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Absorption, Circular Dichroism, and Nuclear Magnetic Resonance Studies of Bis(acetylacetonato)cobalt(III) Complexes Containing 2-Aminoalkylphosphine Chelates with Phosphorus and Nitrogen Donor Atoms

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Bis(acetylacetonato)cobalt(III) complexes containing a variety of 2-aminoalkylphosphines, $NH_2CH_2CH_2P(C_6H_5)_2$, $(CH_3)_2NCH_2CH_2P(C_6H_5)_2$, (*S*)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$, *rac*-$NH_2CH_2CH_2P(CH_3)(C_6H_5)$, (*R*)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$, and $NH_2CH_2CH_2P(CH_3)_2$, and a diphosphine, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ were prepared and resolved (or separated) into optical isomers by SP-Sephadex column chromatography. Absorption, circular dichroism, and ^1H and ^{13}C NMR spectra of the new complexes were measured and the results compared with those of the related complexes. Positions of the 2-aminoalkylphosphine and the related ligands in the spectrochemical series were as follows; $CN^- > NH_2CH_2CH_2P(CH_3)_2 > (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 > NH_2CH_2CH_2P(CH_3)(C_6H_5) \geqq NH_2CH_2CH_2P(C_4H_9)(C_6H_5) > NH_2CH(CH_3)CH_2P(C_6H_5)_2 \geqq NH_2CH_2CH_2P(C_6H_5)_2 \geqq NH_2CH_2CH_2NH_2 > (CH_3)_2NCH_2CH_2P(C_6H_5)_2$. For the ^{13}C NMR spectra, all the signals including those due to two diastereotopic phenyl groups on a phosphorus atom were assigned, and the chemical shifts and the coupling constants were determined. The methyl and carbonyl carbons which are *trans* to a phosphorus atom give a doublet signal due to four-bond ($^4J(C,P) = 6$—7 Hz) and three-bond ($^3J(C,P) = 2$—3 Hz) couplings, respectively, through a cobalt(III) ion.

A 2-aminoalkylphosphine can act as a bidentate ligand with phosphorus and nitrogen donor atoms, forming a five-membered chelate ring. Issleib and his coworkers prepared 2-aminoethyldiphenylphosphine[1)] and its derivatives including those with a chiral phosphorus atom.[2)] However, little metal complexes with such ligands have been prepared[3)] and no cobalt(III) complex seems to be reported. A cobalt(III) ion which belongs to a hard acid would prefer a hard base such as a nitrogen or oxygen donor atom rather than a phosphorus donor atom which belongs to a soft base,[4)] and a few cobalt(III)–phosphine complexes have been known.[5)] Since 2-aminoalkylphosphines have an amino group which can strongly coordinate to a cobalt(III) ion, they might form stable chelate complexes facilitating the bond-formation between cobalt(III) and phosphorus. In this paper, we have prepared bis(acetylacetonato)cobalt(III) complexes of various 2-aminoalkylphosphines, resolved or separated them into optically active forms, and characterized the complexes by absorption, circular dichroism (CD), and ^1H and ^{13}C NMR spectroscopy. The results would be useful for studying detailed stereochemistry of other chiral metal phosphine complexes which recently attract much attention as complex catalysts in asymmetric hydrogenation of some organic compounds.[6)]

Experimental

Free aminophosphines were handled under nitrogen atmosphere until they formed air-stable cobalt(III) complexes. Solvents were dried in the usual way and degassed by distillation in a stream of pure nitrogen. Absorption, CD, and ^1H and ^{13}C NMR spectra were recorded on a Hitachi 323 spectrophotometer, a JASCO J-40 spectropolarimeter, and JEOL JNM-PMX 60 and JNM-FX 100 spectrometers, respectively. Low-temperature absorption and CD measurements were made using a Union Giken SM 404 spectrophotometer and a JASCO J-40 spectropolarimeter, respectively, equipped with a Oxford Cryostat CF 204 and a DTC-2-CLO1 controller.

Preparation of Aminophosphines. *2-Aminoethyldiphenylphosphine*: The method of Issleib and Haferburg[1)] was modified. Small pieces of lithium metal (1.7 g, 240 mmol) were added to a refluxing tetrahydrofuran (THF) solution (300 cm^3) of triphenylphosphine (32.5 g, 120 mmol). The mixture was refluxed for 6 h with stirring to give a deep red solution. *t*-Butyl chloride (11.5 g, 114 mmol) was added dropwise to the solution with stirring under cooling in an ice–salt bath. After 1 h, aziridine (7.0 g, 160 mmol) was added dropwise to the solution at 60 °C, which was then refluxed for 8 h and filtered. To the filtrate was added water (5 cm^3) dropwise and then anhydrous magnesium sulfate (*ca.* 10 g) to remove excess water. The mixture was stirred for 5 h and permitted to stand for a while. The desicant was filtered and the residue was washed with diethyl ether. The filtrate and washings were combined and the solvents were evaporated under reduced pressure. The residue was distilled to give viscous liquid at *ca.* 150 °C and *ca.* 60 Pa. Yield: 6.5 g (60%).

(S)-2-Aminopropyldiphenylphosphine: Hydrogen chloride gas was bubbled into a chloroform solution (50 cm^3) of (*S*)-2-amino-1-propanol[7)] (5 g, 65 mmol), yielding a red oily product. $SOCl_2$ (7 cm^3, 100 mmol) was added to the solution dropwise with stirring. The resulting solution was gradually warmed, refluxed for 4 h, and allowed to stand overnight at room temperature. Needle crystals of (*S*)-1-chloro-2-aminopropane hydrochloride (3.3 g) thus formed were filtered. They were then added to sodium diphenylphosphide which was prepared from 1.8 g of sodium metal and 5.6 g of chlorodiphenylphosphine in liquid ammonia (70 cm^3). The solution was stirred for 3 h and mixed with THF (100 cm^3). Liquid ammonia was evaporated at room temperature, and the solution was filtered. The filtrate was concentrated under reduced pressure and an oily product remained was distilled to give colorless liquid at *ca.* 130 °C and *ca.* 10 Pa. Yield: 1.5 g.

2-Aminoethylmethylphenylphosphine: This was prepared from lithium methylphenylphosphide[8)] and aziridine by a method similar to that for 2-aminoethyldiphenylphosphine. The

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Table 1. Analytical data of the new complexes

Complex		C% Found(Calcd)	H% Found(Calcd)	N% Found(Calcd)
$[Co(acac)_2\{NH_2CH_2CH_2P(C_6H_5)_2\}]PF_6$	**1**	45.50(45.65)	4.84(4.79)	2.17(2.22)
$[Co(acac)_2\{(CH_3)_2NCH_2CH_2P(C_6H_5)_2\}]PF_6$	**2**	47.35(47.36)	5.04(5.20)	2.20(2.12)
$[Co(acac)_2\{NH_2CH(CH_3)CH_2P(C_6H_5)_2\}]PF_6\cdot H_2O$(F-I)	**3a**	45.32(45.25)	5.02(5.17)	2.25(2.11)
$[Co(acac)_2\{NH_2CH(CH_3)CH_2P(C_6H_5)_2\}]PF_6\cdot H_2O$(F-II)	**3b**	45.11(45.25)	5.31(5.17)	2.25(2.11)
$[Co(acac)_2\{NH_2CH_2CH_2P(CH_3)(C_6H_5)\}]B(C_6H_5)_4$(F-I)	**4a**	69.05(69.46)	6.37(6.51)	1.67(1.88)
$[Co(acac)_2\{NH_2CH_2CH_2P(CH_3)(C_6H_5)\}]B(C_6H_5)_4$(F-II)	**4b**	69.99(69.46)	6.56(6.51)	2.33(1.88)
$[Co(acac)_2\{NH_2CH_2CH_2P(CH_3)(C_6H_5)\}]PF_6\cdot 1/2H_2O$(F-II)	**4c**	39.99(39.73)	4.88(4.38)	2.40(2.40)
$[Co(acac)_2\{NH_2CH_2CH_2P(C_4H_9)(C_6H_5)\}]B(C_6H_5)_4$(F-I)	**5a**	70.28(70.32)	7.10(6.93)	2.06(1.78)
$[Co(acac)_2\{NH_2CH_2CH_2P(C_4H_9)(C_6H_5)\}]B(C_6H_5)_4$(F-II)	**5b**	70.27(70.32)	7.20(6.93)	2.10(1.78)
$[Co(acac)_2\{NH_2CH_2CH_2P(CH_3)_2\}]Br\cdot H_2O$	**6**	36.27(36.54)	6.06(6.13)	3.04(3.04)
$[Co(acac)_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}]PF_6$	**7**	54.10(54.01)	4.91(4.78)	——

acac$=C_5H_7O_2^-$

optical resolution was unsuccessful with $(+)_{589}$-di-μ-chloro-bis[(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*]dipalladium(II).[9] Yield: 25%.

Other 2-aminoalkylphosphines: (*R*)-2-Aminoethylbutylphenylphosphine,[10] 2-(dimethylamino)ethyldiphenylphosphine,[11] and 2-aminoethyldimethylphosphine[12] were prepared according to the methods reported.

Preparation of $[Co(acac)_2(L)]^+$ *Complexes.* *L=achiral phosphines*; $NH_2CH_2CH_2P(C_6H_5)_2$, $(CH_3)_2NCH_2CH_2P(C_6H_5)_2$, *and* $NH_2CH_2CH_2P(CH_3)_2$: A methanol solution containing $[Co(acac)_3]$ and an achiral phosphine (1:1) was stirred with active charcoal overnight at room temperature. The resulting dark red solution was filtered, adjusted the pH to *ca.* 7 with hydrochloric acid, and diluted ten times with water. This was passed through a column ($\phi 3\times 120$ cm) of an SP-Sephadex C-25 ion exchanger. The product adsorbed was eluted with a 0.02 mol/dm^3 aqueous solution of Na_2SO_4. A main red violet eluate was saturated with NaCl and the complex was extracted with chloroform except for the case of 2-aminoethyldimethylphosphine complex. The chloroform was removed under reduced pressure and the residue was dissolved in water. The complex was precipitated by the addition of excess $NaPF_6$. The 2-aminoethyldimethylphosphine complex was isolated as tetraphenylborate by the addition of $NaB(C_6H_5)_4$ to the main red violet eluate which had been concentrated under reduced pressure. The tetraphenylborate was converted to bromide with a Dowex 1×8 ion exchanger in methanol.

L=chiral phosphines; (S)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$, *rac*-$NH_2CH_2CH_2P(CH_3)(C_6H_5)$, *and* (R)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$: The complexes were prepared by a method similar to that for 1). By elution with a 0.02 mol/dm^3 aqueous sodium $(+)_{589}$-tartratoantimonate(III) solution, two red violet bands, F-I and F-II were obtained, F-I being eluted faster than F-II. From the eluates, a pair of diastereomers, Λ(*S*) (F-I) and Δ(*S*) (F-II) for the optically active aminophosphines,[13] and Δ(*R*)-Λ(*S*) (F-I) and Δ(*S*)-Λ(*R*) (F-II) for the racemic aminophosphine, were isolated as hexafluorophosphate or tetraphenylborate by a method similar to that described for 1) (Table 1). Δ and Λ represent the absolute configuration of a cobalt(III) ion, and *R* and *S* that of a phosphorus and carbon atom.

Bis(acetylacetonato)[1,2-bis(diphenylphosphino)ethane]cobalt(III) hexafluorophosphate: This was prepared from $[Co(acac)_3]$ and 1,2-bis(diphenylphosphino)ethane (Strem. Chem. Inc.) by a method similar to that for the aminophosphine complexes.

Optical Resolution: Resolutions of the $NH_2CH_2CH_2P(C_6H_5)_2$ and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ complexes were attempted by SP-Sephadex column chromatography using a 0.02 mol/dm^3 aqueous sodium $(+)_{589}$-tartratoantimonate(III) solution as an eluent. However, the bands of enantiomers were separated incompletely, so that the chromatography was repeated until no further increase in $\Delta\varepsilon/\varepsilon$ values for the first and the last fractions was observed. From the eluates, the optical isomers were isolated by a method similar to that for the racemates. Resolutions of the methylphenyl- and dimethyl-phosphine complexes were poor in similar SP-Sephadex column chromatography.

Analytical data of the new complexes are given in Table 1.

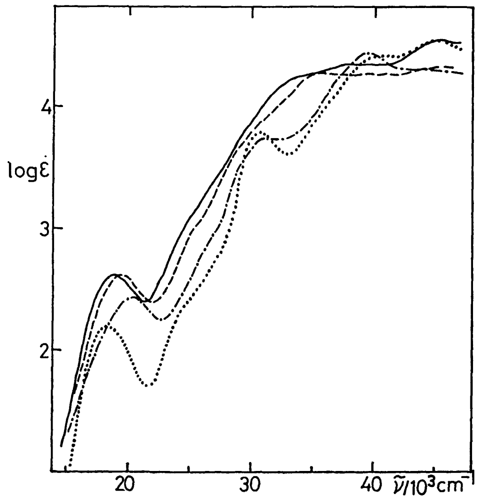

Fig. 1. Absorption spectra of complexes, **1**(———), **4c**(------), **6**(—·—·—·—), and $[Co(acac)_2(en)]ClO_4$ (·········) in ethanol.

Results and Discussion

Absorption Spectra. Reports have been given on the spectrochemical series of various unidentate[14,15] and bidentate[16] phosphine ligands, although there are some discordances among the reports. The bis(acetylacetonato)aminophosphine–cobalt(III) complexes prepared in this study show the first absorption bands around 20000 cm^{-1} with fairly strong intensity. Figure 1 shows absorption spectra of the $NH_2CH_2CH_2P(CH_3)_n(C_6H_5)_{2-n}$ (n=0,1,2) complexes along

Table 2. Absorption (AB) and CD spectral data in the region of the first absorption band

Complex	$\nu^{AB}/10^3$ cm^{-1}(log ε)	$\nu^{CD}/10^3$ cm^{-1}($\Delta\varepsilon$)
1	18.83(2.67)	16.56(−1.83)
		18.18(+1.74)
		20.24(−7.05)
2	18.05(2.56)	
3a	18.92(2.62)	16.64(+2.26)
		18.35(−2.14)
		20.37(+6.97)
3b	18.97(2.61)	16.75(−2.46)
		18.25(+1.31)
		20.28(−8.54)
4a	19.65(2.40)	
4b, 4c	19.51(2.62)	
5a	19.51(2.51)	16.65(+3.25)
		18.59(−3.68)
		20.66(+5.17)
5b	19.49(2.63)	16.58(−1.82)
		18.43(+2.99)
		20.58(−8.00)
6	20.35(2.43)	
7	20.16(2.99)	16.26(−1.22)
		18.38(+8.76)
		20.70(−16.8)
8[a)]	18.58(2.20)	16.67(−1.11)
		19.70(−4.46)
9[b)]	19.0 (1.97)	
	ca. 23.3 (2.45)	

a) **8**: $[Co(acac)_2(NH_2CH_2CH_2NH_2)]ClO_4$, R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965). b) **9**: $K[Co(CN)_2(acac)_2]$.[18)]

with that of the corresponding ethylenediamine complex for comparison. Spectral data of all the aminophosphine and the related complexes are summarized in Table 2. When a phenyl group on a phosphorus atom is replaced by a methyl group, the absorption peaks shift to higher energy. The spectrochemical series of the ligands is determined as $CN^- > NH_2CH_2CH_2P(CH_3)_2 > (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 > NH_2CH_2CH_2P(CH_3)(C_6H_5) \geqq NH_2CH_2CH_2P(C_4H_9)(C_6H_5) > NH_2CH(CH_3)CH_2P(C_6H_5)_2 \geqq NH_2CH_2CH_2P(C_6H_5)_2 \geqq NH_2CH_2CH_2NH_2 > (CH_3)_2NCH_2CH_2P(C_6H_5)_2$, and that of the donor groups as $CN^- > -P(CH_3)_2 > -P(CH_3)(C_6H_5) \geqq -P(C_4H_9)(C_6H_5) > -P(C_6H_5)_2 \geqq -NH_2 > -N(CH_3)_2$. Since a phosphorus donor group occupies a fairly higher position than an acetylacetonate ion in the spectrochemical series, it is expected that the first absorption band of a bis(acetylacetonato)phosphine–cobalt(III) complex splits into two components[17)] as observed for analogous complexes, *cis*-$[Co(CN)_2(acac)_2]^-$ (19000 and *ca.* 23300 cm^{-1})[18)] and *cis*-$[Co(CN)_2(C_2O_4)_2]^{3-}$ (18000 and 23400 cm^{-1}).[19)] The 1,2-bis(diphenylphosphino)ethane complex (**7**) gives only a single broad band at 20160 cm^{-1} at 304 K. However, the band clearly exhibits two components at *ca.* 19400 and 20600 cm^{-1} at 173 K (Fig. 2). The 2-aminoethyldiphenylphosphine complex (**1**) shows no indication of such a splitting even at 173 K.

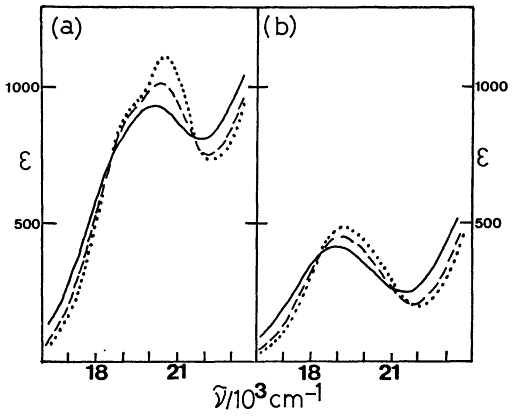

Fig. 2. Absorption spectra of complexes, **7**(a) and **1**(b) at 304 K (———), 223 K(------), and 173 K (·········) in ethanol.

The intensities of the first absorption bands increase with an increase in the number of phenyl groups on a phosphorus atom. Two diastereomers **4a** and **4b** show fairly different intensities from each other (ε(**4b**)/ε(**4a**)$=1.7$). However, the average intensity (2.51) of these isomers is nearly the same as that (2.55) of the diphenylphosphine (**1**) and the dimethylphosphine (**6**) complexes. The difference in intensity between diastereomers **4a** and **4b** might be related with the relative location of a phenyl group to an acetylacetonate ring, since the intensities of **4a** and **4b** are similar to those of the dimethylphosphine (**6**) and the diphenylphosphine (**1**) complexes, respectively. Complexes **4a** and **6**, and **4b** and **1** have a methyl and a phenyl group, respectively, over one acetylacetonate ring (*vide post*, Fig. 7). A similar difference in intensity is seen between diastereomers of the butylphenylphosphine complex, **5a** and **5b**.

The second absorption bands of the present complexes are hidden by intense absorptions due to charge transfer transitions between the ligands and the cobalt(III) ion or internal transitions of the ligands. The absorptions around 30500 and 33000 cm^{-1} could be assigned to those due to the acetylacetonate and phenylphosphine moieties, respectively.

Circular Dichroism Spectra. Absorption and CD spectra of complexes **1**, **7**, and $[Co(acac)_2(NH_2CH_2CH_2NH_2)]^+$ (**8**) are shown in Fig. 3, and the spectral data in Table 2 with those of the related complexes. In the region of the first absorption band, the CD intensities increase remarkably with an increase in absorption intensity. The phosphine complexes **1** and **7** show three CD bands with minus, plus, and minus signs from the low energy side, while the ethylenediamine complex (**8**) two negative CD bands. However, the CD spectrum of complex **8** shows remarkable temperature dependence in the region of the first absorption band and exhibits three

CD bands at 168 K (Fig. 4), the spectral pattern being very similar to those of complexes **1** and **7**. The phosphine complexes also show temperature dependence in the CD, but the spectral patterns remain unchanged (Fig. 4). The enantiomer of the ethylenediamine complex with the negative main CD band has been assigned to Δ configuration.[20] Thus both phosphine complexes in Fig. 3 can be assigned to the same Δ configuration. These enantiomers are those moving more slowly on columns of SP-Sephadex (Experimental).

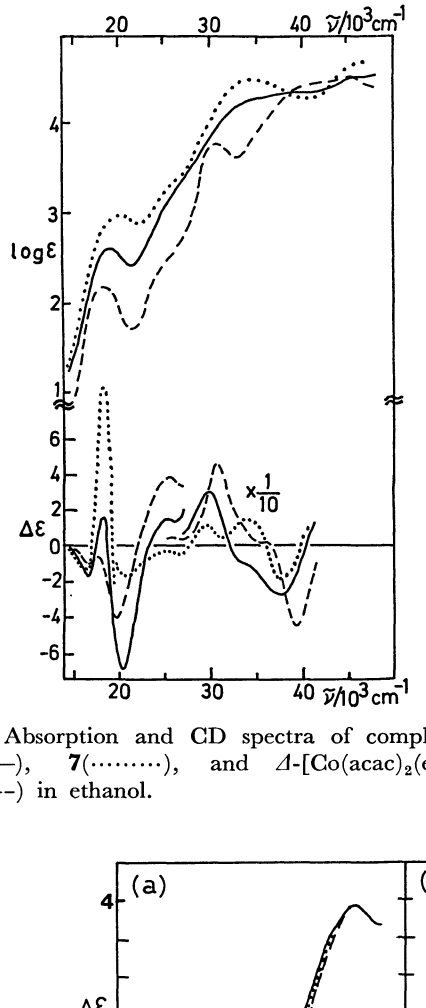

Fig. 3. Absorption and CD spectra of complexes, **1** (———), **7**(·········), and Δ-[Co(acac)$_2$(en)]$^+$ [20] (------) in ethanol.

A pair of diastereomers, $\Delta(S)$ and $\Lambda(S)$ of the (S)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$ complex show CD spectra nearly enantiomeric to each other as observed for the corresponding diastereomers of the (S)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ complex[21] (Fig. 5). The results indicate that the vicinal effects of the chiral ligands to CD are small compared with the configurational effect in these complexes. The vicinal and configurational effect curves were calculated in the usual way[21] (Fig. 6). The configurational effect CD curves of the (S)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$ and (S)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ complexes are nearly the same as the CD spectrum of the $NH_2CH_2CH_2P(C_6H_5)_2$ complex, although the curve of the (S)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ complex in the ultraviolet region deviates a little from the other curves probably because of the substituent variation on the donating phosphorus atom. Thus the additivity rule[22] for the configurational and vicinal effects can be applied to the CD spectra of cobalt(III) phosphine complexes. The vicinal effect CD curve of the (S)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$ chelate ligand should be caused by the chiral conformation and the chiral carbon atom. In general, the effect of a chiral conformation is much stronger than that of a non-ligating chiral atom,[23] and the effect of a δ-gauche chelate ring gives negative CD in the region of the first absorption band.[24] The vicinal effect CD curve of the (S)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$ ligand shows a negative main CD band in this region, indicating the δ-gauche conformation. When the ligand is in the δ-gauche form, the methyl group is disposed equatorially. The vicinal effect CD curve of the (S)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ ligand shows two CD bands with different signs in the region of the first absorption band, the higher energy negative band being stronger than the lower energy positive one (Fig. 6). The chelate conformation of this ligand might not be fixed in a particular chirality, δ or λ,

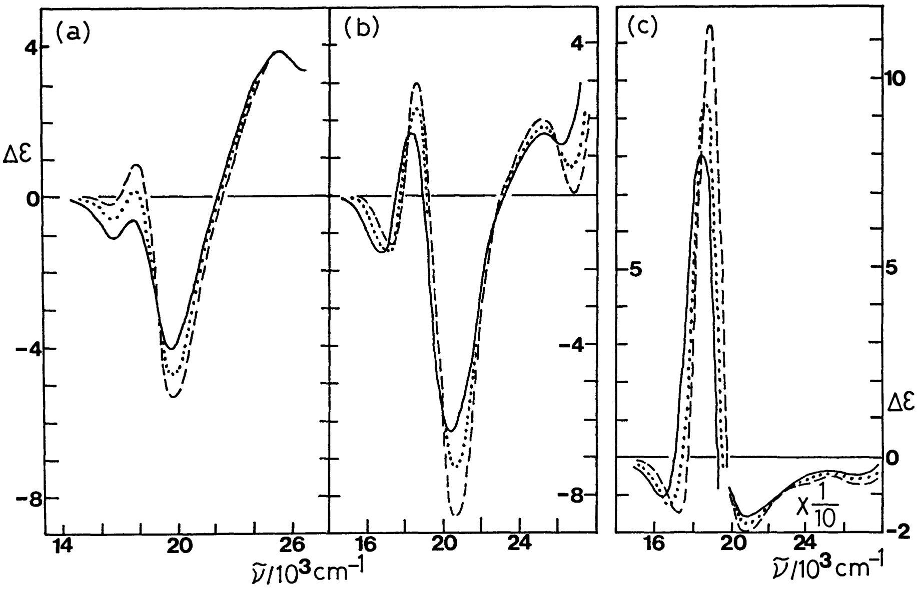

Fig. 4. CD spectra of complexes, Δ-[Co(acac)$_2$(en)]ClO$_4$(a), **1**(b), and **7**(c) at 298 K(———), 223 K(·········), and 168 K(------) in ethanol.

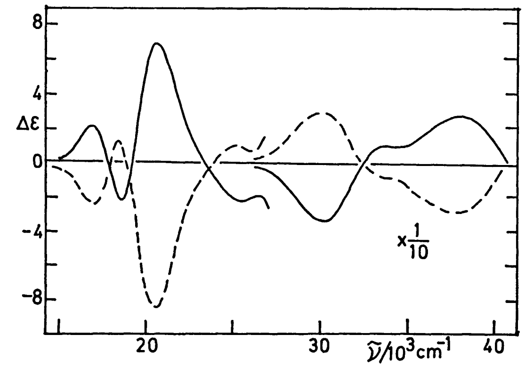

Fig. 5. CD spectra of complexes, **3a**(———) and **3b** (------) in ethanol.

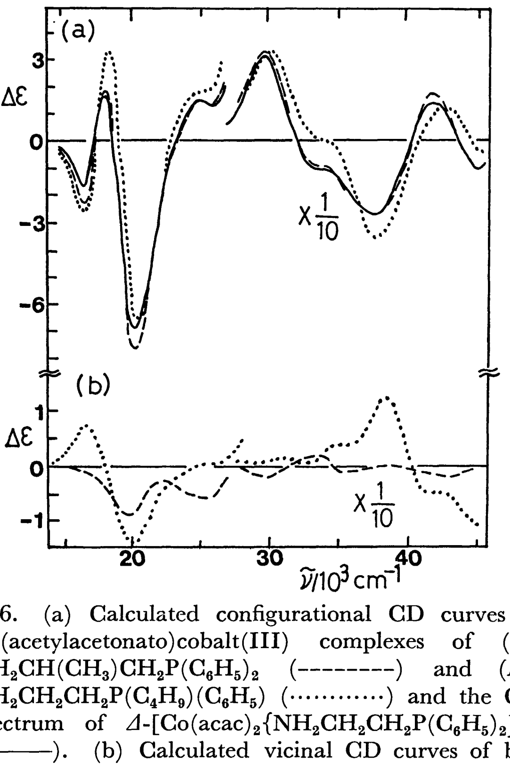

Fig. 6. (a) Calculated configurational CD curves of bis(acetylacetonato)cobalt(III) complexes of (*S*)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$ (--------) and (*R*)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ (············) and the CD spectrum of *Δ*-$[Co(acac)_2\{NH_2CH_2CH_2P(C_6H_5)_2\}]^+$ (———). (b) Calculated vicinal CD curves of bis(acetylacetonato)cobalt(III) complexes of (*S*)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$ (--------) and (*R*)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ (············).

Table 3. ^{1}H NMR spectral data for the acac ligands[a)]

Complex	δ(CH)/ppm		δ(CH$_3$)/ppm	
1	4.93	5.57	1.61 1.96	1.78 2.29
2	4.97	5.69	1.62 1.91	1.77 2.33
3a	4.94	5.55	1.51 1.96	1.80 2.28
3b	4.81	5.56	1.74 1.87	1.77 2.28
4a		5.44 5.50	1.82 2.04	1.97 2.31
4b	4.78	5.58	1.54 2.10	1.86 2.31
5a		5.47 5.52	1.55 2.29	2.05[d)]
5b	4.87	5.57	1.46 2.01	1.91 2.29
6		5.34 5.51	1.95[d)] 2.32	2.00
7	4.93		1.64	1.88
8[b)]		5.64	2.13	2.14
9[c)]		5.55	1.94	2.21

a) Solvent: $CDCl_3$, internal reference: $Si(CH_3)_4$. b) **8**: $[Co(acac)_2(NH_2CH_2CH_2NH_2)]ClO_4$ in CD_3OD, R. J. York, W. D. Bonds Jr., B. P. Cotsoradis, and R. D. Archer, *Inorg. Chem.*, **8**, 789 (1969). c) **9**: $K[Co(acac)_2(CN)_2]$ in CD_3OD.[18)] d) Peak intensity is twice those of others by accidental degeneracy.

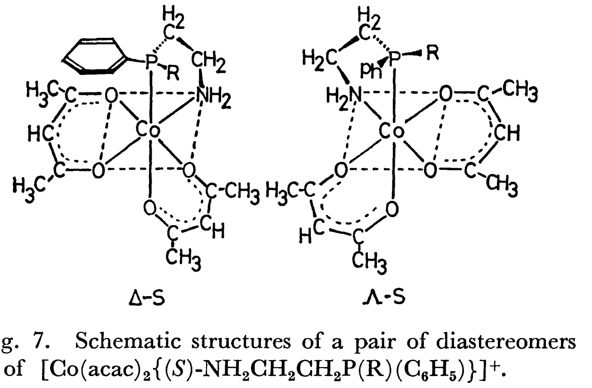

Fig. 7. Schematic structures of a pair of diastereomers of $[Co(acac)_2\{(S)\text{-}NH_2CH_2CH_2P(R)(C_6H_5)\}]^+$.

since X-ray analysis on *trans*-$[CoCl_2\{(S)\text{-}NH_2CH_2CH_2P(C_4H_9)(C_6H_5)\}_2]ClO_4$ reveals that one chelate ring forms a δ-gauche conformation and the other λ-gauche one.[25)] Hence, the vicinal effect of the (*S*)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ ligand should arise primarily from the chiral phosphorus atom. The vicinal effect of such a chiral phosphorus donor atom seems to be as strong as that of a chiral nitrogen donor atom.[26)] The relation between the CD sign and the absolute configuration remains unknown.

^{1}H NMR Spectra. ^{1}H NMR spectral data of the acetylacetonate group and the methyl group of phosphines in the aminophosphine and the related complexes are given in Table 3. The methine and methyl groups of acetylacetonate ligands give two or one, and four or two peaks, respectively, depending on the symmetry of the complexes. The methine signals resonate in two fairly different regions, 4.78—4.99 and 5.34—5.69 ppm. In a pair of diastereomers of the (*S*)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ complex, (**5a**, F-I, *Δ*(*S*)) isomer gives two methine signals in the low field region, whereas (**5b**, F-II, *Δ*(*S*)) isomer one methine signal in the low field and the other in the high field region. The phenyl group on the phosphorus atom in the *Δ*(*S*) isomer is disposed over one acetylacetonate ring and its methine proton is shielded by this phenyl ring to cause the high field shift.[21)] On the other hand, the phenyl group of the *Δ*(*S*)

Table 4. ^{13}C NMR spectral data for the phosphine ligands in δ/ppm[a)]

Complex	P-CH_3	P-CH_2-	N-CH_3	N-CH_2-	P-C_1	*o*-C	*m*-C	*p*-C
1		27.7		42.0	123.5	131.8	128.8	131.5
					127.0	133.5	128.9	132.2
2		24.5	48.8	62.5	123.9	131.8	129.1	131.7
			49.4		127.0	133.4	129.2	132.1
4a[b)]	7.6	29.5		41.5	126.3	132.3	129.0	131.1
4c	5.7	28.4		42.1	127.6	131.2	129.2	132.0
6	7.1	30.7		41.6				
	8.2							
7		23.5			122.8	131.9	128.5	131.2
					127.0	133.8	128.8	132.2
Free ligand[c)]								
I		32.5		39.0	138.4	132.7	128.5	128.7
II	10.7	34.5		38.2	139.3	130.5	127.5	127.6
III		23.8			138.2	132.8	128.5	128.7

a) Solvent: $CDCl_3$, internal reference: $Si(CH_3)_4$. b) The tetraphenylborate was converted to bromide by an ion exchanger. c) $I=NH_2CH_2CH_2P(C_6H_5)_2$, $II=NH_2CH_2CH_2P(CH_3)(C_6H_5)$, $III=(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

Table 5. ^{31}P-^{13}C coupling constants for the phosphine ligands in ^nJ/Hz

Complex	P-CH_3	P-CH_2-	N-CH_2-	P-C_1	*o*-C	*m*-C	*p*-C
1		27.3		48.3	9.0	10.3	4.5
				47.0	7.3	11.0	2.3
2		26.9	2.5	50.0	8.6	9.8	3.7
				47.7	6.1	11.5	2.5
4a[a)]	25.6	28.1		50.0	7.3	10.9	<3
4c	29.3	28.1		47.6	8.5	11.0	3.7
6	29.3	26.9					
	26.9						
7[b)]		42.0		43.5	8.0	10.3	
				45.5	7.3	8.8	
Free ligand[c)]							
I		12.2	20.8	12.2	18.3	7.3	
II	13.4	12.2	17.1	13.5	18.3	6.1	
III		0		13.6	18.5	7.8	

a) The tetraphenylborate was converted to bromide by an ion exchanger. b) All signals are a triplet, the values being $|J_{AX}+J_{BX}|$ of an ABX pattern ($X={}^{13}C$). c) I, II, and III; see Table 4.

isomer is disposed far from two acetylacetonate rings to give their methine signals at similar frequencies in the low field region (Fig. 7). A pair of diastereomers, (**4a**, F-I) and (**4b**, F-II) of the $NH_2CH_2CH_2P(CH_3)(C_6H_5)$ complex give very similar spectra to those of complexes **5a** and **5b**, respectively, and can be assigned to the $\Delta(S)$-$\Delta(R)$ and $\Delta(S)$-$\Lambda(R)$ racemic pairs, respectively. From the strength of such well separated methine signals, the formation ratio of F-II/F-I for the (S)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ complex was determined to be *ca.* 2.7. The same shielding effect of a phenyl group to methine protons of the acetylacetonate ligands is observed for all the other phenylphosphine complexes. The diphosphine complex **7** gives a sharp singlet in the high field region by this effect. No assignment for the methyl group was made because of complexity.

^{13}C NMR Spectra. ^{13}C NMR spectral data of the phosphine complexes and the free ligands measured in this study were summarized in Tables 4, 5, and 6. The assignments were made on the basis of the chemical shifts, the magnitudes of coupling constants, the intensities, and the off-resonance spectra. A representative spectrum (complex **4c**) is shown in Fig. 8.

Spectral Assignments for Diastereotopic Phenyl Carbons: The diphenylphosphine complexes, **1**, **2**, and **7** give complicated spectra in the phenyl region (Fig. 9), since the two phenyl groups in each complex are diastereotopic to each other. Such complicated spectra were successfully assigned by comparing with spec-

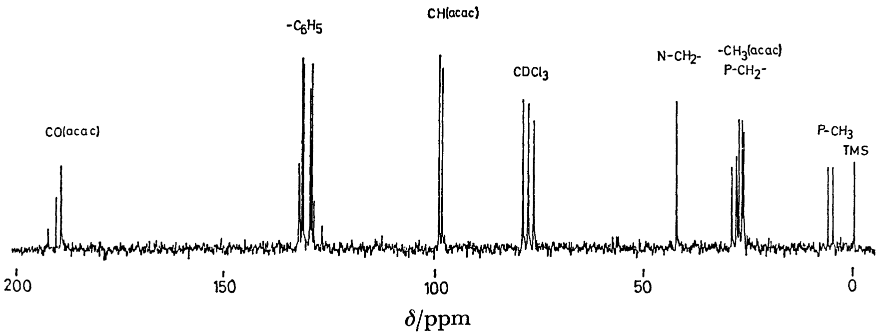

Fig. 8. The ^{13}C NMR spectrum of complex **4c**.

Table 6. ^{13}C NMR spectral data for the acac ligands in δ/ppm (^{n}J(C,P)/Hz)[a)]

Complex	CH_3	CH	CO
1	26.1	98.2	187.7
	26.2		188.8
	26.4		189.5
	27.5(7.3)		191.3(2.3)
2	26.0	98.5	187.7
	26.2	98.8	189.0
	26.5		189.9
	27.6(7.3)		191.4(2.5)
4a	26.6	98.6	188.8
	26.8		189.2
	27.1		190.9
	27.8(6.1)		191.0(3.7)
4c	26.2	98.1	188.5
	26.6	98.9	188.6
	27.3		189.7
	27.9(6.1)		191.5(3.8)
6	26.5	98.8	188.3
	26.8		189.1
	27.5		190.9
	28.1(6.1)		191.6(3.7)
7	26.3	98.2	186.8
	27.4		189.5
$[Co(acac)_3]$	27.5	97.6	189.2

a) Solvent: $CDCl_3$, internal reference: $Si(CH_3)_4$.

tra of the methylphenylphosphine complexes, **4a** and **4c**. These complexes are a pair of diastereomers formed with the ligand having a single phenyl group and thereby give a simple spectrum in the phenyl region (Fig. 10). The spectrum of **4c** isomer in Fig. 10 consists of four kinds of doublets. The carbon bonded to the phosphorus atom (P–C_1) and the *p*-carbon were assigned on the bases of the off-resonance and the intensities. The *o*- and *m*-carbons can be assigned from their chemical shifts. It is known that the chemical shift of *m*-carbon of a monosubstituted benzene remains almost unchanged from that of benzene, 128.7 ppm.[27)] Thus the doublet at 129.2 ppm is assigned to the *m*-carbon and the remaining doublet at 131.2 ppm to the *o*-carbon. Table 5 gives the coupling constants, ^{n}J(C,P) observed from the spectra.

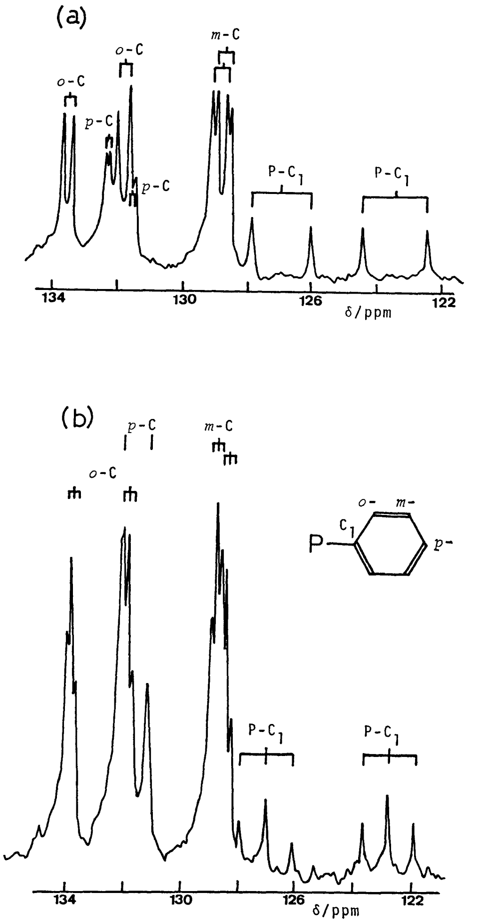

Fig. 9. ^{13}C NMR spectra of complexes, **1**(a) and **7**(b) in the phenyl region.

The spectrum in the phenyl region of another isomer, **4a** was similarly assigned, although the doublet of the *p*-carbon is overlapped by one of the doublet signals of the *o*-carbon. With the aid of the chemical shifts and the coupling constants for these isomers, the complicated phenyl signals of the diphenylphosphine complexes, **1**, **2**, and **7** were assigned (Fig. 9 and Tables 4 and 5).

Carbon-Phosphorus Couplings through a Cobalt(III) Ion: Four methyl and four carbonyl carbons of two acetylacetonate ligands in the aminophosphine complexes exhibit fairly different chemical shifts in the region of each kind of carbons (Fig. 11 and Table 6). Furthermore, each one of the methyl and carbonyl carbons

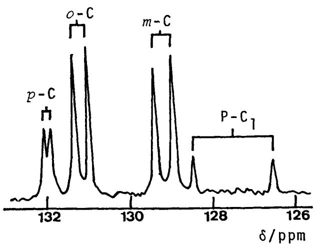

Fig. 10. The ^{13}C NMR spectrum of complex **4c** in the phenyl region.

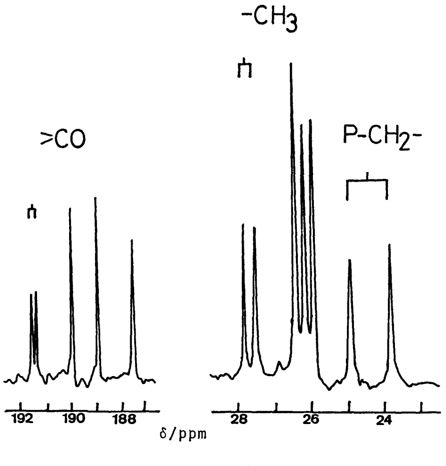

Fig. 11. ^{13}C NMR spectra of complex **2** in the methyl and carbonyl regions.

gives a doublet due to coupling with a phosphorus atom *trans* to the carbon, ^4J(C,P) and ^3J(C,P), respectively. Both doublet are observed at the lowest field among each kind of carbons and the values of ^4J(C,P) for the methyl and ^3J(C,P) for the carbonyl carbons are 6—7 and 2—4 Hz, respectively. Such long-range couplings through a cobalt(III) ion would be useful for assigning structures of cobalt(III)–phosphine complexes. No coupling between carbon and phosphorus in the *cis* positions is observed.

Spectral Parameters in Free and Complexed Aminoalkylphosphines: Spectral data of the free and complexed aminoalkylphosphines are given in Tables 4 and 5. The effects of coordination of the ligands on spectral parameters are summarized as follows.

1) Carbons bonded to a phosphorus atom shift to an upfield upon coordination, and the coupling constants, ^1J(C,P) become much larger.
2) Methylene carbons bonded to a nitrogen atom shift slightly to a downfield upon coordination, and no coupling with a phosphorus atom is observed.
3) Chemical shifts of P–C$_1$ and *o*-carbon atoms depend largely on the kind of compounds, but those of *m*- and *p*-carbon atoms do not. Such trends are similar to those for monosubstituted benzenes.

These features will provide useful information not only for assigning ^{13}C NMR spectra of cobalt(III) phosphine complexes, but also for elucidating bonding properties between a phosphorus atom and a cobalt(III) ion.

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