Preparation and Characterization of Cobalt(III) Complexes Containing 4,7-Diphenyl-4,7-diphosphadecane-1,10-diamine and 4,8-Diphenyl-4,8-diphosphaundecane-1, 11-diamine, $NH_2(CH_2)_3P(C_6H_5)$-$(CH_2)_nP(C_6H_5)(CH_2)_3NH_2$ (n=2,3)

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Twelve new cobalt(III) complexes of the types, *cisα*-[Co(L)(*rac*(*P*)-323 or 333NPPN)]$^{p+}$ (L=2,4-pentanedionate (acac) and oxalate (ox) ions) (four complexes) and *cisβ*-[Co(L)(*rac*(*P*)- or *meso*(*P*)-323 or 333NPPN)]$^{p+}$ (eight complexes) were prepared and characterized by ^{1}H NMR and absorption spectra, where *rac*(*P*)- and *meso*(*P*)-323NPPN denote *rac*(*P*)- and *meso*(*P*)-$NH_2(CH_2)_mP(C_6H_5)(CH_2)_nP(C_6H_5)(CH_2)_mNH_2$ with m=3 and n=2, and 333NPPN the ligand with m=3 and n=3. Reactivities of the complexes towards hydrochloric acid were examined and compared with those of the corresponding 222NPPN (m=2, n=2) and 232NPPN (m=2, n=3) complexes. All the *cisα* isomers yield the *cisα*-dichloro complexes, the 333NPPN and 222NPPN complexes being more reactive than the 232NPPN and 323NPPN complexes in which five- and six-membered chelate rings of NPPN are involved. For the *cisβ* isomers, the acac complexes afford [Co(acac)(Cl)(mnmNPPNH$^+$)]$^{2+}$ except the *rac*(*P*)- and *meso*(*P*)-333NPPN complexes which give the *trans*-dichloro complexes, while all the ox complexes liberate the ox ion to yield the dichloro complex of the *cisα*, *cisβ*, or *trans* configuration. For both *cisβ*-acac and -ox isomers, the 222NPPN and 232NPPN complexes are more reactive than those of 323NPPN and 333NPPN, and the *meso*(*P*)-complexes are more reactive than the *rac*(*P*)-complexes.

In a previous paper,[1] we reported the preparation of stereoisomers of 2,4-pentanedionato (acac) and oxalato (ox) cobalt(III) complexes containing a linear quadridentate ligand with two chiral phosphorus donor atoms, $NH_2(CH_2)_2P(C_6H_5)(CH_2)_nP(C_6H_5)(CH_2)_2NH_2$ (n=2: 222NPPN, n=3: 232NPPN), and their novel reactivities towards hydrochloric acid. For example, the *cisβ* isomers of the acac complexes dissociate the amino group trans to the phosphorus donor atom of NPPN reversibly depending on the acidity of solution to form [Co(acac)-(H_2O)(NPPNH$^+$)]$^{2+}$, while the *cisα* isomers yield *cisα*-dichloro complexes in hydrochloric acid. These properties are quite different from those of analogous tetramine complexes[2] which are stable under the same conditions. In order to examine whether such chemical properties depend on the size of chelate rings of NPPN ligands, we have prepared 4,7-diphenyl-4,7-diphosphadecane-1,10-diamine (323NPPN) and 4,8-diphenyl-4,8-diphosphaundecane-1,11-diamine (333NPPN) complexes of cobalt(III) (Fig. 1).

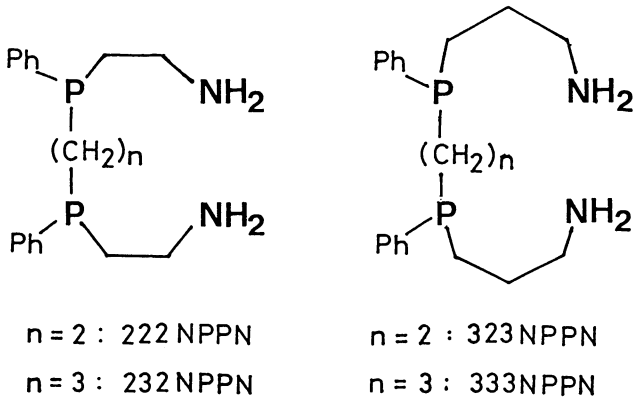


Fig. 1. Linear quadridentate phosphine ligands of the NPPN-type.

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 spectra were recorded on a Hitachi U3400 spectrophotometer, and ^{1}H and ^{13}C NMR spectra on a Hitachi R-90H spectrometer.

Preparation of Ligands. 323NPPN and 333NPPN were prepared by a method similar to that for 333NPPN reported by Meek et al.,[3] except that (3-aminopropyl)phenylphosphine was obtained from (3-aminopropyl)diphenylphosphine and sodium.

(3-Aminopropyl)diphenylphosphine, $NH_2CH_2CH_2CH_2P(C_6H_5)_2$. The reported method for $NH_2CH_2CH_2CH_2P(C_6H_5)_2$ was reduction of $NCCH_2CH_2P(C_6H_5)_2$ with $LiAlH_4$.[4] In the present paper, it was prepared from $NH_2CH_2CH_2CH_2Cl$ and $NaP(C_6H_5)_2$. A liquid ammonia solution (300 cm^3) containing $P(C_6H_5)_3$ (65 g, 0.247 mol) and sodium metal (13 g, 0.565 mol) was stirred for 3 h at −78 °C. To the resulting red-orange solution were added $NH_2CH_2CH_2CH_2Cl \cdot HCl$ (Tokyo Kasei Kogyo Co., Ltd.) (32.5 g, 0.25 mol) and tetrahydrofuran (THF) (300 cm^3) by portions. After stirring for 2 h at −78 °C, liquid ammonia was allowed to evaporate slowly. The THF solution was refluxed for 8 h at 60—70 °C, and then the solvent was evaporated under reduced pressure. The residue was distilled at 150—160 °C/ca. 60 Pa to give a colorless viscous liquid. Yield: 48 g (80%).

(3-Aminopropyl)phenylphosphine, $NH_2CH_2CH_2CH_2PH(C_6H_5)$. To a liquid ammonia solution (300 cm^3) of sodium metal (8 g, 0.348 mol) was added (3-aminopropyl)diphenylphosphine (40 g, 0.164 mol) dropwise with stirring at −78 °C. The solution was stirred for 2 h to give an yellow-orange solution. Water (10 cm^3) was added by portions with care,

yielding a colorless solution. Liquid ammonia was evaporated, and the residue was stirred with a mixture of water (200 cm^3) and diethyl ether (200 cm^3). The ethereal layer was separated from water and dried over Na_2SO_4 (5 g) overnight. The solvent was evaporated and the residue was distilled at 95—100°/ca. 60 Pa to yield a colorless liquid. Yield: 22 g (80%).

4,7-Diphenyl-4,7-diphosphadecane-1,10-diamine (323NPPN), $NH_2(CH_2)_3P(C_6H_5)(CH_2)_2P(C_6H_5)(CH_2)_3NH_2$. A THF solution (50 cm^3) of (3-aminopropyl)phenylphosphine (10 g, 59.8 mmol) was added dropwise with stirring at 0 °C to sodium metal (1.5 g, 65.2 mmol) in THF (50 cm^3). After a while the orange solution was warmed at 20 °C, stirred for 6 h and cooled to 0 °C. To the solution was added a THF solution of 1,2-dichloroethane (2.9 g, 29.3 mmol) dropwise with stirring at 0 °C, and then the colorless solution was stirred at 25 °C for 5 h. The solvent THF was evaporated, and diethyl ether was added to precipitate NaCl, which was filtered off. The filtrate was evaporated under vacuum, yielding a colorless oily product. Yield: 15 g (70%). This was used for preparing Co(III) complexes without further purification.

4,8-Diphenyl-4,8-diphosphaundecane-1,11-diamine (333NPPN), $NH_2(CH_2)_3P(C_6H_5)(CH_2)_3P(C_6H_5)(CH_2)_3NH_2$. This ligand was prepared by the same method as that for 323NPPN using 1,3-dichloropropane instead of 1,2-dichloroethane. Yield: 16 g (73%).

Preparation of Cobalt(III) Complexes. *cis*α-[Co(acac)(*rac*(*P*)-323NPPN)]{$B(C_6H_5)_4$}$_2$·1/2$(CH_3)_2CO$ (A-I), *cis*β-[Co(acac)(*rac*(*P*)-323NPPN)]{$B(C_6H_5)_4$}$_2$·H_2O (A-II), and *cis*β-[Co(acac)(*meso*(*P*)-323NPPN)]{$B(C_6H_5)_4$}$_2$ (A-III). A methanol solution (100 cm^3) containing [Co(acac)$_3$] (590 mg, 1.66 mmol) and 323NPPN (600 mg, 1.67 mmol) was stirred at room temperature overnight. The dark orange solution was diluted with water (2 dm^3) and applied on a column (ϕ 4 cm×70 cm) of SP-Sephadex C-25. The adsorbed products were eluted with a 0.1 mol dm^{-3} NaCl aqueous solution. Three large orange bands (**A-I**, **A-II**, **A-III** in the order of elution) and two small red bands developed. Each eluate of **A-I** and **A-II** was evaporated to dryness under reduced pressure at 40 °C. The orange complex in the residue was extracted with ethanol, and the extract was evaporated again to dryness under reduced pressure. The residue was dissolved in water (10 cm^3). On addition of an aqueous solution of $NaB(C_6H_5)_4$, complexes **A-I** and **A-II** were precipitated and recrystallized from a mixture of acetone and water (2:1, 15 cm^3). Yield: **A-I**, 430 mg (33%); **A-II**, 150 mg (8%). The eluate of **A-III** was diluted ten times with water, and rechromatographed using a column (ϕ 3 cm×70 cm) of SP-Sephadex C-25 and a 0.1 mol dm^{-3} Na_2SO_4 aqueous solution. After elution of a small reddish orange band, the eluate of a large orange band (**A-III**) was collected and worked up by the same manner as for **A-I** and **A-II**. Yield: 350 mg (18%). Found for **A-I**: C, 75.54; H, 7.11; N, 2.28%. Calcd for [Co(acac)(323NPPN)]{$B(C_6H_5)_4$}$_2$·1/2$(CH_3)_2CO$=$C_{74.5}H_{80}N_2P_2O_{2.5}B_2Co$: C, 75.45; H, 6.80; N, 2.36%. Found for **A-II**: C, 74.40; H, 6.96; N, 2.27%. Calcd for [Co(acac)(323NPPN)]{$B(C_6H_5)_4$}$_2$·H_2O=$C_{73}H_{79}N_2P_2O_3B_2Co$: C, 74.63; H, 6.78; N, 2.38%. Found for **A-III**: C, 75.70; H, 6.81; N, 2.33%. Calcd for [Co(acac)(323NPPN)]{$B(C_6H_5)_4$}$_2$=$C_{73}H_{77}N_2P_2O_2B_2Co$: C, 75.79; H, 6.71; N, 2.42%. These three complexes are soluble in acetone and acetonitrile, but insoluble in water, methanol and ethanol.

***cis*α-[Co(acac)(*rac*(*P*)-333NPPN)]{$B(C_6H_5)_4$}$_2$·$2H_2O$ (B-I), *cis*β-[Co(acac)(*rac*(*P*)-333NPPN)]{$B(C_6H_5)_4$}$_2$·1/$2H_2O$ (B-II), and *cis*β-[Co(acac)(*meso*(*P*)-333NPPN)]{$B(C_6H_5)_4$}$_2$·1/$2H_2O$ (B-III).** A methanol solution (150 cm^3) containing [Co(acac)$_3$] (810 mg, 2.27 mmol) and 333NPPN (850 mg, 2.27 mmol) was stirred at 50 °C for 30 min, and then at room temperature for 6 h. The resulting brown solution was diluted with water (3 dm^3) and applied on a column (ϕ 4 cm×70 cm) of SP-Sephadex C-25. By elution with a 0.1 mol dm^{-3} NaCl aqueous solution, three large orange bands (**B-I**, **B-II**, **B-III** in the order of elution) and a small red one appeared. From eluates of the orange bands, complexes **B-I**, **B-II**, and **B-III** were isolated as tetraphenylborates by methods similar to those for complexes **A-I** and **A-II**. Yields: **B-I**, 370 mg (14%); **B-II**, 640 mg (24%); **B-III**, 620 mg (23%). Found for **B-I**: C, 73.95; H, 6.97; N, 2.31%. Calcd for [Co(acac)(333NPPN)]{$B(C_6H_5)_4$}$_2$·$2H_2O$=$C_{74}H_{83}N_2P_2O_4B_2Co$: C, 73.64; H, 6.93; N, 2.32%. Found for **B-II**: C, 75.63; H, 6.99; N, 2.19%. Found for **B-III**: C, 75.25; H, 6.96; N, 2.34%. Calcd for [Co(acac)(333NPPN)]{$B(C_6H_5)_4$}$_2$·1/$2H_2O$=$C_{74}H_{80}N_2P_2O_{2.5}B_2Co$: C, 75.33; H, 6.83; N, 2.34%. Solubilities of the complexes are quite similar to those of the 323NPPN analogues.

***cis*α-[Co(ox)(*rac*(*P*)-323NPPN)]$B(C_6H_5)_4$·H_2O·$(CH_3)_2CO$ (C-I), *cis*β-[Co(ox)(*rac*(*P*)-323NPPN)]$B(C_6H_5)_4$·$(CH_3)_2CO$ (C-II), and *cis*β-[Co(ox)(*meso*(*P*)-323NPPN)]$B(C_6H_5)_4$ (C-III).** A methanol solution (15 cm^3) of 323NPPN (695 mg, 1.93 mmol) was added to a solution of K_3[Co(ox)$_3$]·$3H_2O$ (953 mg, 1.93 mmol) in a mixture of water (20 cm^3) and methanol (120 cm^3). The resulting brown solution was stirred overnight and filtered. The filtrate was diluted with water (2 dm^3), and applied on a column (ϕ 3 cm×120 cm) of SP-Sephadex C-25. By elution with a 0.05 mol dm^{-3} NaCl aqueous solution, three large orange bands (**C-I**, **C-II**, **C-III** in the order of elution) and several slow-moving small reddish bands developed. Each eluate of the three orange bands was evaporated to dryness under reduced pressure at 40 °C. The orange complex in the residue was extracted with ethanol. The extract was evaporated again to dryness under reduced pressure, and the residue was dissolved in water (10 cm^3). On addition of an aqueous $NaB(C_6H_5)_4$ solution, the aqueous solution yielded a precipitate of the complex. Complexes **C-I** and **C-II** were recrystallized from a mixture of acetone and water (2:1, 10 cm^3), while complex **C-III** was not recrystallized because of its insolubility in solvents useful for recrystallization. Yields: **C-I**, 90 mg (6%); **C-II**, 400 mg (25%); **C-III**, 270 mg (17%). Found for C-I: C, 65.41; H, 6.43; N, 2.98%. Calcd for [Co(ox)(323NPPN)]$B(C_6H_5)_4$·H_2O·$(CH_3)_2CO$=$C_{49}H_{58}N_2P_2O_6BCo$: C, 65.20; H, 6.48; N, 3.10%. Found for **C-II**: C, 66.48; H, 6.55; N, 3.09%. Calcd for [Co(ox)(323NPPN)]$B(C_6H_5)_4$·$(CH_3)_2CO$=$C_{49}H_{56}N_2P_2O_5BCo$: C, 66.52; H, 6.38; N, 3.17%. Found for **C-III**: C, 66.70; H, 6.27; N, 3.36%. Calcd for [Co(ox)(323NPPN)]$B(C_4H_5)_4$=$C_{46}H_{50}N_2P_2O_4BCo$: C, 66.84; H, 6.10; N, 3.39%. Complexes **C-I** and **C-II** are soluble in acetone and acetonitrile, but insoluble in water and methanol. Complex **C-III** is soluble in dimethyl sulfoxide, slightly soluble in acetone and acetonitrile, and insoluble in water and methanol.

***cis*α-[Co(ox)(*rac*(*P*)-333NPPN)]$B(C_6H_5)_4$·$2(CH_3)_2CO$ (D-I), *cis*β-[Co(ox)(*rac*(*P*)-333NPPN)]$B(C_6H_5)_4$·$2(CH_3)_2CO$ (D-II), and *cis*β-[Co(ox)(*meso*(*P*)-333NPPN)]$B(C_6H_5)_4$ (D-III).** These complexes were prepared by the same method as that for the 323NPPN complexes. Yields: **D-I**, 7%; **D-II**, 36%; **D-III**, 30%. Found for **D-I**: C, 66.67; H, 6.52; N, 2.66%. Found for **D-II**: C, 66.93; H, 6.63; N, 2.85%. Calcd for

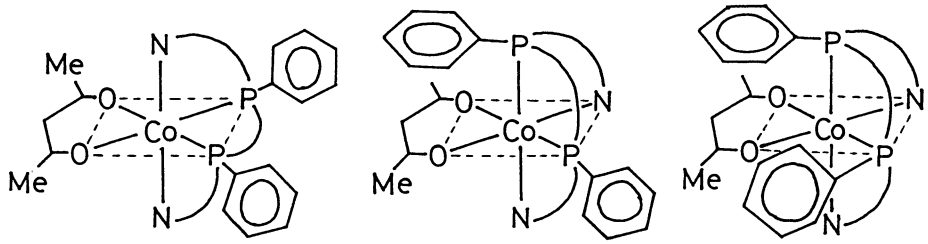
[Co(ox)(333NPPN)]$B(C_6H_5)_4 \cdot 2(CH_3)_2CO$=$C_{53}H_{64}N_2P_2O_6BCo$: C, 66.53; H, 6.74; N, 2.93%. Found for **D-III**: C, 67.07; H, 6.32; N, 3.35%. Calcd for [Co(ox)(333NPPN)]$B(C_6H_5)_4$=$C_{47}H_{52}N_2P_2O_4BCo$: C, 67.15; H, 6.24; N, 3.33%. The complexes show similar solubilities to those of the corresponding isomers of the 323NPPN complex.

Reactions of the Complexes with Hydrochloric Acid. All the complexes were converted to the chlorides, which were readily soluble in water, by treating with Dowex 1×8 (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 used for studying the reactivity of the complex in water or hydrochloric acid without further purification.

Results and Discussion

The [Co(acac or ox)(mnmNPPN)]$^{p+}$ (*m*, *n*=2, 3) complexes can have three possible geometrical isomers, *cisα-rac(P)*, *cisβ-rac(P)*, and *cisβ-meso(P)* (Fig. 2). The *meso(P)*-ligand can not form the *cisα* isomer, since the two terminal P–N chelate arms point to the same apical site with respect to the P–Co–P plane. These three isomers of [Co(acac or ox)(323NPPN or 333NPPN)]$^{p+}$ were obtained by reactions of [Co(acac)$_3$] or $[Co(ox)_3]^{3-}$ with 323NPPN or 333NPPN according to methods for the 232NPPN complexes described in a previous paper.[1] The structures of the acac complexes were assigned on the basis of ^{1}H NMR spectral data (Table 1). Complexes **A-I** and **B-I** show only one methyl signal of acac and are assigned to the *cisα-rac(P)* isomer, while other acac complexes **A-II**, **A-III**, **B-II**, and **B-III** are *cisβ* isomers, since they give two kinds of methyl signal. Of these complexes, **A-III** and **B-III** exhibit one of the two methyl signals at a remarkably high field, δ=0.93 and 1.04, respectively, compared with other methyl signals (δ=1.55—2.19). One methyl group in the *cisβ*-[Co(acac)(*meso(P)*-NPPN)]$^{2+}$-type complexes is located over the phenyl ring bonded to the phosphorus atom trans to the oxygen atom of acac (Fig. 2(c)), and is shielded by this phenyl group as reported for the corresponding 232NPPN complex.[1] Thus complexes **A-III** and **B-III** are assigned to the *cisβ-meso(P)* isomer, and the other **A-II** and **B-II** complexes to the *cisβ-rac(P)* isomer. Both *cisβ-rac(P)* and *cisβ-meso(P)* isomers have a phenyl group over the acac chelate ring, and show the methine proton signal of acac at a higher field than those of the *cisα* isomers (Table 1 and Fig. 2).

For the ox complexes, the *cisα* isomers (**C-I** and **D-I**) can be assigned from a similarity of the visible absorption spectra to those of the acac complexes. The *cisα* isomers show a nearly symmetrical first d–d band, while the *cisβ* isomers give a band with a shoulder in this region (Fig. 3). The spectra of the *cisβ-rac(P)* and *cisβ-*



(a) *cisα-rac(P)* (b) *cisβ-rac(P)* (c) *cisβ-meso(P)*

Fig. 2. Three possible isomers of [Co(acac)(*mnm*NPPN)]$^{2+}$.

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)*-323NPPN)]$^{2+}$	(**A-I**)	2.29		5.85	21.83 (2.70)	
cisβ-[Co(acac)(*rac(P)*-323NPPN)]$^{2+}$	(**A-II**)	1.55	1.99	4.85	22.46 (3.04)	
cisβ-[Co(acac)(*meso(P)*-323NPPN)]$^{2+}$	(**A-III**)	0.93	2.19	4.97	18.9 (2.4)[c]	22.85 (3.06)
cisα-[Co(acac)(*rac(P)*-333NPPN)]$^{2+}$	(**B-I**)	2.18		5.77	20.73 (2.62)	
cisβ-[Co(acac)(*rac(P)*-333NPPN)]$^{2+}$	(**B-II**)	1.57	1.95	5.20	19.7 (2.5)[c]	22.27 (2.79)
cisβ-[Co(acac)(*meso(P)*-333NPPN)]$^{2+}$	(**B-III**)	1.04	2.16	4.99	19.2 (2.4)[c]	22.27 (2.79)
cisα-[Co(ox)(*rac(P)*-323NPPN)]$^{+}$	(**C-I**)				22.06 (2.50)	
cisβ-[Co(ox)(*rac(P)*-323NPPN)]$^{+}$	(**C-II**)				22.38 (2.82)	
cisβ-[Co(ox)(*meso(P)*-323NPPN)]$^{+}$	(**C-III**)				18.8 (2.2)[c]	22.77 (2.96)
cisα-[Co(ox)(*rac(P)*-333NPPN)]$^{+}$	(**D-I**)				21.15 (2.48)	
cisβ-[Co(ox)(*rac(P)*-333NPPN)]$^{+}$	(**D-II**)				19.6 (2.3)[c]	22.07 (2.58)
cisβ-[Co(ox)(*meso(P)*-333NPPN)]$^{+}$	(**D-III**)				19.6 (2.4)[c]	22.12 (2.67)

a) δ, solvent $(CD_3)_2SO$. b) First absorption band $\tilde{\nu}/10^3$ cm^{-1} (log ε), solvent CH_3CN except for **C-III** and **D-III** (solvent $(CH_3)_2SO$). c) Shoulder.

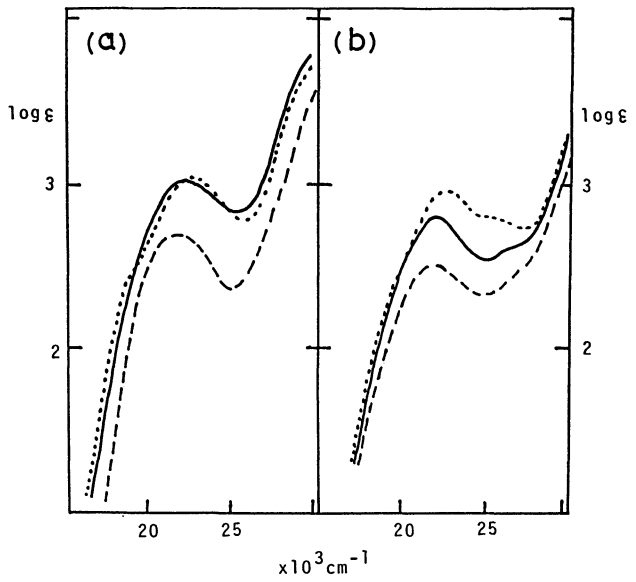


Fig. 3. Absorption spectra of (a) isomers **A-I** (——), **A-II** (——), **A-III** (·····), and (b) isomers **C-I** (——), **C-II** (——), **C-III** (·····).

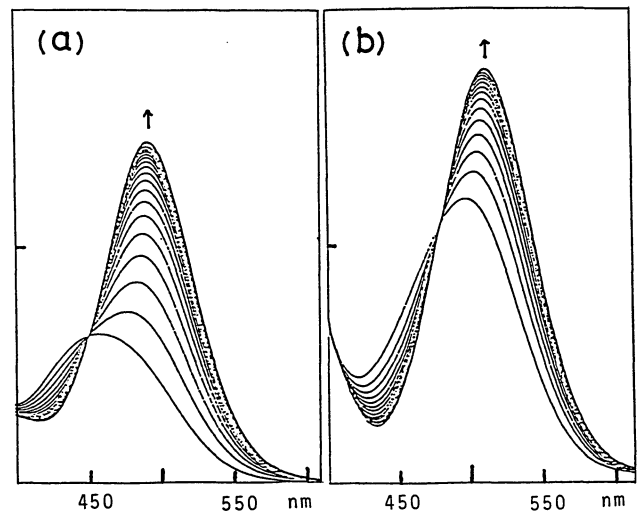


Fig. 4. Changes in absorption spectra of (a) isomer **A-I** in concd HCl recorded at 30 min intervals at 25 °C, and (b) isomer **B-I** in concd HCl recorded at 2 min intervals at 15 °C.

meso(*P*) isomers have a similar pattern, and no assignment can be made for the two *cisβ* isomers. Hence we derived the acac complexes from the ox complexes by treating with Li(acac), and assigned complexes **C-II** and **D-II** as the *cisβ-rac*(*P*) isomer and complexes **C-III** and **D-III** as the *cisβ-meso*(*P*) isomer.

The data of absorption spectra are given in Table 1. The spectra of the 333NPPN complexes are very similar to those of the corresponding 323NPPN and the previously reported 232NPPN[1] complexes. The first d–d bands of the *cisα* isomers shift to the higher energy side in the order of complexes, 333NPPN<232NPPN<323NPPN<222NPPN. The complexes where the central P–Co–P chelate forms a five-membered ring show the band at higher energy than those containing a six-membered P–Co–P chelate ring. The *cisβ* isomers have all a broad d–d band, and their peak positions do not differ appreciably among the complexes.

The water-soluble chlorides of *cisα*-[Co(acac)(323 or 333NPPN)]$^{2+}$ are stable in water and dil HCl (ca. 1 mol dm^{-3}), but react gradually with concd HCl, changing the color of solutions from orange to red. Figure 4 shows the spectral changes with time. The spectra change with an isosbestic point, and the changes are very similar to those observed for the corresponding 232NPPN and 222NPPN complexes in concd HCl.[1] The products isolated by reactions of the 232NPPN and 222NPPN complexes with concd HCl were *cisα*-[$CoCl_2$(232 or 222NPPN)]$^+$.[1] The spectral changes of the 323NPPN and 333NPPN complexes in concd HCl indicate the formation of *cisα*-[$CoCl_2$(323 or 333NPPN)]$^+$, since their final spectra are very similar to those of the 232NPPN and 222NPPN complexes under the same conditions. The half-life times of the reactions are 390 min at 20 °C for the 323NPPN complex and 6 min at 15 °C for the 333NPPN complex, while those of the 222NPPN and 232NPPN complexes were 87 min and 364 min at 20 °C, respectively.[1] The reactivity of *cisα*-[Co(acac)(*mnm*NPPN)]$^{2+}$ towards concd HCl decreases in the order of the 333NPPN>222NPPN >232NPPN≈323NPPN complexes. The differences in reactivity of the complexes seem to result from steric factors as indicated by molecular models. The 333NPPN complex is the most crowded structure, and the 222NPPN complex involves strain arising from the NPPN skeleton formed by three small five-membered chelate rings. These crowded 333NPPN and strained 222NPPN complexes would be less stable than the 232NPPN and 323NPPN complexes in which such unfavorable conditions are reduced to some extent.

The *cisα*-[Co(ox)(323 or 333NPPN)]Cl complexes in HCl solutions show similar spectral changes, and the final spectra coincide with those of the corresponding acac complexes in concd HCl, indicating the formation of the same *cisα*-dichloro complexes. The ox complexes are more reactive towards HCl than the acac complexes. The half-life times of the reactions in 2 mol dm^{-3} HCl at 30 °C are 43 min for the 323NPPN complex and 3 min for the 333NPPN complex, while it was 220 min for the 232NPPN complex.[1] Thus the reactivity towards HCl decreases in the order of the 333NPPN>323NPPN>232NPPN complexes. The 333NPPN complex is also the most reactive towards HCl as well as the acac analog. For the ox complexes, there is a fairly large difference in reactivity between the 323NPPN and 232NPPN complexes, in contrast to their acac complexes with similar reactivity described above.

The chlorides of *cisβ*-[Co(acac)(*rac*(*P*)- or *meso*(*P*)-323NPPN)]$^{2+}$ are stable in water and fairly strong HCl (ca. 5 mol dm^{-3}) solutions, but react slowly with concd

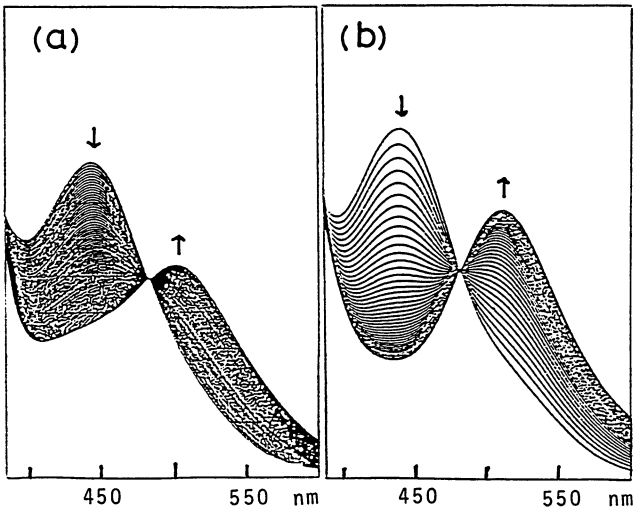


Fig. 5. Changes in absorption spectra of isomers **A-II** (a) and **A-III** (b) in concd HCl at 25 °C recorded at 60 min and 30 min intervals, respectively.

HCl. Figure 5 shows that the spectra of these *rac*(*P*) and *meso*(*P*) complexes change with an isosbestic point at 482 nm and 480 nm, respectively. The colors of solutions change from orange to red. The spectra of the red solutions show the first d–d band at 502 nm for the *rac*(*P*) and 509 nm for the *meso*(*P*) complexes. These values and spectral patterns are quite similar to those of [Co(acac)Cl(*rac*(*P*)- or *meso*(*P*)-232NPPNH$^+$)]$^{2+}$ (505 and 513 nm, respectively) reported in a previous paper.[1] The liberated amino group of the 232NPPN complexes in HCl solutions was found to be the one at the position trans to phosphorus, as shown in Fig. 6, from the ^{1}H NMR spectra of the complexes in DCl.[1] The red concd HCl solutions of the *rac*(*P*)- and *meso*(*P*)-323NPPN complexes turned orange by dilution with water. From the dilute solutions the original complexes were recovered by column chromatography, although some decomposition to Co(II) species occured for both complexes. These observations are also the same as those for the 232NPPN complexes. Therefore, the spectral changes of *cisβ*-[Co(acac)(*rac*(*P*)- or *meso*(*P*)-323NPPN)]$^{2+}$ in concd HCl are also attributable to the dissociation of the amino group trans to phosphorus to form [Co(acac)Cl(*rac*(*P*)- or *meso*(*P*)-323NPPNH$^+$)]$^{2+}$ shown in Fig. 6, although the ^{1}H NMR

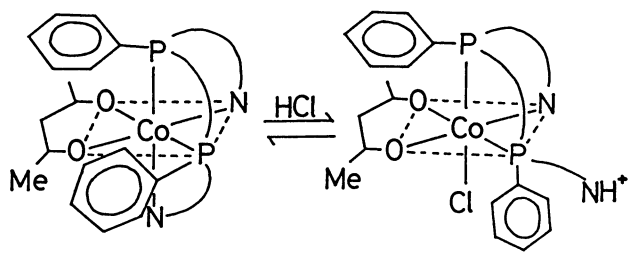


Fig. 6. Dissociation of one amino group of *cisβ*-[Co(acac)(323NPPN)]$^{2+}$ in concd HCl.

spectra in DCl did not show the liberated amino group because of the insufficient acidity of DCl for the 323NPPN complexes. The half-life times at 40 °C in concd HCl are 720 and 75 min for the *rac*(*P*)- and *meso*(*P*)-323NPPN complexes, respectively. The corresponding 232NPPN complexes are more reactive and dissociate the amino group fairly rapidly in 0.1 mol dm^{-3} HCl at room temperature.[1] The remarkable reactivity of the 232NPPN complexes may be attributed to the larger strain of the five-membered chelate ring of the leaving amino group linked meridionally with the P–Co–P chelate ring. The half-life time of 720 min for the reaction of *cisβ*-[Co(acac)(*rac*(*P*)-323NPPN)]$^{2+}$ in concd HCl at 40 °C is much longer than that of the reaction of the *cisα* isomer to *cisα*-[CoCl$_2$(*rac*(*P*)-323NPPN)]$^+$ (21 min at 40 °C in concd HCl), while the corresponding 232NPPN complexes are more stable in the *cisα* isomer than the *cisβ* isomer.

The *cisβ*-[Co(acac)(*rac*(*P*)- or *meso*(*P*)-333NPPN)]$^{2+}$ complexes show different reactivity from the other *cisβ*-acac complexes. The complexes, which are stable in water, react slowly with concd HCl to give a green-brown solution. These solutions exhibit a band around 630 nm, which can be assigned to the split component (Ia) of the first d–d band of the *trans*-[CoCl$_2$(NPPN)]$^+$-type complex.[5] The *trans*-dichloro complexes seem to decompose gradually in concd HCl, since the bands show weak structures characteristic of [CoCl$_4$]$^{2-}$ with passage of time. The reactivity of [Co(acac)(333NPPN)]$^{2+}$ towards HCl is *cisα-rac*(*P*) isomer$\gg$*cisβ-meso*(*P*) isomer$>$*cisβ-rac*(*P*) isomer. The 333NPPN complexes are also more stable in the *cisβ* form than the *cisα* form.

All the isomers of *cisβ*-[Co(ox)(323 or 333NPPN)]Cl are stable in water, but react with concd HCl. Both spectra of *rac*(*P*)- and *meso*(*P*)-323NPPN complexes in concd HCl change in a similar rate with isosbestic points. The final spectrum of the *rac*(*P*) isomer coincides with that of *cisα*-[CoCl$_2$(*rac*(*P*)-323NPPN)]$^+$ yielded from *cisα*-[Co(acac)(*rac*(*P*)-323NPPN)]$^{2+}$ in concd HCl, while that of the *meso*(*P*) isomer shows the first d–d band at 511 nm. The reaction product could not be isolated because of poor crystallization and a small amount. However, the product was tentatively assigned to *cisβ*-[CoCl$_2$(*meso*(*P*)-323NPPN)]$^+$ from the peak position of the d–d band. No starting oxalato complex was detected from the reaction product by column chromatography. The *cisβ* isomers of *rac*(*P*)- and *meso*(*P*)-333NPPN complexes are more reactive than those of the 323NPPN complexes. The orange solutions of the two 333NPPN complexes in 8 mol dm^{-3} HCl slowly turn dark green, and the spectra exhibit a band around 620 nm, which is characteristic of the *trans*-dichloro complex. The *meso*(*P*) isomer is more reactive than the *rac*(*P*) isomer, and its spectral change in a HCl solution has isosbestic points. For the *rac*(*P*) isomer, there is no isosbestic point in the spectra, indicating the presence of a rather stable intermediate

during the reaction of the *cisβ*-oxalato to *trans*-dichloro complexes. However, no further studies were made in this paper.

From the present and the previous papers,[1] the following features are pointed out for the [Co(acac or ox)(*mnm*NPPN)]$^{p+}$-type complexes. (1) The [Co(acac or ox)(*mnm*NPPN)]$^{p+}$ (*m*, *n*=2, 3) complexes yielded all of the three possible isomers (*cisα-rac*(*P*), *cisβ-rac*(*P*), and *cisβ-meso*(*P*)) except that the 222NPPN complex formed no *cisβ-rac*(*P*) isomer. On the other hand, the analogous tetramine (*mnm*NNNN) complexes of the type, [Co(bidentate)(*mnm*NNNN)]$^{p+}$ often afford particular isomers. For example, the 232NNNN complex yields only the *cisβ-rac*(*N*) isomer,[6] and the 323NNNN complex two isomers, *cisβ-rac*(*N*) and *cisβ-meso*(*N*), no *cisα-rac*(*N*) isomer being known.[7] Only known complex of 333NNNN is *cisβ*-[Co(sal)(333NNNN)]$^{+}$ (sal=salycilate ion),[8] and it is reported that [Co(ox)-(333NNNN)]$^{+}$ is too unstable to be isolated,[9] in contrast to the stable 333NPPN complex. The formation of all possible isomers in the *mnm*NPPN complexes may be related in part to the optical stability of a phosphorus donor atom. In the *mnm*NNNN complexes, inversion of the secondary amine group takes place rather easily, and the complexes tend to be stabilized in particular isomers. (2) All *cisα*-[Co(acac or ox)(*rac*(*P*)-NPPN)]$^{p+}$ react with hydrochloric acid to yield *cisα*-[$CoCl_2$(*rac*(*P*)-NPPN)]$^{+}$, and the 222NPPN and 333NPPN complexes are more reactive than the 232NPPN and 323NPPN complexes where the NPPN skeletal structures are formed by a combination of five- and six-membered chelate rings. The *cisα*-[Co(acac)(222NNNN)]$^{2+}$ complex is quite stable under the same conditions.[1] (3) Except the 333NPPN complexes, all *cisβ*-[Co(acac)-(NPPN)]$^{2+}$ in HCl solutions dissociate the amino group trans to phosphorus of NPPN reversibly depending on the acidity of solution, yielding [Co(acac)(Cl or H_2O)($NPPNH^{+}$)]$^{p+}$. Such a reversible dissociation of an amino end group of chelate has never been reported for cobalt(III) complexes. The *cisβ*-[Co(acac)(*rac*(*P*)- or *meso*(*P*)-333NPPN)]$^{2+}$ complexes yield the *trans*-dichloro complex by reaction with concd HCl. (4) All *cisβ*-[Co(ox)(NPPN)]$^{+}$ release the oxalate ion in hydrochloric acid to form the *cisα*-, *cisβ*-, or *trans*-dichloro complex. No dissociation of the amino group of NPPN was observed. (5) In hydrochloric acid solutions, the 222NPPN and 232NPPN complexes are more stable in the *cisα* isomer than the *cisβ* isomer, while the 323NPPN and 333NPPN complexes are more stable in the *cisβ* isomer than the *cisα* isomer. For each NPPN, the *cisβ-rac*(*P*) isomer is more stable than the *cisβ-meso*(*P*) isomer.

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