Preparation, and Structural and Spectroscopic Characterization of Cobalt(III) Phosphine Complexes of the Type, $[Co(CN)_{4-2n}(acac)_n(P)_2]^{(n-1)+}$ (acac=Acetylacetonate Ion, n=0,1,2, and P=$P(CH_3)_x(C_6H_5)_{3-x}$, x=0,1,2,3)

Kazuo KASHIWABARA, Katsuaki KATOH, Tomoji OHISHI, Junnosuke FUJITA,* and Muraji SHIBATA**

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

*** Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920*

(Received June 15, 1981)

A series of the complexes, $[Co(CN)_{4-2n}(acac)_n(P)_2]^{(n-1)+}$ (acac=acetylacetonate ion, P=$P(CH_3)_x(C_6H_5)_{3-x}$) and several related complexes were prepared. For $[Co(acac)_2(P)_2]^+$, the $P(CH_3)_3$ and $P(CH_3)(C_6H_5)_2$ complexes afford only the *cis* and the *trans* isomers, respectively, while the $P(CH_3)_2(C_6H_5)$ complex forms both *cis* and *trans* isomers. No $P(C_6H_5)_3$ ligand gave the bis(acac)-type complex. The *trans* isomers show a strong absorption band in the region of the first absorption band, which is assumed to involve charge transfer transitions between the cobalt(III) ion and a phosphine, while the *cis* isomers give usual absorption spectra, exhibiting the first d-d absorption band of medium intensity. The methyl and phenyl groups on a phosphorus atom in both *cis* and *trans* isomers show triplet signals in the ^1H and ^{13}C NMR spectra due to virtual coupling. A *trans*(P,P) configuration was assigned to all the complexes of $[Co(CN)_2(acac)(P)_2]$ on the basis of the NMR and electronic spectra. For $[Co(CN)_4(P)_2]^-$, a *trans* configuration was assigned from the electronic spectra.

Little work has been reported for cobalt(III) complexes containing unidentate phosphines,[1] except for those of organo cobalt(III)- and bis(dimethylglyoximato)cobalt(III)-type, the latter type of which has been studied extensively as a model compound of Vitamin B_{12}.[2,3] In previous papers,[4,5] one of the present authors (M.S.) prepared several cobalt(III) complexes containing triphenylphosphine. Very recently we succeeded in isolating a pair of geometrical isomers of the bis(acetylacetonato)bis(dimethylphenylphosphine)cobalt(III) complex, and clarified some chemical and spectroscopic properties.[6] The difference in electronic spectra between the isomers was quite remarkable. In this paper, we extended the study to complexes of the type, $[Co(CN)_{4-2n}(acac)_n(P)_2]^{n-1}$ (acac=acetylacetonate ion, n=0,1,2) containing a series of phosphines, $P(CH_3)_x(C_6H_5)_{3-x}$ (x=0,1,2,3). Cyanide and acetylacetonate ions appear to afford fairly stable cobalt(III) complexes with unidentate phosphine ligands. Chemical properties such as stability and geometrical isomerism of those complexes would depend on the kinds of not only phosphine ligands, but also other ligands coexisting in a complex.

Experimental

The phosphine ligands were prepared according to the methods reported,[7] and handled under nitrogen atmosphere until they formed cobalt(III) complexes. Solvents were dried in the usual way and degassed in a stream of nitrogen. Absorption, and ^1H and ^{13}C NMR spectra were recorded on a Hitachi 323 spectrophotometer, and JEOL JNM-PMX 60 and JNM-FX 100 spectrometers, respectively.

trans-$[Co(acac)_2(PMePh_2)_2]PF_6$ *and* trans-$[Co(acac)_2(H_2O)(PMePh_2)]PF_6$. Methyldiphenylphosphine ($PMePh_2$) (0.9 g, 4.5 mmol) was added to a mixture of $[Co(acac)_3]$ (0.7 g, 2 mmol) and a small amount of active charcoal in ethanol (60 cm³). The mixture was stirred at 25 °C for a day, and filtered. The dark red brown filtrate was diluted to 4 dm³ with a mixture of water and ethanol (2:1). The solution was poured onto a small column of SP-Sephadex C-25 (ϕ2 cm×3 cm) in the Na^+ form. After the column had been thoroughly washed with a mixture of water and ethanol (2:1), the product adsorbed was eluted with a 0.05 mol/dm³ NaCl solution in a mixture of water and ethanol (2:1). The eluate gave a red brown precipitate on addition of $NaPF_6$. The precipitate was filtered and dissolved in a small amount of CH_2Cl_2. The solution was mixed with ethanol and stored in a refrigerator to give red brown crystals of *trans*-$[Co(acac)_2(PMePh_2)_2]PF_6$. Yield: 35%. The corresponding *cis* complex was not yielded.

A methanol solution (*ca.* 30 cm³) of *trans*-$[Co(acac)_2(PMePh_2)_2]PF_6$ (*ca.* 50 mg) was allowed to stand for a while at room temperature, and then chromatographed by use of a column of Sephadex LH-20 (ϕ2.7 cm×50 cm). By elution with methanol, the band was separated into two, the first blue-green and the second red brown (the starting complex) bands. The effluent of the first band was concentrated to a small volume under reduced pressure. The concentrate was mixed with a small amount of water and allowed to stand at room temperature to yield blue-green crystals of *trans*-$[Co(acac)_2(H_2O)(PMePh_2)]PF_6$.

cis- *and* trans-$[Co(acac)_2(PMe_2Ph)_2]PF_6$, *and* trans-$[Co(acac)_2(H_2O)(PMe_2Ph)]PF_6$. These complexes were prepared by modifiing the method reported previously.[6] A mixture of $[Co(acac)_3]$ (0.7 g, 2 mmol), PMe_2Ph (0.55 g, 4 mmol), and a small amount of active charcoal in ethanol (60 cm³) was stirred at room temperature for 2 h, and filtered. The red brown filtrate was diluted with water to 3 dm³. The solution was poured onto a small column (ϕ 2.7 cm×3 cm) of SP-Sephadex C-25, and then the column was washed with water. The Sephadex adsorbed the product was charged on the top of an SP-Sephadex C-25 column (ϕ 2.7 cm×50 cm). By elution with an aqueous 0.02 mol/dm³ NaCl solution, the column showed two bands. The fraction of the first blue-violet band was concentrated to a small volume under reduced pressure. The concentrate gave a blue-violet precipitate on addition of $NaPF_6$. The precipitate was dissolved in a mixture of methanol and water (5:1). The solution was allowed to stand at room temperature to give blue-violet crystals of *trans*-$[Co(acac)_2(H_2O)(PMe_2Ph)PF_6$. Yield: *ca.* 15%. The effluent of the second red brown band gave red brown crystals of *cis*-$[Co(acac)_2(PMe_2Ph)_2]PF_6$ by the same method as the above. Yield: *ca.* 50%.

The *trans*-$[Co(acac)_2(PMe_2Ph)_2]PF_6$ complex was obtained by adding a slight excess of PMe_2Ph to an ethanol solu-

tion of *trans*-$[Co(acac)_2(H_2O)(PMe_2Ph)]PF_6$, red orange crystals being deposited in *ca.* 15 min. Yield: 80%.

cis-$[Co(acac)_2(PMe_3)_2]PF_6$. Red crystals of this complex were obtained by a method similar to that for the PMe_2Ph complex, using PMe_3 instead of PMe_2Ph. Yield: 50%. The formation of the corresponding *trans* isomer and the aqua complex was not observed in column chromatography.

$[Co(acac)_2(Ph_2PCH_2CH_2PPh_2)]PF_6$. This complex was prepared by the method reported previously.[8]

$[Co(acac)_2(Me_2PCH_2CH_2PMe_2)]PF_6$. A methanol solution (100 cm^3) containing $[Co(acac)_3]$ (0.25 g, 0.7 mmol) and 1,2-bis(dimethylphosphino)ethane (0.1 g, 0.7 mmol) was stirred at room temperature for 20 h. A mixture of diethyl ether and water (400 cm^3, 1:3) was added to the resulting orange solution in order to extract the unreacted free diphosphine into the diethyl ether. The diethyl ether layer was separated off, and the aqueous solution was diluted ten times with water. The solution was chromatographed by a method similar to that for the PMe_2Ph complex. The first orange eluate was evaporated to dryness under reduced pressure, and the residue was extracted with chloroform. The extract was evaporated to dryness, and the residue was again dissolved in water. Red crystals of the complex were obtained on addition of $NaPF_6$. Yield: *ca.* 20%.

trans(P,P)-$[Co(CN)_2(acac)(PPh_3)_2]$. This complex was prepared by the method reported previously.[4]

trans(P,P)-$[Co(CN)_2(acac)(PMePh_2)_2]$. A mixture of $K[Co(CN)_2(acac)_2]$[9] (0.7 g, 2 mmol) and $PMePh_2$ (0.8 g, 4 mmol) in ethanol (60 cm^3) was stirred at 30 °C for 6 h. The resulting orange yellow solution was concentrated under reduced pressure to *ca.* 15 cm^3. An orange precipitate of the crude complex was obtained on standing, which was filtered. The filtrate was chromatographed by use of an alumina column (ϕ 4 cm × 50 cm) and a mixture of hexane and ethanol (1:10). The orange yellow eluate was concentrated to a small volume. The concentrate was rechromatographed by use of a Sephadex LH-20 column (ϕ 3 cm × 60 cm) and a mixture of hexane and ethanol (5:1). Another crop of the complex was obtained by evaporating the eluate to dryness under reduced pressure. The combined first and second crops were recrystallized from a mixture of dichloromethane and ethanol (4:1). Yield: *ca.* 55%.

trans(P,P)-$[Co(CN)_2(acac)(PMe_2Ph)_2]$. This complex was prepared by a method similar to that for the $PMePh_2$ complex, using PMe_2Ph instead of $PMePh_2$. The eluate which was obtained by rechromatography with a Sephadex LH-20 column was concentrated to a small volume under reduced pressure. The concentrate was mixed with a small amount of water and allowed to stand, yielding orange yellow crystals of the complex. Yield: *ca.* 25%.

trans(P,P)-$[Co(CN)_2(acac)(PMe_3)_2]$ *and* cis-$[Co(CN)(acac)_2(PMe_3)]$. A mixture of $K[Co(CN)_2(acac)_2]$ (0.7 g, 2 mmol) and PMe_3 (0.2 g, 2.6 mmol) in methanol (100 cm^3) was stirred for 20 h at room temperature. The resulting orange solution was chromatographed by using an alumina column (ϕ2 cm × 30 cm) and methanol. The eluate was concentrated to a small volume under reduced pressure. The concentrate was rechromatographed by use of a Sephadex LH-20 column (ϕ2 cm × 50 cm) and a mixture of hexane and ethanol (10:1). Each eluate of the first red and the second orange bands was evaporated to dryness, and the residue was dissolved in a small amount of chloroform. The chloroform solutions obtained from the first and the second eluates gave crystals of red *cis*-$[Co(CN)(acac)_2(PMe_3)]$ and orange *trans*(P,P)-$[Co(CN)_2(acac)(PMe_3)_2]$, respectively, on addition of hexane. Yield: *ca.* 7% for each complex.

cis-$[Co(CN)_2(acac)(Ph_2PCH_2CH_2PPh_2)]$. A mixture of $K[Co(CN)_2(acac)_2]$ (0.2 g, 0.6 mmol) and $Ph_2PCH_2CH_2PPh_2$ (0.25 g, 0.6 mmol) in methanol (100 cm^3) was stirred at 55 °C for 4 h. The resulting orange solution was evaporated to dryness, and the residue was extracted with hot benzene. The extract afforded orange crystals of the complex on standing at room temperature. Yield: 50%.

trans(P,P)-$K[Co(CN)_4(PPh_3)_2]$. The previous method[5] was modified. A mixture of PPh_3 (5.2 g, 20 mmol) and $K_3[Co(CN)_5I]$[10] (4.3 g, 10 mmol) in glacial acetic acid (70 cm^3) was stirred at 75 °C for 6 h, and filtered. The yellow filtrate was mixed with water (500 cm^3) and stored in a refrigerator to yield a yellow precipitate. It was filtered, washed with benzene in order to remove free PPh_3, and then dissolved in a mixture of dichloromethane and methanol (1:1). The solution was chromatographed by use of a Sephadex LH-20 column (ϕ1.5 cm × 30 cm) and a mixture of dichloromethane and methanol (1:1). The first main yellow eluate was concentrated to a small volume under reduced pressure. The concentrate was mixed with a small amount of water and stored in a refrigerator to yield orange crystals of the complex. Yield: 15%.

trans(P,P)-$Na[Co(CN)_4(PMePh_2)_2]$. The method of Maki and Ohshima[11] for the PPh_3 complex was modified. A suspension of $Na_5[Co(SO_3)_2(CN)_4]3H_2O$[12] (1.2 g, 3.5 mmol) and $PMePh_2$ (1.1 g, 5.5 mmol) in glacial acetic acid (40 cm^3) was stirred at 75 °C for 7 h. The resulting orange yellow solution was evaporated to dryness under reduced pressure. The residue was extracted with methanol, and the extract was evaporated to dryness. The residue was again extracted with methanol. The extract was concentrated to *ca.* 20 cm^3 under reduced pressure to yield a yellow precipitate. It was filtered and dissolved in methanol. The methanol solution was chromatographed by use of a Sephadex LH-20 column (ϕ1.5 cm × 30 cm) and methanol. The first main yellow eluate was concentrated to a small volume. The concentrate was mixed with a small amount of water and stored in a refrigerator to give orange crystals of the complex. Yield: 10%. The complex can also be prepared from $K_3[Co(CN)_5I]$ and $PMePh_2$ by a method similar to that for the PPh_3 complex.

trans(P,P)-$K[Co(CN)_4(PMe_2Ph)_2]$. A mixture of PMe_2Ph (2.2 g, 16 mmol) and $K_3[Co(CN)_5I]$ (3.4 g, 8 mmol) in a mixture (60 cm^3) of dioxane and water (5:2) was stirred at 50 °C for 4 h, and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was extracted with a mixture of methanol and dichloromethane (3:1). The extract was chromatographed by use of a Sephadex LH-20 column (ϕ 1.5 cm × 30 cm) and a mixture of methanol and dichloromethane (3:1). The first main yellow eluate was concentrated to a small volume. The concentrate was mixed with a small amount of ethanol and stored in a refrigerator to yield yellow crystals of the complex. Yield: 10%.

$K[Co(CN)_4(Ph_2PCH_2CH_2PPh_2)]$. A mixture of $K_3[Co(CN)_5I]$ (4.3 g, 10 mmol) and $Ph_2PCH_2CH_2PPh_2$ (4.0 g, 10 mmol) in a mixture (100 cm^3) of dioxane and water (7:3) was stirred at 75 °C for 7 h, and filtered. The filtrate was evaporated to dryness under reduced pressure, and the residue was extracted with methanol. The extract was evaporated to dryness, and the residue was again extracted with methanol. The extract was chromatographed by use of a Sephadex LH-20 column (ϕ 1.5 cm × 30 cm) and methanol. The second main yellow eluate was concentrated to a small volume under reduced pressure. The concentrate was mixed with a small amount of ethanol and stored

Table 1. Elemental analyses and absorption spectral data

Complex	C (%) Found(Calcd)	H (%) Found(Calcd)	N (%) Found(Calcd)	$\tilde{\nu}/10^3$ cm^{-1} (log ε)	Solvent
trans-$[Co(acac)_2(PMePh_2)_2]PF_6$	53.53(53.88)	4.96(5.02)	—	21.5(4.13)	a)
trans-$[Co(acac)_2(PMe_2Ph)_2]PF_6$	46.03(46.03)	5.22(5.35)	—	22.8(4.13)	a)
cis-$[Co(acac)_2(PMe_2Ph)_2]PF_6$	45.75(46.03)	5.03(5.33)	—	18.4(2.49), 21.3(2.6)*	b)
cis-$[Co(acac)_2(PMe_3)_2]PF_6$	34.66(34.67)	5.77(5.82)	—	18.8(2.40) 22.6(2.6)*	b)
$[Co(acac)_2(Ph_2PCH_2CH_2PPh_2)]PF_6$	54.10(54.01)	4.91(4.78)	—	20.2(2.99)	b)
$[Co(acac)_2(Me_2PCH_2CH_2PMe_2)]PF_6$	34.56(34.80)	5.67(5.48)	—	19.3(2.4),* 23.4(2.9)*	b)
trans-$[Co(acac)_2(H_2O)(PMePh_2)]PF_6$	44.37(44.53)	4.81(4.71)	—	16.6(2.51)	b)
trans-$[Co(acac)_2(H_2O)(PMe_2Ph)]PF_6\cdot 0.5H_2O$	38.14(38.11)	4.99(4.99)	—	17.4(2.53)	b)
cis-$[Co(acac)_2(CN)(PMe_3)]$	46.83(46.55)	6.64(6.58)	3.59(3.88)	19.4(2.2),* 23.5(2.7)*	b)
trans(P,P)-$[Co(CN)_2(acac)(PPh_3)_2]$	69.86(70.30)	5.45(5.08)	3.75(3.81)	20.9(3.58)	a)
trans(P,P)-$[Co(CN)_2(acac)(PMePh_2)_2]$	64.63(64.91)	5.52(5.46)	4.29(4.59)	22.3(3.57)	b)
trans(P,P)-$[Co(CN)_2(acac)(PMe_2Ph)_2]\cdot H_2O$	55.21(54.77)	6.22(6.20)	5.74(5.55)	23.7(3.55)	b)
trans(P,P)-$[Co(CN)_2(acac)(PMe_3)_2]$	43.07(43.10)	6.76(6.96)	7.35(7.73)	24.5(3.26)	b)
cis-$[Co(CN)_2(acac)(Ph_2PCH_2CH_2PPh_2)]$	65.10(65.14)	5.00(5.13)	4.44(4.60)	23.4(3.12)	b)
trans-$K[Co(CN)_4(PPh_3)_2]\cdot 0.5H_2O$	66.15(65.30)	4.74(4.30)	7.48(7.62)	26.5(3.3)*	b)
trans-$Na[Co(CN)_4(PMePh_2)_2]\cdot 4H_2O$	54.12(54.14)	5.07(5.14)	8.53(8.42)	28.6(3.3)*	b)
trans-$K[Co(CN)_4(PMe_2Ph)_2]\cdot 2.5H_2O$	46.15(45.89)	4.94(5.20)	10.78(10.70)	29.2(3.25)	b)
$K[Co(CN)_4(Ph_2PCH_2CH_2PPh_2)]\cdot 0.5H_2O$	58.94(59.11)	3.98(4.13)	9.08(9.19)	29.6(2.92)	b)

*: Shoulder. a) CH_2Cl_2. b) CH_3OH.

Table 2. ^{1}H NMR spectral data, δ (J/Hz)[a]

Complex	acac -CH_3	acac -CH	P-CH_3	Solvent
trans-$[Co(acac)_2(PMePh_2)_2]PF_6$	1.52	4.47	2.10(t, 8.0)	b)
trans-$[Co(acac)_2(PMe_2Ph)_2]PF_6$	1.71	4.94	1.71(t, 8.3)	c)
cis-$[Co(acac)_2(PMe_2Ph)_2]PF_6$	1.91	5.43	1.35(t, 13.4)	b)
	2.04		1.41(t, 14.1)	
cis-$[Co(acac)_2(PMe_3)_2]PF_6$	1.83	5.48	m	b)
	2.17			
$[Co(acac)_2(Ph_2PCH_2CH_2PPh_2)]PF_6$	1.64	4.93	—	b)
	1.88			
$[Co(acac)_2(Me_2PCH_2CH_2PMe_2)]PF_6$	1.76	5.42	m	b)
	2.18			
cis-$[Co(CN)(acac)_2(PMe_3)]$	1.82	5.42	1.56(d, 13.2)	b)
	1.88	5.50		
	2.11			
	2.30			
trans(P,P)-$[Co(CN)_2(acac)(PPh_3)_2]$	1.07	4.58	—	b)
trans(P,P)-$[Co(CN)_2(acac)(PMePh_2)_2]$	1.12	4.71	2.41(t, 8.4)	b)
trans(P,P)-$[Co(CN)_2(acac)(PMe_2Ph)_2]\cdot H_2O$	1.18	4.68	2.06(t, 8.4)	b)
trans(P,P)-$[Co(CN)_2(acac)(PMe_3)_2]$	1.90	5.28	1.67(t, 8.0)	b)
cis-$[Co(CN)_2(acac)(Ph_2PCH_2CH_2PPh_2)]$	1.11	4.96	—	b)
	1.93			
trans-$Na[Co(CN)_4(PMePh_2)_2]\cdot 4H_2O$	—	—	2.41(t, 9.0)	d)
trans-$K[Co(CN)_4(PMe_2Ph)_2]\cdot 2.5H_2O$	—	—	2.06(t, 9.0)	e)

a) J refers to the interval of two outer peaks of a triplet, and d: doublet, m: multiplet. b) $CDCl_3$. c) CD_2Cl_2. d) CD_3OD. e) D_2O.

in a refrigerator to yield yellow crystals of the complex. Yield: 20%.

Analytical data of the complexes are given in Table 1.

Results and Discussion

The $[Co(acac)_2(P)_2]^+$ *Complexes.* In a previous paper,[6] we have prepared *cis*- and *trans*-$[Co(acac)_2(PMe_2Ph)_2]^+$ and *trans*-$[Co(acac)_2(H_2O)(PMe_2Ph)]^+$

TABLE 3. ^{13}C NMR SPECTRAL DATA FOR PHOSPHINE LIGANDS, δ (J/Hz)[a]

Complex	P-CH_3	P-C_6H_5 P-C_1	*o*-C	*m*-C	*p*-C	Solvent
trans-$[Co(acac)_2(PMePh_2)_2]PF_6$	7.4(24.4)	128.3(39.1)	132.5(9.8)	128.9(8.5)	131.4	c)
trans-$[Co(acac)_2(PMe_2Ph)_2]PF_6$	9.1(24.4)	131.7(40.4)	131.3(9.7)	129.4(9.9)	131.5	d)
cis-$[Co(acac)_2(PMe_2Ph)_2]PF_6$	9.6(29.0) 10.6(29.3)	131.3(45.1)	130.9(8.6)	129.6(9.8)	131.9	d)
cis-$[Co(acac)_2(PMe_3)_2]PF_6$	11.9(29.3)	—	—	—	—	c)
cis-$[Co(CN)(acac)_2(PMe_3)]$	12.2(30.5)[b]	—	—	—	—	c)
trans(P,P)-$[Co(CN)_2(acac)(PPh_3)_2]$	—	129.9(41.6)	135.3(9.8)	128.3(9.8)	130.7	c)
trans(P,P)-$[Co(CN)_2(acac)(PMePh_2)_2]$	15.7(34.2)	130.7(43.9)	133.8(9.8)	128.5(9.8)	130.7	c)
trans(P,P)-$[Co(CN)_2(acac)(PMe_2Ph)_2]\cdot H_2O$	12.4(32.5)	132.3(40.8)	130.9(9.1)	128.3(8.8)	130.1	c)
trans(P,P)-$[Co(CN)_2(acac)(PMe_3)_2]$	13.4(29.3)	—	—	—	—	c)
trans-$Na[Co(CN)_4(PMePh_2)_2]\cdot 4H_2O$	18.6(35.2)	134.9(50.0)	134.5(9.8)	129.0(9.8)	131.7	e)
trans-$K[Co(CN)_4(PMe_2Ph)_2]\cdot 2.5H_2O$	17.1(36.1)	137.1(47.9)	131.8(8.8)	129.4(9.8)	131.4	e)

a) J refers to the interval of two outer peaks of a triplet. b) Doublet. c) $CDCl_3$. d) CD_2Cl_2. e) CD_3OD.

by a reaction of $[Co(acac)_3]$ with PMe_2Ph in ethanol in the presence of active charcoal. The geometrical configurations of these complexes can be easily assigned on the basis of the ^1H and ^{13}C NMR spectra (Tables 2 and 3). The bis(PMe_2Ph) complexes isolated as hexafluorophosphate are insoluble in water, but soluble in common organic solvents such as ethanol or dichloromethane. The *cis* isomer is quite stable in such solvents. The corresponding *trans* isomer is stable in dichloromethane, but hydrolyzes in ethanol (not anhydrous) to afford *trans*-$[Co(acac)_2(H_2O)(PMe_2Ph)]^+$ which is stable to further hydrolysis. The hydrolysis is depressed in the presence of excess PMe_2Ph Thus the *trans* bis(PMe_2Ph) isomer in hydrous ethanol gives the following equilibrium:

$$trans\text{-}[Co(acac)_2(PMe_2Ph)_2]^+ + H_2O \rightleftharpoons trans\text{-}[Co(acac)_2(H_2O)(PMe_2Ph)]^+ + PMe_2Ph$$

The *trans* bis(PMe_2Ph) isomer in ethanol slowly isomerizes to the *cis* isomer on addition of active charcoal, attaining an equilibrium between the two isomers. In fact the *cis* isomer also isomerizes to the *trans* isomer under the same conditions, the *cis* isomer being predominant at equilibrium at room temperature as indicated by the preparative experiment.

The $PMePh_2$ and PMe_3 ligands used in this study give only *trans*-$[Co(acac)_2(PMePh_2)_2]^+$ and *cis*-$[Co(acac)_2(PMe_3)_2]^+$, respectively under similar experimental conditions to that for the PMe_2Ph complex. The *trans*-$[Co(acac)_2(H_2O)(PMePh_2)]^+$ complex was derived from the *trans* bisphosphine complex by hydrolysis. These experimental results including those of the PMe_2Ph complex suggest that the $[Co(acac)_2(P)_2]^+$-type complex is stabilized in the *cis* isomer, unless there is steric hindrance between two phosphine ligands in the *cis* positions. The preponderance of *cis* coordination of phosphine ligands will be brought about by the strong *trans* effect of a phosphine ligand.[13] The $PMePh_2$ ligand might be too bulky to occupy *cis* positions in the bis(acac)cobalt(III) complex. No PPh_3 reacted with $[Co(acac)_3]$ in ethanol in the presence of active charcoal. On raising the reaction temperature reduction of Co(III) took place.

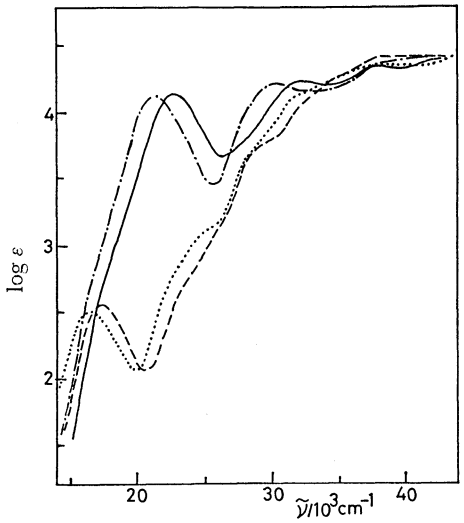

Fig. 1. Absorption spectra of *trans*-$[Co(acac)_2(PMe_2Ph)_2]^+$ (——), *trans*-$[Co(acac)_2(PMePh_2)_2]^+$ (—·—), *trans*-$[Co(acac)_2(H_2O)(PMe_2Ph)]^+$ (----), and *trans*-$[Co(acac)_2(H_2O)(PMePh_2)]^+$ (·····).

The absorption spectra of *trans*-$[Co(acac)_2(P)_2]^+$ and *trans*-$[Co(acac)_2(H_2O)(P)]^+$ ($P=PMePh_2$, PMe_2Ph) are compared in Fig. 1. The spectra of the *trans* bisphosphine complexes differ markedky from those of the aqua complexes; the formers show a very strong band around 22000 cm^{-1}. The *cis*-$[Co(acac)_2(P)_2]^+$ ($P=PMe_2Ph$, PMe_3) complexes exhibit no such strong bands in this region (Fig. 2). The strong bands of the *trans* bisphosphine complexes can be assigned to a charge transfer transition between the Co(III)–phosphine because of the strong intensity. The bands have a shoulder in the low energy side, which can be assigned to a part of the first d-d band. The aqua complexes show clearly the first d-d band, and the spectra resemble that of *trans*-$[Co(acac)_2(NH_3)_2]^+$ which gives the first d-d band at 18500 cm^{-1} ($\log \varepsilon = 1.89$).[14] The *cis*-$[Co(acac)_2(P)_2]^+$ ($P=PMe_2Ph$, PMe_3) complexes give a band at *ca.* 18500 cm^{-1} and a shoulder at *ca.* 22000 cm^{-1}. They can be assigned to two split components of the first d-d band. The Me_2-

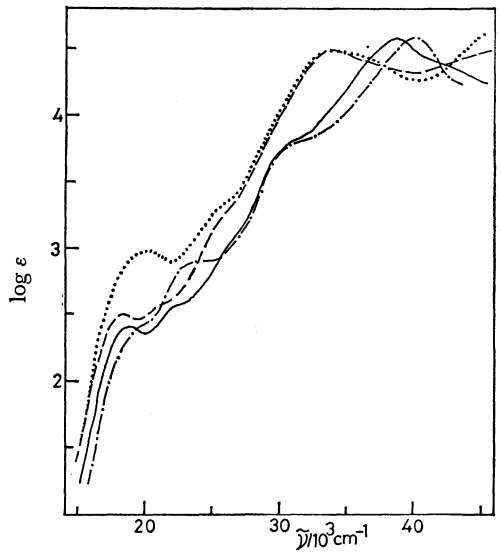

Fig. 2. Absorption spectra of *cis*-$[Co(acac)_2(PMe_3)_2]^+$ (——), *cis*-$[Co(acac)_2(PMe_2Ph)_2]^+$ (----), $[Co(acac)_2(Me_2PCH_2CH_2PMe_2)]^+$ (—·—), and $[Co(acac)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (·····).

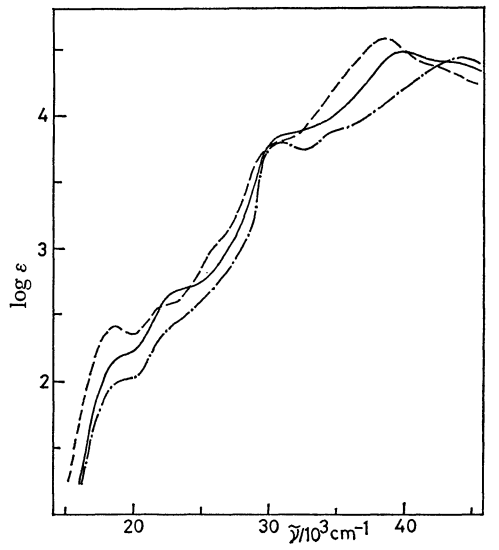

Fig. 3. Absorption spectra of *cis*-$[Co(acac)_2(PMe_3)_2]^+$ (----), *cis*-$[Co(CN)(acac)_2(PMe_3)]$ (——), and *cis*-$[Co(CN)_2(acac)_2]^-$ (—·—).

$PCH_2CH_2PMe_2$ complex also shows two components of the first d-d band, although the spectral pattern is somewhat different from that of the above bisphosphine complexes. The $Ph_2PCH_2CH_2PPh_2$ complex gives a broad, fairly strong single d-d band at 20200 cm^{-1}, but the band splits into two components (19400 and 20600 cm^{-1}) at 173 K.[8] A similar splitting spectral pattern in the first d-d band region has been observed for *cis*-$[Co(CN)_2(acac)_2]^-$ [4] (Fig. 3) and *cis*-$[Co(CN)_2(C_2O_4)_2]^{3-}$.[15] In the ultraviolet region, all the complexes show complicated spectra due to absorptions arising from intramolecular transitions of the ligands and charge transfer transitions between the cobalt(III) ion and the ligands. In the complexes of each type including other cyano complexes studied here, both d-d and charge transfer bands are shifted remarkably depending on the kind of phosphine ligands. The shift occurs to the high energy side in the following order of ligands; $PPh_3 < PMePh_2 < PMe_2Ph \approx Ph_2PCH_2CH_2PPh_2 < PMe_3 < Me_2PCH_2CH_2PMe_2$. This order agrees with the decreasing order of the cone angles (θ(degree), steric effect) of phosphines given by Tolman;[16] $PPh_3(145) > PMePh_2(136) > Ph_2PCH_2CH_2PPh_2(125) \geq PMe_2Ph(122) > PMe_3(118) > Me_2PCH_2CH_2PMe_2(107)$. It also agrees with the decreasing order of the substituent additivity values ($\Sigma\chi_i$ (cm^{-1}), electronic effect) given by the same author;[16] $PPh_3(12.9) > PMePh_2(11.2) > PMe_2Ph(9.5) > PMe_3(7.8)$.

Figure 3 shows the absorption spectra of *cis*-$[Co(CN)_n(acac)_2(PMe_3)_{2-n}]^{(n-1)+}$ (n=0,1,2). By replacing the PMe_3 ligand by a cyanide ion, the first absorption band remains almost unshifted, but decreases the intensity. The band or shoulder around 30000 cm^{-1} can be assigned to a transition between the Co(III)–acac. The bands at 38800 cm^{-1} and 39900 cm^{-1} of the bisphosphine and the monocyano complexes, respectively, can be assigned to a transition between the Co(III)–PMe_3.

The ^1H NMR spectral data for the methyl and methine parts of the complexes are summarized in Table 2. Except for the *cis*-$[Co(acac)_2(PMe_2Ph)_2]^+$ complex, the methine protons of acac of the bis(acac) complexes with the phosphine ligand having a phenyl group resonate at a remarkably high field (4.47—4.94 ppm) as compared with those of the complexes with the trialkylphosphine ligand (5.42—5.50 ppm). A phenyl ring of the phosphine ligand in the former complexes comes over an acetylacetonate ring so that the methine proton should be shielded by the phenyl ring to cause the high field shift.[8] The methine proton of *cis*-$[Co(acac)_2(PMe_2Ph)_2]^+$ shows no such high field shift. The two PMe_2Ph ligands in this complex would be prohibited to rotate freely around the Co–P bond, and the conformation with the two phenyl rings stacking each other seems to be stable from studies with molecular models. When the complex has such a conformation, the methyl group(s) of the phosphine is placed over the acetylacetonate ring, and the resonance value of the methine proton would be similar to that in the PMe_3 complex. The P–CH_3 groups in $[Co(acac)_2(P)_2]^+$ (P=PMe_2Ph, $PMePh_2$) give triplet signals due to so-called virtual coupling, although those of the trialkylphosphine complexes become multiplets. The *cis* PMe_2Ph complex exhibits two kinds of the P–CH_3 signals, indicating the *cis*, chiral structure. The carbons of the methyl and phenyl groups on phosphorus except for the *p*-carbon also show triplet signals in the ^{13}C NMR spectra of both *cis* and *trans* bisphosphine complexes (Table 3). The spectral assignment was made according to the reference.[8] Thus there exists virtual coupling in both *cis* and *trans* bisphosphine complexes. In planar complexes, such virtual coupling is, in general, observed for only a *trans* isomer.[17] For some octahedral complexes of the *cis* type, however, the coupling has been reported to be remarkable.[18] Virtual coupling as a diagnosis for the *trans* arrangement of two phosphorus donor atoms seems to be limited to only planar complexes.

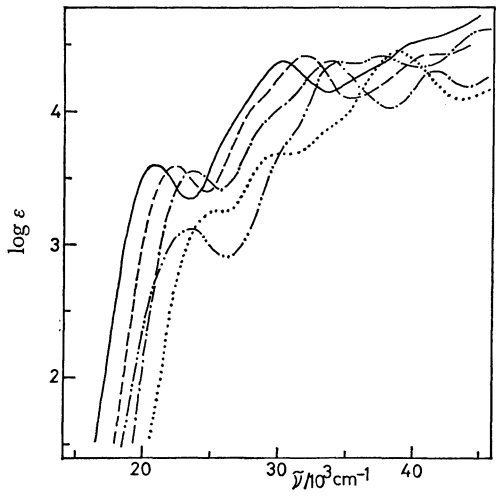

Fig. 4. Absorption spectra of *trans*(P,P)-[$Co(CN)_2$-(acac)$(PPh_3)_2$] (——), *trans*(P,P)-[$Co(CN)_2$(acac)-$(PMePh_2)_2$] (----), *trans*(P,P)-[$Co(CN)_2$(acac)-$(PMe_2Ph)_2$] (—·—), *trans*(P,P)-[$Co(CN)_2$(acac)-$(PMe_3)_2$] (·····), and *cis*-[$Co(CN)_2$(acac)$(Ph_2PCH_2$-$CH_2PPh_2)$] (—··—).

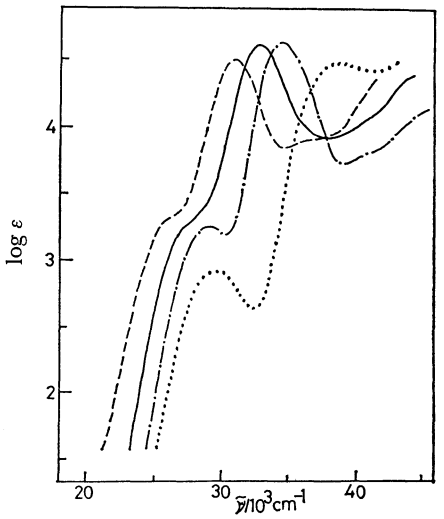

Fig. 5. Absorption spectra of *trans*-$[Co(CN)_4(PPh_3)_2]^-$ (----), *trans*-$[Co(CN)_4(PMePh_2)_2]^-$ (——), *trans*-$[Co(CN)_4(PMe_2Ph)_2]^-$ (—·—), and $[Co(CN)_4(Ph_2PCH_2$-$CH_2PPh_2)]^-$ (·····).

The $[Co(CN)_2(acac)(P)_2]$ *Complexes.* The $[Co(CN)_2(acac)(P)_2]$-type complex has three possible geometrical isomers, *trans*(P,P), *trans*(C,C), and *trans*(P,C) isomers. In this study, the reactions between *cis*-$[Co(CN)_2(acac)_2]^-$ and $P(CH_3)_n(C_6H_5)_{3-n}$ (n=0,1,2, or 3) afforded only one isomer for each phosphine ligand. All the complexes isolated can be assigned to either a *trans*(P,P) or a *trans*(C,C) configuration from the ^1H and ^{13}C NMR spectra (Tables 2 and 3). In addition the remarkable high field shift of the methine proton signals of acac in the complexes containing a phenylphosphine derivative as compared with that of the PMe_3 complex strongly suggests that the complexes have one or two phosphine ligands at the coordination sites perpendicular to the acetylacetonate ring. Thus the bisphosphine complexes except for the PMe_3 complex can be assigned to the *trans*(P,P) isomers. This assignment is supported by absorption spectra of those complexes. The complexes show the strong first d-d band as compared with that of the corresponding $Ph_2PCH_2CH_2PPh_2$ complex which is easily assigned to the *cis* isomer by appearance of two kinds of the methyl signals of acac in the ^1H NMR spectrum (Fig. 4). The bisphosphine complexes of a *cis*(P,P) type would show the first d-d band weaker than that of the $Ph_2PCH_2CH_2PPh_2$ complex by analogy with spectra of the $[Co(acac)_2(P)_2]^+$-type complexes as stated previously. The PMe_3 complex shows the weaker first d-d band than those of the other three bisphosphine complexes, but it is still stronger than that of the $Ph_2PCH_2CH_2PPh_2$ complex, suggesting the *trans*(P,P) isomer.

The preference of the *trans*(P,P) configuration in the $[Co(CN)_2(acac)(P)_2]$-type complex would result from the stronger *trans* effect of a cyanide ion than that of a phosphine. In general, ligands which exhibit a strong *trans* effect tend to avoid the *trans* positions to each other.[13] Hence the *trans*(C,C) and *trans*(P,C) configurations will be less favorable than the *trans*(P,P) configuration. Further, the bulkiness of phosphine ligands would still facilitate the *trans*(P,P) configuration.

The $[Co(CN)_4(P)_2]^-$ *Complexes.* There are two possible geometrical isomers, *cis* and *trans*, for the $[Co(CN)_4(P)_2]$-type complex. In this study, only one isomer was obtained for each of the bisphosphine complexes of this type. For the structural assignment of the bisphosphine complexes, no NMR spectra give useful information. However, the complexes show absorption spectra similar to one another, indicating the same geometrical configuration, although the spectra shift remarkably depending on the kind of the phosphine ligands (Fig. 5). In addition, the complexes exhibit a strong band or shoulder in the first d-d band region, the intensities of which are much stronger than that of the corresponding band of $[Co(CN)_4(Ph_2PCH_2CH_2PPh_2)]^-$. Thus the bisphosphine complexes can be assigned to the *trans*(P,P) configuration on the same consideration as that described for the other phosphine complexes. The reason for the preference of the *trans*(P,P) configuration in the $[Co(CN)_4(P)_2]^-$-type complex is not clear. When the strength of the *trans* effect of cyanide and phosphine ligands is taken into account, the *cis*(P,P) configuration would be more favorable than the *trans*-(P,P) one as stated previously. There might be a factor that stabilizes the planar-type coordination of four cyanide ligands in the complexes concerned.

This work was partly supported by the Kurata Research Grant of the Kurata Foundation. The authors wish to thank Dr. T. Ito of Institute for Molecular Science for obtaining ^{13}C NMR spectra.

References

1) "Transition Metal Complexes Containing Phosphorus, Arsenic and Antimony Ligands," ed by C. A. McAuliffe, Macmillan Press, London (1973); C. A. McAuliffe and W. Levason, "Phosphine, Arsine and Stibine Complexes of the Transition Elements," Elsevier, Amsterdam (1979).

2) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964).
3) W. C. Trogler and L. G. Marzilli, *Inorg. Chem.*, **14**, 2942 (1975); R. C. Stewart and L. G. Marzilli, *ibid.*, **16**, 424 (1977).
4) H. Nishikawa, K. Konya, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **41**, 1492 (1968).
5) K. Watanabe, H. Nishikawa, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **42**, 1150 (1969).
6) K. Kashiwabara, K. Katoh, J. Fujita, H. Nishikawa, and M. Shibata, *Chem. Lett.*, **1981**, 575.
7) L. Maier, "Organic Phosphorus Compounds," ed by L. Maier and G. M. Kosolapott, Wiley, New York (1972), Vol. 1, p. 1.
8) K. Kashiwabara, I. Kinoshita, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **54**, 725 (1981).
9) L. J. Boucher, C. G. Coe, and D. R. Herring, *Inorg. Chim. Acta*, **11**, 123 (1974).
10) A. W. Adamson, A. Chiang, and E. Zinato, *J. Am. Chem. Soc.*, **91**, 5467 (1969).
11) N. Maki and K. Ohshima, *Bull. Chem. Soc. Jpn.*, **43**, 3970 (1970).
12) L. Cambi and E. Paglia, *Gazz. Chim. Ital.*, **88**, 691 (1970); H. H. Chen, M. S. Taso, R. W. Garer, P. H. Tewari, and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).
13) For example, F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley & Sons, New York (1967), Chap. 5.
14) R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).
15) S. Fujinami and M. Shibata, *Bull. Chem. Soc. Jpn.*, **46**, 3443 (1973).
16) C. A. Tolman, *Chem. Rev.*, **77**, 183 (1978).
17) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc., A*, **1966**, 770.
18) G. M. Bancraft and E. T. Libbey, *Can. J. Chem.*, **51**, 1482 (1973).