$(232NPPN) which forms a six-membered P–Co–P chelate ring upon coordination.

Experimental

The phosphine ligands were prepared and handled under an atmosphere of nitrogen until they formed cobalt(III) complexes. All solvents used for the preparation were made oxygen-free by bubbling nitrogen for 20 min immediately before use. Absorption and ^{1}H and ^{13}C NMR spectra were recorded on Hitachi U3400 and R-90HS spectrometers, respectively.

Preparation of Ligands. 3,7-Diphenyl-3,7-diphosphanonane-1,9-diamine (232NPPN). The ligand was prepared by a method similar to that for 222NPPN.[1,3)] To (2-aminoethyl)phenylphosphine (9.7 g, 63 mmol) in dry tetrahydrofuran (THF) (200 cm^3) was added dropwise a 15% hexane solution of butyl lithium (50 cm^3) over a period of 1 h with stirring. After further stirring for 1 h, 1,3-dibromopropane (6.4 g, 32 mmol) was added dropwise, the solution was refluxed for 3 h, and cooled to room temperature. Water (2 cm^3) was added dropwise, the solvent THF was evaporated, and to the residue were added water (200 cm^3) and then diethyl ether (200 cm^3) with stirring. The ethereal layer was separated, dried over $MgSO_4$ (ca. 5 g) overnight, filtered, and evaporated to give an oily product. It was heated at ca. 100 °C under highly reduced pressure (ca. 135 Pa) to remove by-products and starting materials. The 232NPPN ligand was not distilled under such conditions and used for preparing cobalt(III) complexes without further purification. Yield: 60%

3,6-Diphenyl-3,6-diphosphaoctane-1,8-diamine (222NPPN). This ligand was prepared by the same method as that described in a previous paper.[1)]

Preparation of Cobalt(III) Complexes.[††] ***cisα*-[Co(acac)(*rac*(*P*)-232NPPN)](ClO_4)$_2$ · $2H_2O$ (A-I), *cisβ*-[Co(acac)(*rac*(*P*)-232NPPN)]{B(C_6H_5)$_4$}$_2$ · 2(CH_3)$_2$CO (A-II) and *cisβ*-[Co(acac)(*meso*(*P*)-232NPPN)](ClO_4)$_2$ · H_2O (A-III).** To [Co(acac)$_3$][4)] (550 mg, 1.55 mmol) in methanol (100 cm^3) was added 232NPPN (535 mg, 1.55 mmol) in methanol (10 cm^3), and the mixture was stirred overnight. The resulting brown solution was evaporated to dryness under reduced pressure. The residue was stirred in a mixture of water (200 cm^3) and diethyl ether (100 cm^3). The aqueous layer was separated, diluted with water (5 dm^3), and applied on a column (ϕ4.5 cm×50 cm) of SP-Sephadex C-25. The adsorbed products were eluted with an aqueous 0.1 mol dm^{-3} NaCl solution (pH 7), yielding three large orange bands (**A-I**, **A-II**, and **A-III** in the order of elution) and two small red bands. Each eluate of the three orange bands was evaporated to dryness under reduced pressure at 40 °C, and the residue was

---

[†] Present address: Department of General Education, School of Commerce, Senshu University, Higashi-mita 2-1-1, Tama-ku, Kawasaki 214.

[††] Caution; The perchlorates of cobalt(III) phosphine complexes are potentially explosive, and should be handled carefully.

mixed with ethanol to extract the orange complex. The ethanol solution was evaporated again to dryness under reduced pressure, and the residue was dissolved in water (10 cm^3). Complexes **A-I** and **A-III** were isolated from these solutions by addition of $NaClO_4$ (2 g) and recrystallized from hot methanol by adding $NaClO_4$ (1 g) in water (10 cm^3). Complex **A-II** was isolated in a similar way by addition of $NaB(C_6H_5)_4$ (0.1 g) and recrystallized from a mixture of acetone and methanol (3 : 1, 10 cm^3) by adding water (10 cm^3). Yields **A-I**: 125 mg (20%), **A-II**: 155 mg (9%), **A-III**: 125 mg (20%). Found for **A-I**: C, 39.10; H, 5.54; N, 3.94%. Calcd for *cisα*-[Co(acac)(*rac*(*P*)-232NPPN)]$(ClO_4)_2 \cdot 2H_2O = C_{24}H_{39}N_2O_{12}P_2Cl_2Co$: C, 38.99; H, 5.32; N, 3.79%. Found for **A-II**: C, 74.73; H, 7.06; N, 2.20%. Calcd for *cisβ*-[Co(acac)(*rac*(*P*)-232NPPN)]$\{B(C_6H_5)_4\}_2 \cdot 2(CH_3)_2CO = C_{78}H_{87}N_2O_4P_2B_2Co$: C, 74.41; H, 6.96; N, 2.22%. Found for **A-III**: C, 40.38; H, 5.34; N, 4.06%. Calcd for *cisβ*-[Co(acac)(*meso*(*P*)-232NPPN)]$(ClO_4)_2 \cdot H_2O = C_{24}H_{37}N_2O_{11}P_2Cl_2Co$: C, 39.96; H, 5.17; N, 3.88%. Complexes **A-I** and **A-III** are soluble in methanol, ethanol, acetone, and acetonitrile, but insoluble in water. Complex **A-II** is soluble in acetone and acetonitrile, but insoluble in methanol, ethanol, and water. Structures of the complexes are described later.

***cisα*-[Co(acac)(*rac*(*P*)-222NPPN)]$\{B(C_6H_5)_4\}_2 \cdot H_2O \cdot 2(CH_3)_2CO$ (B-I) and *cisβ*-[Co(acac)(*meso*(*P*)-222NPPN)]$\{B(C_6H_5)_4\}_2 \cdot 3H_2O \cdot (CH_3)_2CO$ (B-II).** To [Co(acac)$_3$] (1.6 g, 4.5 mmol) in methanol (200 cm^3) were added 222NPPN (1.5 g, 4.5 mmol) in methanol (20 cm^3) and active charcoal (200 mg). The mixture was stirred overnight at room temperature and filtered. The filtrate was diluted with water (5 dm^3), mixed with concd hydrochloric acid (3 cm^3), and applied on a column (ϕ4.5 cm×50 cm) of SP-Sephadex C-25. By elution with 0.1 mol dm^{-3} Na_2SO_4 (pH ca. 2) the column gave a large orange yellow and a large orange red band and several small red bands. The eluate of the orange yellow band was evaporated to dryness under reduced pressure, and the orange complex was extracted from the residue with ethanol. The extract was evaporated again to dryness under reduced pressure, and the residue was dissolved in water (15 cm^3). Orange crystals (**B-I**) were precipitated on addition of an aqueous $NaB(C_6H_5)_4$ solution to the solution and recrystallized from a mixture of acetone and water (2 : 1). Yield: 1.84 g (36%). Found: C, 73.22; H, 6.95; N, 2.21%. Calcd for *cisα*-[Co(acac)(*rac*(*P*)-222NPPN)]$\{B(C_6H_5)_4\}_2 \cdot H_2O \cdot 2(CH_3)_2CO = C_{77}H_{87}N_2P_2O_5B_2Co$: C, 73.17; H, 6.94; N, 2.22%.

The eluate of the orange red band became red in color on standing, but the color turned orange yellow when adjusted its pH at ca. 7 with Na_2CO_3. On addition of $NaB(C_6H_5)_4$ the solution, which had been adjusted the pH at ca. 7, gave a pale orange precipitate, which was recrystallized from acetone and water to form orange crystals (**B-II**). Yield: 520 mg (10%). Found: C, 71.68; H, 6.81; N, 2.10%. Calcd for *cisβ*-[Co(acac)(*meso*(*P*)-222NPPN)]$\{B(C_6H_5)_4\}_2 \cdot 3H_2O \cdot (CH_3)_2CO = C_{74}H_{85}N_2P_2B_2O_6Co$: C, 71.56; H, 6.90; N, 2.26%. The complex is stable in the solid state, but the chloride (vide infra) which is soluble in water decomposes slowly in water at about 40 °C. The solubilities of the 222NPPN complexes are quite similar to that of the tetraphenylborate of 232NPPN complex.

***cisα*-[Co(ox)(*rac*(*P*)-232NPPN)]PF_6 (C-I), *cisβ*-[Co(ox)(*rac*(*P*)-232NPPN)]$B(C_6H_5)_4 \cdot 3.5H_2O$ (C-II), and *cisβ*-[Co(ox)(*meso*-(*P*)-232NPPN)]PF_6 (C-III).** To $K_3[Co(ox)_3] \cdot 3H_2O$$^{5)}$ (820 mg, 1.66 mmol) in a mixture (80 cm^3) of methanol and water (7 : 1) was added 232NPPN (565 mg, 1.63 mmol) in methanol (10 cm^3). The mixture was stirred for 6 h at room temperature and filtered. On dilution with water (500 cm^3) the filtrate gave a white precipitate which was filtered off. The filtrate was further diluted with water (4 dm^3) and applied on a column (ϕ3 cm×130 cm)of SP-Sephadex C-25. By elution with 0.1 mol dm^{-3} NaCl, a large yellow-orange and a large orange band, and then a small red band developed. The yellow-orange eluate was diluted ten times with water and applied again on a small column (ϕ3 cm×10 cm) of SP-Sephadex C-25. The adsorbed complex was eluted with 1.0 mol dm^{-3} NaCl, and the eluate was mixed with an aqueous solution of $NaB(C_6H_5)_4$. A pale orange precipitate was formed, filtered, washed with water, and dissolved in acetone (20 cm^3). By addition of water (10 cm^3) and by slow evaporation of acetone by standing, the solution gave orange crystals of **C-II**, which were filtered, washed with water and dried in air. Yield: 160 mg (12%). Found: C, 61.51; H, 5.86; N, 3.08%. Calcd for *cisβ*-[Co(ox)(*rac*(*P*)-232NPPN)]$B(C_6H_5)_4 \cdot 3.5H_2O = C_{45}H_{54}N_2P_2O_{7.5}BCo$: C, 61.73; H, 6.33; N, 3.20%.

The eluate of the slower-moving orange band was evaporated to dryness under reduced pressure at 40 °C, and the residue was mixed with ethanol to remove NaCl. Sodium chloride was filtered off, and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of water, and the solution was applied again on a column (ϕ4.5 cm×40 cm) of SP-Sephadex C-25. By elution with 0.1 mol dm^{-3} Na_2SO_4, an yellow and an orange band developed. Each eluate was evaporated to dryness under reduced pressure at 40 °C, and the complex was extracted with ethanol. The extract was concentrated to ca. 5 cm^3 under reduced pressure and mixed with a saturated aqueous solution of NH_4PF_6 (ca. 2 cm^3). The mixture was cooled in ice to yield orange crystals, which were filtered, washed with cold water and dried in air. Yield: 250 mg (24%) for **C-I** and 180 mg (17%) for **C-III**. Found for **C-I**: C, 39.51; H, 4.49; N, 4.45%. Calcd for *cisα*-[Co(ox)(*rac*(*P*)-232NPPN)]$PF_6 = C_{21}H_{28}N_2P_3O_4F_6Co$: C, 39.52; H, 4.42; N, 4.39%. Found for **C-III**: C, 39.53; H, 4.42; N, 4.41%. Calcd for *cisβ*-[Co(ox)(*meso*(*P*)-232NPPN)]$PF_6 = C_{21}H_{28}N_2P_3O_4F_6Co$: C, 39.53; H, 4.42; N, 4.39%.

Complexes **C-I** and **C-III** are soluble in methanol and acetone, slightly souble in water and ethanol, and insoluble in diethyl ether. Complex **C-II** is soluble in acetone and acetonitrile, and insoluble in water, methanol, and ethanol.

***cisα*-[Co(en)(*rac*(*P*)-232NPPN)]$(ClO_4)_3 \cdot H_2O \cdot CH_3OH$.** To [Co(en)$_3$]$Cl_3$$^{6)}$ (750 mg, 2.17 mmol) in a mixture (50 cm^3) of methanol and water (5 : 3) were added 232NPPN (750 mg, 2.17 mmol) in methanol (15 cm^3) and active charcoal (200 mg). The mixture was stirred overnight at room temperature and filtered. The filtrate was diluted with water (3 dm^3, pH ca. 4) and applied on a column (ϕ3 cm×110 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.2 mol dm^{-3} Na_2SO_4, giving a large orange-yellow band and several small red and orange bands. There was no spectroscopic evidence of [Co(en)(232NPPN)]$^{3+}$ in the eluates of small bands. The eluate of the orange-yellow band was evaporated to dryness under reduced pressure, and the complex was extracted with ethanol. The extract was evaporated again to dryness under reduced pressure, and the residue was dissolved in water. On addition of $NaClO_4$

orange crystals were precipitated, filtered, and recrystallized from hot methanol. Yield: 187 mg (11%). Found: C, 32.56; H, 5.79; N, 7.21%. Calcd for *cisα*-[Co(en)(*rac*(*P*)-232NPPN)]-$(ClO_4)_3 \cdot H_2O \cdot CH_3OH=C_{22}H_{42}N_4P_2O_{15}Cl_3Co$: C, 32.47; H, 5.20; N, 6.88%.

The complex is soluble in acetone, acetonitrile, and methanol, and insoluble in water.

Reactions of the Complexes with Hydrochloric Acid. All the complexes were converted to the chlorides, which were readily soluble in water, by stirring with Dowex 1X8 (Cl^- form) in a mixture of acetone and water (2:1). The resin was filtered off, and the filtrate was evaporated to dryness under reduced pressure. The residue was soluble in water and used for examining the reactivity of the complex in water or hydrochloric acid without further purification.

The chloride of **A-I** was dissolved in a small amount of concd HCl. After 24 h the resulting red solution was concentrated in a desiccator over NaOH, yielding red crystals which were filtered and washed with diethyl ether. Found: C, 40.13; H, 5.15; N, 4.93%. Calcd for *cisα*-[$CoCl_2$(*rac*(*P*)-232NPPN)]$Cl \cdot 1.5HCl=C_{19}H_{29.5}N_2P_2Cl_{4.5}Co$: C, 40.29; H, 5.25; N, 4.95%. Each chloride of **A-II** and **A-III** was dissolved in 0.1 mol dm^{-3} HCl, and the solution was allowed to stand for 24 h. The resulting red solution was evaporated to dryness under reduced pressure at 40 °C to give a dark red complex. Found for the complex from **A-II**: C, 42.83; H, 6.14; N, 4.54%. Calcd for [Co(acac)Cl(*rac*(*P*)-232NPPNH$^+$)]-$Cl_2 \cdot 1.5H_2O \cdot HCl=C_{24}H_{40}N_2P_2O_{3.5}Cl_4Co$: C, 42.75; H, 5.98; N, 4.15%. Found for the complex from **A-III**: C, 41.42; H, 5.96; N, 4.09%. Calcd for [Co(acac)Cl(*meso*(*P*)-232NPPNH$^+$)]-$Cl_2 \cdot 3H_2O \cdot HCl=C_{24}H_{43}N_2P_2O_5Cl_4Co$: C, 41.11; H, 6.18; N, 3.99%. These chloro complexes liberate the chloride ion rapidly in water and dil HCl, and decompose in concd HCl to give Co(II) species.

The reaction of **B-I** with concd HCl also afforded a red complex, which was isolated in a similar way. Found: C, 37.62; H, 4.99; N, 4.92%. Calcd for *cisα*-[$CoCl_2$(*rac*(*P*)-222NPPN)]$Cl \cdot 2HCl=C_{18}H_{28}N_2P_2Cl_5Co$: C, 37.89; H, 4.95; N, 4.91%. The color of orange **B-II** changed slowly to red in 0.1 mol dm^{-3} HCl, indicating the same dissociation of one amino group of 222NPPN as occurred in isomers **A-II** and **A-III**. However, the complex decomposed during the course of isolation.

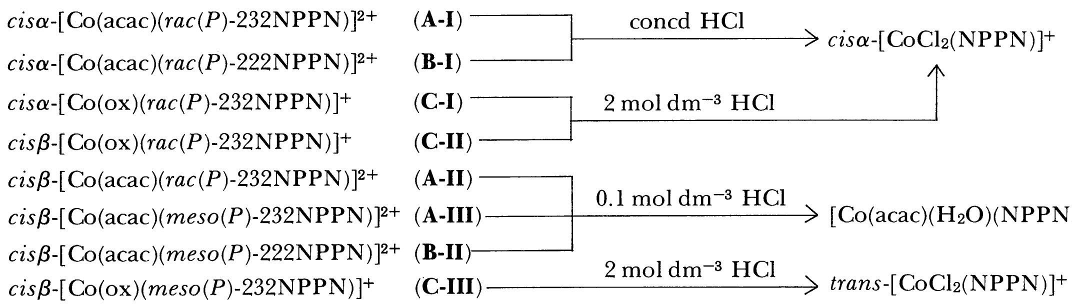
The chloride of **C-I** was more reactive to HCl and yielded a red complex by the reaction with 2 mol dm^{-3} HCl. The absorption spectrum of the product was identical with that of *cisα*-[$CoCl_2$(*rac*(*P*)-232NPPN)]$^+$(19950 cm^{-1}(log ε=2.79), 25600 cm^{-1}(log ε=2.5)(shoulder)). Both isomers **C-II** and **C-III** in 0.1 mol dm^{-3} HCl solutions showed little change in absorption spectra. However, an orange-yellow soluton of **C-II** in 2 mol dm^{-3} HCl slowly turned red, from which *cisα*-[$CoCl_2$(*rac*-(*P*)-232NPPN)]$^+$ was obtained. Isomer **C-III** in a 2 mol dm^{-3} HCl solution changed the color slowly from orange-yellow to green. The absorption spectrum of the green solution showed a band at 620 nm and a shoulder around 500 nm which were characteristic of *trans*-[$CoCl_2$(232NPPN)]$^+$(vide infra). The green complex slowly decomposed to cobalt(II) species and was failed in isolation.

The products yielded by reactions of the complexes with hydrochloric acid are summarized in Scheme 1. The reaction rates and spectral changes for representative complexes are described later.

Results and Discussion

The 232NPPN and 222NPPN ligands have two chiral phosphorus atoms which are stable to racemization, and exist in the racemic (*RR*,*SS*) and meso(*RS*) forms. In a previous paper,[1)] we isolated *trans*-[$CoCl_2$(*rac*(*P*)-222NPPN)]$^+$ in a yield of 32% from the reaction product of [$CoCl(NH_3)_5]Cl_2$ and 222NPPN. The corresponding *meso*(*P*)-222NPPN complex was rather unstable and decomposed to Co(II) species and an oily material during the course of isolation. The instability of this complex may be attributable to a strained structure (envelop conformation) of the central five-membered P–Co–P chelate ring. In this study, we have obtained a mixture of *trans*-[$CoCl_2$(*rac*-(*P*)-232NPPN)]$^+$ and -[$CoCl_2$(*meso*(*P*)-232NPPN)]$^+$ in a yield of ca. 60% by a method similar to that for the 222NPPN complex. However, attempts to separate them were unsuccessful. In column-chromatography the complex was adsorbed strongly on ion-exchangers and eluted hardly with even 5 mol dm^{-3} HCl or NaCl.

The reactions of [$Co(acac)_3$] with 232NPPN and with 222NPPN yielded three (**A-I**, **A-II**, and **A-III**) and two (**B-I** and **B-II**) isomers of the [Co(acac)(NPPN)]$^{2+}$-type complex, respectively. For this type of complex, there are three possible geometrical or diastereomeric isomers. (Fig. 1) Each isomer has its antipode, but other diastereomers such as *cisα*-(*Λ*-*RR*(*P*)/*Δ*-*SS*(*P*)) are not possible. The chiralities of phosphorus atoms of these NPPN ligands are related to the geometrical structures of [Co(acac)(NPPN)]$^{2+}$. The *rac*(*P*)-NPPN



Scheme 1.

Table 1. ^{1}H NMR and Absorption Spectral Data

Complex		^{1}H NMR (acac)$^{a)}$			Absorption$^{b)}$		
		-CH$_3$		=CH-			
cisα-[Co(acac)(*rac*(*P*)-232NPPN)]$^{2+}$	(**A-I**)	2.00		5.60	21.3(2.66)		
cisβ-[Co(acac)(*rac*(*P*)-232NPPN)]$^{2+}$	(**A-II**)	1.69	1.75	4.91	20.0(2.6)^{sh},	22.8(2.94)	
cisβ-[Co(acac)(*meso*(*P*)-232NPPN)]$^{2+}$	(**A-III**)	1.29	1.96	4.82	19.1(2.5)^{sh},	22.8(2.97)	
cisα-[Co(acac)(*rac*(*P*)-222NPPN)]$^{2+}$	(**B-I**)	2.13		5.71	22.2(2.88)		
cisβ-[Co(acac)(*meso*(*P*)-222NPPN)]$^{2+}$	(**B-II**)	1.10	2.07	5.00	18.4(2.5)^{sh},	22.7(3.02)	
cisα-[Co(ox)(*rac*(*P*)-232NPPN)]$^{+}$	(**C-I**)				21.4(2.64)		26.4(2.4)$^{sh\,c)}$
cisβ-[Co(ox)(*rac*(*P*)-232NPPN)]$^{+}$	(**C-II**)				20.2(2.5)^{sh},	22.6(2.67)	26.8(2.8)$^{sh\,c)}$
cisβ-[Co(ox)(*meso*(*P*)-232NPPN)]$^{+}$	(**C-III**)				19.4(2.3)^{sh},	23.5(2.81)	26.5(2.84)$^{c)}$
cisα-[Co(en)(*rac*(*P*)-232NPPN)]$^{3+}$					21.8(2.6)^{sh},	23.7(2.69)	

a) δ/ppm from TMS, solvent $(CD_3)_2SO$. b) First absorption band, $\tilde{\nu}/10^3\,cm^{-1}$ ($\log \varepsilon$), solvent; CH_3CN for the acac complexes, CH_3OH for the ox complexes, and H_2O for the en complex, sh; shoulder. c) Second absorption band.

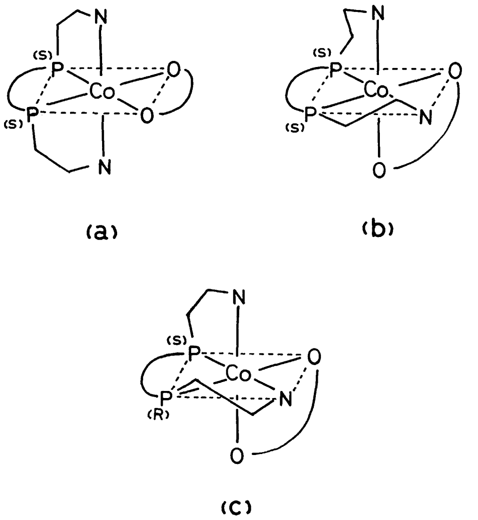


Fig. 1. Three possible isomers of [Co(acac)(NPPN)]$^{2+}$: (a) *cisα*-(*Λ*-*SS*(*P*)/*Δ*-*RR*(*P*)), (b) *cisβ*-(*Δ*-*SS*(*P*)/*Λ*-*RR*(*P*)), (c) *cisβ*-(*Δ*-*RS*(*P*)/*Λ*-*SR*(*P*)).

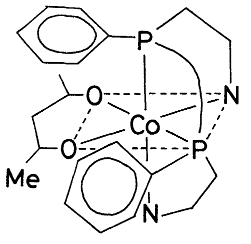


Fig. 2. A schematic structure of *Δ*-*cisβ*-[Co(acac)-(*RS*(*P*)-NPPN)]$^{2+}$.

ligand can form both cis*α* and cis*β* isomers, while the *meso*(*P*)-NPPN ligand affords only the cis*β* isomer, since two terminal P-N chelate arms of the *meso*(*P*)-ligand point to the same apical site with respect to the P–Co–P plane. Approximate symmetries of the cis*α* and cis*β* isomers are C_2 and C_1, respectively. Thus isomers **A-I** and **B-I** which show only one methyl signal of acac in the ^{1}H NMR spectra can be assigned to the cis*α* structure, and isomers **A-II**, **A-III**, and **B-II** which give two kinds of methyl signal to the cis*β* one (Table 1). The assignment for two cis*β* isomers of the *rac*(*P*)- and *meso*(*P*)-NPPN complexes can also be made from the chemical shift of methyl groups of acac in the ^{1}H NMR spectra. Table 1 shows that isomers **A-III** and **B-II** exhibit one of the two methyl signals at a remarkably high field, 1.29 and 1.10 ppm, respectively compared with other methyl signals (1.69—2.13 ppm). Molecular models indicate that one methyl group in *cisβ*-[Co(acac)(*meso*(*P*)-NPPN)]$^{2+}$ is located over the phenyl ring bonded to the phosphorus atom trans to the oxygen atom of acac as shown in Fig. 2. The high field shift of the methyl signal is attributable to the shielding effect of this phenyl group. The *cisβ*-[Co(acac)(*rac*(*P*)-NPPN)]$^{2+}$ complex has a structure that both methyl groups are not strongly shielded by phenyl groups. Thus isomer **A-II** is assigned to *cisβ*-[Co(acac)(*rac*(*P*)-232NPPN)]$^{2+}$, and isomers **A-III** and **B-II** to *cisβ*-[Co(acac)(*meso*(*P*)-232NPPN)]$^{2+}$ and *cisβ*-[Co(acac)(*meso*(*P*)-222NPPN)]$^{2+}$, respectively. The third isomer of 222NPPN complex, *cisβ*-[Co(acac)(*rac*-(*P*)-222NPPN)]$^{2+}$ was not obtained by the reaction of [Co(acac)$_3$] with 222NPPN.

As Fig. 2 shows, the other phenyl ring bonded to the phosphorus atom trans to the nitrogen atom is situated over the acac chelate ring. A similar structure is also formed in *cisβ*-[Co(acac)(*rac*(*P*)-232NPPN)]$^{2+}$, while both phenyl rings in the cis*α* isomer are disposed away from the acac chelate ring. Thus all the cis*β* isomers show the methine proton signal of acac at a higher field than that of the cis*α* isomer (Table 1). Such a high field shift of the methine proton of acac has been observed in our previous studies and often used to assign the geometry of complexes.[7]

Absorption spectra of isomers **A-I**, **A-II**, and **A-III** are shown in Fig.3 and the data of the first d-d bands are given in Table 1. The first d-d band of isomer **A-I** (cis*α*) is nearly symmetric in shape, while those of cis*β* isomers, **A-II** and **A-III** are broad and show a distinct shoulder on the low energy side. The spectra of 222NPPN complexes are quite similar to those of the corresponding isomers of the 232NPPN complex.

Since the order of ligand field strengths of donor atoms will be P>N>O as observed in many Co(II) phosphine complexes,[8] the splitting of the first d-d band is expected to be larger for the cisβ isomer than for the cisα isomer from Yamatera's rule.[9]

The chlorides of isomers **A-I** and **B-I** are stable in water and dil HCl (ca. 1 mol dm^{-3}), but react gradually in concd HCl, the color of solutions changing from orange to red (See Experimental section). Figure 4 shows the spectral change of isomer **A-I** in concd HCl recorded at 1 h intervals at 23.5 °C. An isosbestic point is seen at 473 nm, and the plots of ln $(D_t - D_\infty)$ against time gives a straight line. The product isolated was *cis*α-[CoCl$_2$(*rac*(*P*)-232NPPN)]$^+$ as characterized by elemental analysis, absorption and ^{13}C NMR spectra (DMSO-d_6, -CH$_2$-; δ=24.97(s), 25.03(t), 29.44(t), 33.29-(s)) (Scheme 1). Isomer **B-I** in concd HCl reacts in a similar manner to yield *cis*α-[CoCl$_2$(*rac*(*P*)-222NPPN)]$^{2+}$. The half-life times of the reactions at 20 °C are 364 min for isomer **A-I** and 87 min for isomer **B-I**, isomer **A-I** being more stable than isomer **B-I**. For a tetramine analog *cis*α-[Co(acac)(trien)]$^{2+}$ (trien=NH$_2$-CH$_2$CH$_2$NHCH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$),[10] no spectral change was observed in concd HCl at room temperature over 24 h. The difference in reactivity of acac

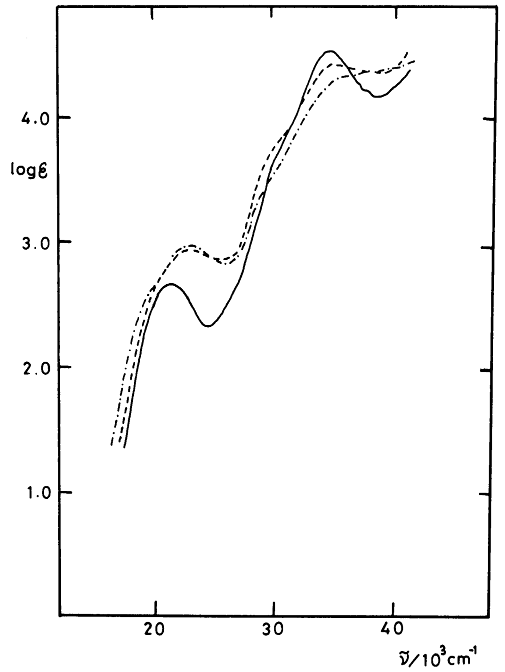


Fig. 3. Absorption spectra of isomers **A-I** (——), **A-II** (----), and **A-III** (-·-·-) in CH$_3$CN.

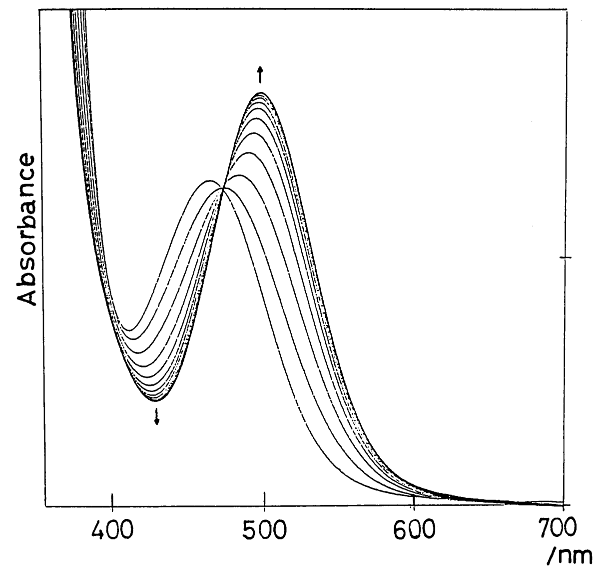


Fig. 4. Change in absorption spectrum of isomer **A-I** in concd HCl recorded at 1 h intervals at 23.5 °C. Trends of spectral changes with time are shown by arrows.

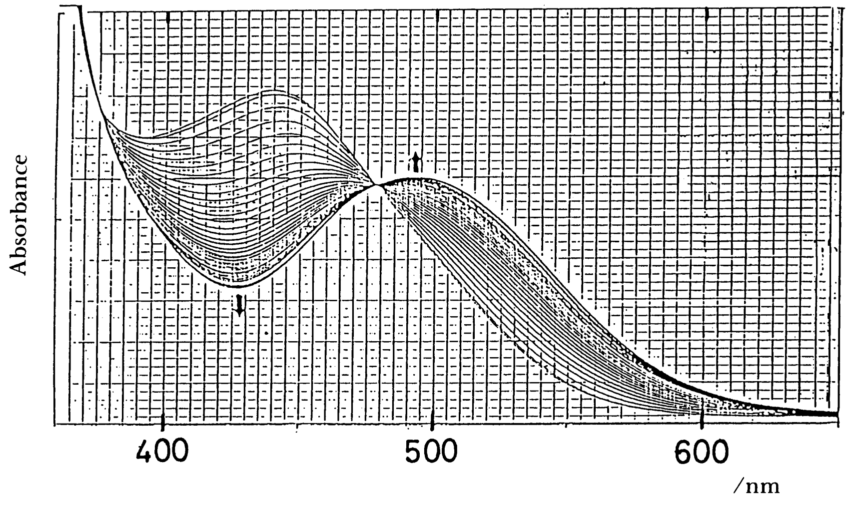


Fig. 5. Change in absorption spectrum of isomer **A-II** in 0.1 mol dm^{-3} HCl recorded at 1 h intervals at 23.5 °C.

between the NPPN and trien complexes may be attributable to the stronger trans effect of the phosphine donor group than that of the amine donor group. The reason for the rate difference between isomers **A-I** and **B-I** is not clear, but it may be related to the size of the central P–P chelate ring. The *rac*(*P*)-222NPPN ligand which forms a smaller five-membered P–P chelate ring will coordinate to the Co(III) ion with a shorter Co–P distance than that of a larger six-membered P–P chelate ring in the *rac*(*P*)-232NPPN complex, and the phosphine donor group will have a stronger trans effect on the acac ligand in the trans positions and will make it more labile.

The chlorides of isomers **A-II** and **A-III** are stable in water, while the chloride of isomer **B-II** decomposes slowly in water at 40 °C. These three isomers decompose fairly rapidly in concd HCl to give Co(II) species. In dil HCl (pH 1) the isomers change gradually from orange to red in color, although isomer **B-II** accompanies very slow decomposition to Co(II). Figure 5 shows a spectral change of isomer **A-II** with time in 0.1 mol dm^{-3} HCl at 23.5 °C. The spectra change with isosbestic points at 376 and 478 nm. The reaction rates increase in the order of **A-II**<**A-III**<**B-II**. From the 0.1 mol dm^{-3} HCl solutions of isomers **A-II** and **A-III**, red complexes formulated, respectively as [Co(acac)Cl(*rac*(*P*)-232NPPNH$^+$)]Cl$_2$ · 1.5H$_2$O · HCl and [Co(acac)Cl(*meso*(*P*)-232NPPNH$^+$)]Cl$_2$ · 3H$_2$O · HCl were isolated. The product from isomer **B-II** was not obtained because of decomposition during the course of isolation. These red complexes of 232NPPN show the first d-d band at 516 nm in ethanol solutions, but the band shifts to 495 nm in aqueous and dil HCl solutions, indicating rapid replacement of Cl$^-$ by water. In ^{1}H NMR spectra the two red complexes give the signals of acac at the same positions, 1.60 and 1.84 ppm for the methyl protons, and 4.87 ppm for the methine proton. The methyl signal at 1.29 ppm of isomer **A-III** shifts to a lower field in the red complex. The result indicates that in the red complex the shielding of the methyl group by the phenyl group is removed by dissociation of the amino group in the position trans to the phosphorus atom (Fig. 2). Similar structures can be assigned to the other red complexes from **A-II** and **B-II** from similarity of the ^{1}H NMR and absorption spectra to those of the red complex from isomer **A-III**. All the red complexes formed in acidic solutions revert to the original orange complexes by neutralizing the solutions. The dissociation reactions of the amino group take place by protonation to the nitrogen atom. An analogous tetramine complex *cisβ*-[Co(acac)(232-tet)]$^{2+}$ (232-tet= NH$_2$CH$_2$CH$_2$NH(CH$_2$)$_3$NHCH$_2$CH$_2$NH$_2$)$^{10)}$ shows no spectral change in dil and concd HCl solutions at room temperature over 24 h. The dissociation of the amino group by protonic acids in the present phosphine complexes may also be attributable to the trans effect of the phosphine donor group.

Three isomers (**C-I**, **C-II**, and **C-III**) of [Co(ox)-(232NPPN)]$^+$ were obtained by reaction of [Co(ox)$_3$]$^{3-}$ with 232NPPN. Isomer **C-I** is assigned to *cisα*-[Co(ox)(*rac*(*P*)-232NPPN)]$^+$ from the ^{13}C NMR spectrum (CD$_3$CN, –CH$_2$–; δ=19.80(s), 23.47(t), 31.13(t), 42.72(s)). The isomer is stable in water and methanol, but more reactive to HCl than isomer **A-I** of the acac complex and affords *cisα*-[CoCl$_2$(*rac*(*P*)-232NPPN)]$^+$ in 2 mol dm^{-3} HCl at room temperature. The spectrum of isomer **C-I** in 2 mol dm^{-3} HCl changes with an isosbestic point at 464 nm, and the half-life time is 220 min at 30 °C (Fig. 6(a)). The chloride of isomer **C-II** isomerizes to isomer **C-I** in water, methanol, or acetonitrile very slowly (several days at room temperature) as confirmed by ^{13}C NMR and absorption spectra, and column-chromatography. The isomer affords isomer **A-II** of the acac complex by reaction with Li(acac) at room temperature. Thus

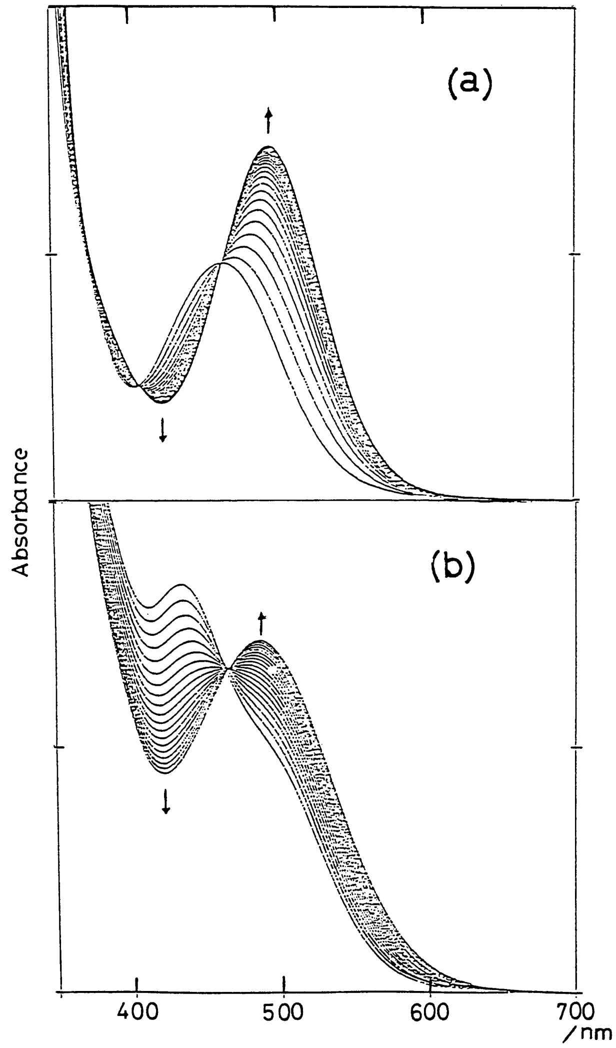


Fig. 6. Changes in absorption spectra of (a) isomer **C-I** and (b) isomer **C-II** in 2 mol dm^{-3} HCl recorded at 1 h intervals at 23.5 °C (a) and 50 °C (b).

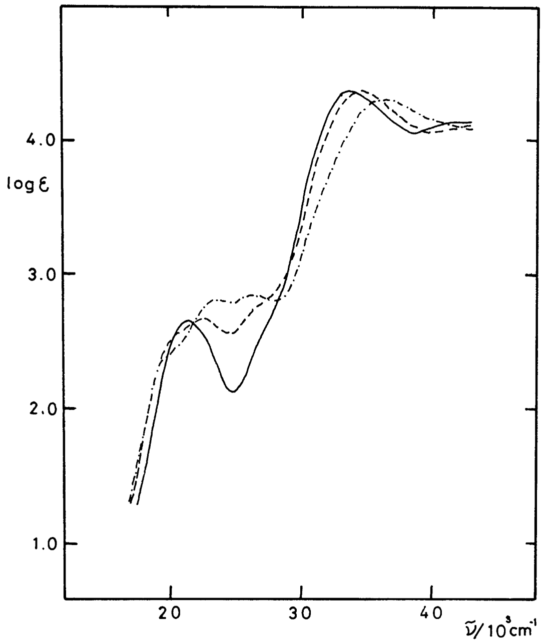


Fig. 7. Absorption spectra of isomers **C-I** (——), **C-II** (----), and **C-III** (-·-·-) in CH_3OH.

isomer **C-II** can be assigned to *cisβ*-[Co(ox)(*rac*(*P*)-232NPPN)]$^+$. The remaining isomer **C-III** is assigned to *cisβ*-[Co(ox)(*meso*(*P*)-232NPPN)]$^+$. The isomer is stable in water and methanol, and reacts with Li(acac) to yield isomer **A-III** of the acac complex.

Both cisβ isomers of the ox complex in acidic solution have different reactivity from that of the corresponding isomers of the acac complex, where one amino group of the 232NPPN ligand is liberated from the Co(III) ion. The chloride of isomer **C-II** in 2 mol dm^{-3} HCl changes to *cisα*-[$CoCl_2$(*rac*(*P*)-232NPPN)]$^+$, and the spectral change has an isosbestic point at 463 nm (Fig. 6(b)). For isomer **C-III**, the orange 2 mol dm^{-3} HCl solution slowly turns green, and its spectrum is very similar to that of *trans*-[$CoCl_2$(232NPPN)]$^+$, although the green complex decomposes very slowly to Co(II) under the experimental conditions. Thus neither cisβ isomer of the ox complex dissociates the amino group of the NPPN ligand, and the oxalate ion is liberated by acids, in contrast with the cisβ isomers of the acac complex.

Absorption spectra of three isomers of the ox complex are shown in Fig. 7, and the data are listed in Table 1. The spectral patterns are similar to those of the corresponding isomers of the acac complex, although the ox complexes show a peak or shoulder assignable to the second d-d band which is not observed clearly for the acac complexes. The similarity in spectra between the ox and acac complexes will support the assignment for isomers of these complexes.

Either reaction of [$Co(en)_3$]$^{3+}$ with 232NPPN or *trans*-[$CoCl_2$(232NPPN)]$^+$ with en affords only *cisα*-[Co(en)(*rac*(*P*)-232NPPN)]$^{3+}$, which was assigned on the basis of the ^{13}C NMR spectrum (D_2O, $-CH_2-$; δ=19.41(s), 25.26(t), 29.52(t), 44,49(s), 46.00(s)). No fraction indicative of the cisβ isomer is observed in column-chromatography. The cisα isomer is stable and does not react with even concd HCl. The en complex of 222NPPN also forms only the cisα isomer with *rac*(*P*)-222NPPN.[1] The *meso*(*P*)-NPPN ligand does not form the cisβ-en complex. The instability of this isomer seems to come from the steric crowding between the amino group of en and the phenyl group as indicated in Fig. 2. The property that the present 232NPPN complexes are more stable in the cisα isomer than the cisβ one is quite different from the corresponding complexes of 232-tet[2] and 232PNNP ($(C_6H_5)_2PCH_2CH_2NH(CH_2)_3NHCH_2CH_2P(C_6H_5)_2$)[11] which form only the cisβ isomer.

The authors wish to thank Grant-in-Aid for Scientific Research No. 61430013 from the Ministry of Education, Science and Culture.

References

1) M. Atoh, H. Sugiura, Y. Seki, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **60**, 1699 (1987).

2) M. Saburi and S. Yoshikawa, "Stereoselectivity in Octahedral Complexes," in "Chemistry of Octahedral Complexes," Kagaku Sosetsu, No. 13, (1976), Chap. 7, p. 109.

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

4) "Inorg. Synth.," Vol. V, p. 188.

5) "Inorg. Synth.," Vol. I, p. 37.

6) "Inorg. Synth.," Vol. II, p. 221.

7) a) K. Kashiwabara, I. Kinoshita, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **54**, 725 (1981). b) S. Hayakawa, H. Nishikawa, K. Kashiwabara, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **54**, 3593 (1981). c) K. Kashiwabara, K. Katoh, T. Ohishi, J. Fujita, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **55**, 149 (1982). d) T. Ohishi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1553 (1983). e) K. Katoh, H. Sugiura, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 3580 (1984). f) M. Takata, K. Kashiwabara, H. Ito, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **58**, 2247 (1985). g) M. Atoh, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **59**, 1001 (1986).

8) a) I. Kinoshita, K. Kashiwabara, J. Fujita, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **54**, 2683 (1981). b) M. Atoh, I. Kinoshita, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **55**, 3179 (1982). c) I. Kinoshita, Y. Yokota, K. Matsumoto, S. Ooi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1067 (1983). d) T. Ohishi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 3441 (1983). e) T. Ohishi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **60**, 583 (1987).

9) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).

10) *cisα*-[Co(acac)(trien)]$^{2+}$ and *cisβ*-[Co(acac)(232-tet)]$^{2+}$ were prepared by the reaction of Li(acac) with *trans*-[$CoCl_2$(trien or 232-tet)]$^+$, respectively.

11) Min-Ho Jung, M. Atoh, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **61**, 3503 (1988).