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Synthesis, Characterization, and Isomerization of *trans*- and *cis*-$[CoCl_2(1,2\text{- or }1,3\text{-diphosphine})_2]^+$ and Related Complexes

Tomoji Ohishi, Kazuo Kashiwabara, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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A number of new diphosphine complexes of cobalt(III), *trans*- and *cis*-$[CoCl_2$(dmpe, dmpp, dbpe, or dpee$)_2]^+$, *trans*- and *cis*-$[CoBr_2(dmpe)_2]^+$, *trans*- and *cis*-$[CoCl(H_2O)(dmpe)_2]^{2+}$, *trans*-$[Co(I_2$ or BrI$)(dmpe)_2]^+$, and $[Co(CO_3)$(dmpp or dbpe)$]^+$ have been prepared and characterized, where dmpe, dmpp, dbpe, and dpee denote 1,2-bis(dimethylphosphino)ethane, 1,3-bis(dimethylphosphino)propane, 1,2-bis(dibutylphosphino)ethane, and *cis*-1,2-bis(diphenylphosphino)ethylene, respectively. The trans isomers of the dihalogeno complexes are stable to aquation, while the cis isomers release one of the halide ions in water fairly rapidly to yield *cis*-$[CoX(H_2O)(\text{diphosphine})_2]^+$ which isomerizes to the trans isomer on exposure of ultraviolet light. The *cis*-$[CoCl_2(\text{diphosphine})_2]^+$ complexes in methanol or ethanol solution isomerize to the trans isomer, and the rates were followed spectrophotometrically in the temperature range of 39.0—65.0 °C. The rates have a first-order dependence on the complex concentration. Both the ΔH^* and ΔS^* values for the isomerization increase in the order diphosphine=dmpe<dmpp<dbpe<dpee. This order coincides with the increasing order in cone angle of phosphine ligands, and suggests that the difference in rates among the complexes comes from a steric factor. Absorption spectra of all the complexes have been recorded and the results compared with those of the corresponding ethylenediamine complexes.

Since the first synthesis of cobalt(III)-diphosphine complexes, *trans*-$[CoX_2\{(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2\}_2]^+$ ($X=Cl^-$, Br^-, and I^-) by Wymore and Bailar,[1] several complexes of this type have been prepared with $(CH_3)_2PCH_2CH_2P(CH_3)_2$,[2,3] $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$,[4] $o\text{-}C_6H_4[P(CH_3)_2]_2$,[5] $o\text{-}C_6H_4[P(C_6H_5)_2]_2$,[6] and *cis*-$(C_6H_5)_2PCHCHP(C_6H_5)_2$.[7] To our knowledge, however, no cis isomer of those complexes is known. This paper reports the first examples of *cis*-$[CoX_2(\text{diphosphine})_2]^+$, where X is Cl^- or Br^-, and diphosphine is $(CH_3)_2PCH_2CH_2P(CH_3)_2$=dmpe, $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$=dmpp, $(C_4H_9)_2PCH_2CH_2P(C_4H_9)_2$=dbpe, or *cis*-$(C_6H_5)_2PCHCHP(C_6H_5)_2$=dpee. A pair of trans and cis isomers of $[CoX_2(\text{diphosphine})_2]^+$ will be useful for studying physical and chemical properties of a cobalt(III)-phosphine complex which consists of a hard Lewis acid and a soft Lewis base. In this paper we report synthesis, absorption spectra and cis to trans isomerization of the new complexes, and compare the results with those of the corresponding ethylenediamine (en) complexes.

Experimental

Phosphine ligands were handled under an atmosphere of nitrogen until they formed cobalt(III) complexes. All solvents used for preparing ligands and complexes were deoxygenated by bubbling nitrogen for 20 min immediately before use. Absorption and ^{1}H NMR spectra were recorded on a Hitachi 323 spectrophotometer and a Jeol-PMX 60 spectrometer, respectively.

Phosphine Ligands. The dpee ligand was obtained from Strem Chemicals, Inc. and used as received. The dmpe[8] and dmpp[4] ligands were prepared according to literature methods, and dbpe was prepared by the following method. To $(C_4H_9)_2PH$[9] (11.4 g, 78 mmol) in dry THF (400 cm^3) was added dropwise LiC_4H_9 (15% hexane solution, 39.94 g) with stirring. After 1 h 1,2-dichloroethane (3.86 g, 39 mmol) was added to the resulting orange solution. Stirring was continued for 3 h to give a colorless solution. The solvent was removed under reduced pressure, and the oily residue was shaken with a mixture of chloroform (100 cm^3) and water (100 cm^3) to extract LiCl into water. The chloroform layer was separated, dried over Na_2SO_4 (3 g), and evaporated under reduced pressure to yield a light yellow oil of dbpe, which was used for preparing complexes without further purification.

Preparation of Complexes.† *trans*-$[CoCl_2(dmpe)_2]ClO_4$. The complex was prepared by the published method.[2]

***trans*-$[CoBr_2(dmpe)_2]ClO_4$.** An ethanol solution (5 cm^3) of dmpe (2.06 g, 14 mmol) was added to an ethanol solution (250 cm^3) of $CoBr_2\cdot6H_2O$ (2.02 g, 6.2 mmol) with stirring. After 1 h concd HBr (1 cm^3) was added, and air was bubbled through the solution for 10 h. The resulting green solution was concentrated to 100 cm^3 under reduced pressure. On addition of $NaClO_4$ (1 g) in ethanol (5 cm^3) the concentrate gave green crystals, which were filtered and recrystallized from hot methanol. Yield: 2.1 g (55%). Found: C, 23.45; H, 4.99%. Calcd for $C_{12}H_{32}Br_2ClCoO_4P_4$: C, 23.30; H, 5.21%. The complex is soluble in methanol, ethanol, and acetonitrile.

***trans*-$[CoI_2(dmpe)_2]ClO_4\cdot0.5CH_3OH$.** This complex was prepared by a method similar to that for *trans*-$[CoBr_2(dmpe)_2]^+$. A methanol solution (100 cm^3) containing dmpe (240 mg, 1.6 mmol) and $CoI_2\cdot6H_2O$ (337 mg, 0.8 mmol) was stirred for 20 min and then was mixed with concd HI (1 cm^3) and $NaClO_4$ (150 mg). Air was bubbled through the solution for 6 h. The resulting dark brown solution was concentrated to 50 cm^3 under reduced pressure. The concentrate was cooled at −5 °C for 10 h to give brownish-violet crystals, which were filtered, washed with a mixture (20 cm^3) of methanol and diethyl ether (2:1), and air-dried. Yield: 200 mg (33%). Found: C, 21.02; H, 4.59%. Calcd for $C_{12.5}H_{34}ClCoI_2O_{4.5}P_4$: C, 20.61; H, 4.84%. The complex is soluble in DMF and DMSO.

***cis*-$[CoCl_2(dmpe)_2]ClO_4$.** Crystals of $[Co(CO_3)(dmpe)_2]ClO_4\cdot1.5NaClO_4\cdot H_2O$[10] (736 mg, 1.15 mmol) were soaked in ice-cold concd HCl (20 cm^3) at 0 °C. After 1 h the result-

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†All of the perchlorate salts of cobalt(III)-phosphine complexes described below are potentially explosive, and should be handled carefully.

ing red solution was mixed with an ice-cold aqueous solution (3 cm^3) of $NaClO_4$ (300 mg) and was cooled at −5 °C for 10 h. Red crystals deposited were filtered and recrystallized from acetonitrile (20 cm^3) by adding diethyl ether (50 cm^3). Yield: 340 mg (52%). Found: C, 27.23; H, 6.45%. Calcd for $C_{12}H_{32}C_{13}CoO_4P_4$: C, 27.21; H, 6.09%. The complex is soluble in methanol and acetonitrile.

***cis*-[CoBr$_2$(dmpe)$_2$]ClO$_4$·0.5CH$_3$CN·H$_2$O.** The complex was prepared by the same method as for *cis*-$[CoCl_2(dmpe)_2]^+$ using concd HBr instead of concd HCl. Yield: 38%. Found: C, 21.71; H, 5.32, N, 1.21%. Calcd for $C_{13}H_{35.5}N_{0.5}Br_2ClCoO_5P_4$: C, 21.76; H, 5.45; N, 1.07%. The complex is soluble in methanol and acetonitrile.

***trans*-[CoCl$_2$(dmpp)$_2$]ClO$_4$·0.5H$_2$O.** The complex was prepared by the method of Cloyd and Meek.[4)]

[Co(CO$_3$)(dmpp)$_2$]ClO$_4$·H$_2$O. To a solution of *trans*-$[CoCl_2(dmpp)_2]ClO_4 \cdot 0.5H_2O$ (200 mg, 0.35 mmol) in a mixture (100 cm^3) of acetonitrile and water (4 : 1) were added K_2CO_3 (97.6 mg, 0.7 mmol) in water (3 cm^3) and active charcoal (100 mg). The mixture was stirred for 30 min and filtered. The filtrate was evaporated to dryness under reduced pressure, and the complex was extracted with methanol (20 cm^3). On addition of diethyl ether (50 cm^3) the extract gave a yellow precipitate, which was filtered, washed with a mixture (50 cm^3) of methanol and diethyl ether (1 : 5), and air-dried. Yield: 150 mg (78%). Found: C, 31.74; H, 6.78%. Calcd for $C_{15}H_{38}ClCoO_8P_4$: C, 31.94; H, 6.17%. The complex is soluble in methanol and ethanol.

***cis*-[CoCl$_2$(dmpp)$_2$]ClO$_4$·0.5H$_2$O.** The complex was prepared from $[Co(CO_3)(dmpp)_2]ClO_4 \cdot H_2O$ and concd HCl by a method similar to that for *cis*-$[CoCl_2(dmpe)_2]^+$. Yield: 48%. Found: C, 29.54; H, 6.19%. Calcd for $C_{14}H_{37}Cl_3CoO_{4.5}P_4$: C, 29.67; H, 6.58%. The complex is soluble in methanol and acetonitrile.

***trans*-[CoCl$_2$(dbpe)$_2$]PF$_6$·H$_2$O.** An ethanol solution (100 cm^3) containing $CoCl_2 \cdot 6H_2O$ (193 mg, 0.81 mmol) and dbpe (684 mg, 1.62 mmol) was stirred for 40 min, and then concd HCl (1 cm^3) was added. Air was bubbled through the solution for 10 h. The resulting dark green solution was evaporated to dryness under reduced pressure, and the residue was dissolved in methanol (50 cm^3). The methanol solution was shaken with hexane (100 cm^3) to extract free dbpe into hexane. This procedure was repeated several times, and the methanol layer was separated and concentrated to 20 cm^3 under reduced pressure. To the concentrate were added water (10 cm^3) and NH_4PF_6 (500 mg) dissolved in a mixture (3 cm^3) of water and methanol (1 : 1). The mixture was stored in a refrigerator for 10 h to yield green crystals, which were filtered, washed with a mixture (30 cm^3) of water and ethanol (4 : 1), and air-dried. Yield: 110 mg (15%). Found: C, 46.46; H, 9.47%. Calcd for $C_{36}H_{82}Cl_2CoF_6OP_5$: C, 46.50; H, 8.89%. The complex is soluble in methanol, ethanol, chloroform, and diethyl ether.

[Co(CO$_3$)(dbpe)$_2$]PF$_6$·1.5H$_2$O. To *trans*-$[CoCl_2(dbpe)_2]PF_6 \cdot H_2O$ (200 mg, 0.22 mmol) in a mixture (100 cm^3) of methanol and water (4 : 1) were added K_2CO_3 (100 mg, 0.72 mmol) in water (5 cm^3) and active charcoal (ca. 100 mg). The mixture was stirred for 4 h and filtered. The filtrate was evaporated to dryness under reduced pressure, and the complex was extracted with ethanol (20 cm^3). The extract was concentrated to 10 cm^3 and mixed with a solution of NH_4PF_6 (500 mg) in a mixture (3 cm^3) of water and ethanol (4 : 1). The mixture was stored in a refrigerator for 10 h to yield orange crystals, which were filtered, washed with a mixture (30 cm^3) of water and ethanol (4 : 1), and air-dried. Yield: 80 mg (41%). Found: C, 47.89; H, 9.04%. Calcd for $C_{37}H_{83}CoF_6O_{4.5}P_5$: C, 47.89; H, 9.02%. The complex is soluble in methanol and ethanol.

***cis*-[CoCl$_2$(dbpe)$_2$]PF$_6$·H$_2$O.** Ice-cold concd HCl (1 cm^3) was added to an ethanol solution (2 cm^3) of $[Co(CO_3)(dbpe)_2]PF_6 \cdot 1.5H_2O$ (70 mg, 0.075 mmol) at 0 °C, the color of the solution changing slowly from yellow to red. To the red solution was added NH_4PF_6 (200 mg) in water (0.5 cm^3), and the mixture was stored in a refrigerator for 10 h to give red-violet crystals, which were filtered, washed with a mixture (10 cm^3) of ethanol and water (1 : 5), and air-dried. Yield: 20 mg (29%). Found: C, 46.83; H, 9.56%. Calcd for $C_{36}H_{82}Cl_2CoF_6OP_5$: C, 46.50; H, 8.89%. The complex is soluble in methanol and ethanol.

***trans*-[CoCl$_2$(dpee)$_2$]ClO$_4$.** The complex was prepared according to the literature method.[7)]

***cis*-[CoCl$_2$(dpee)$_2$]BF$_4$.** Ice-cold concd HCl (1 cm^3) was added dropwise to an ethanol solution (6 cm^3) of $[Co(O_2)(dpee)_2]BF_4$[7)] (100 mg, 0.103 mmol) at 0 °C. After a while the resulting red-violet solution was mixed with $NaBF_4$ (200 mg) in water (1 cm^3), and was allowed to stand at 5 °C for 10 h to yield red-violet crystals, which were filtered and dissolved in a minimum amount of ethanol–dichloromethane (5 : 1). The solution was applied on a column (ϕ 2.5×20 cm) of Toyopearl TSK-GEL, and the adsorbed products were eluted with ethanol. An yellow-green (major product) and a red-violet (minor product) band appeared. The eluate of the red-violet band was collected and evaporated to dryness under reduced pressure below 30 °C. The residue was dissolved in ethanol (5 cm^3), and diethyl ether (5 cm^3) was added. The solution was allowed to stand at 5 °C for 10 h to give violet crystals, which were filtered, washed with a mixture (20 cm^3) of diethyl ether and ethanol (5 : 1), and air-dried. Yield: 20 mg (19%). Found: C, 62.68; H, 4.62%. Calcd for $C_{52}H_{44}BCl_2CoF_4P_4$: C, 61.87; 4.39%. The complex is soluble in ethanol and dichloromethane.

***trans*-[CoBrI(dmpe)$_2$]ClO$_4$.** To a methanol solution (50 cm^3) of *trans*-$[CoBr_2(dmpe)_2]ClO_4$ (200 mg, 0.32 mmol) was added dropwise a methanol solution (3 cm^3) of NaI (50 mg, 0.33 mmol) with stirring. The solution was stirred for 3 h at 45 °C, and then concentrated under reduced pressure to 5 cm^3. On cooling at 0 °C brown crystals were precipitated, filtered, washed with a mixture (30 cm^3) of methanol and diethyl ether (1 : 1), and air-dried. Yield: 150 mg (70%). Found: C, 21.71; H, 4.87%. Calcd for $C_{12}H_{32}BrClCoIO_4P_4$: C, 21.66; H, 4.84%. The complex is soluble in methanol and ethanol.

***cis*-[CoCl(H$_2$O)(dmpe)$_2$](PF$_6$)$_2$·CH$_3$CN.** To an acetonitrile solution (3 cm^3) of *cis*-$[CoCl_2(dmpe)_2]ClO_4$ (100 mg, 0.19 mmol) was added water (40 cm^3). The solution was stirred at room temperature for 15 min, the color of the solution changing from red to yellow. On addition of NH_4PF_6 (500 mg) in water (3 cm^3) a yellow precipitate was obtained. It was filtered, washed with water (50 cm^3), and air-dried. Yield: 110 mg (85%). Found: C, 23.07; H, 5.01; N, 1.88%. Calcd for $C_{14}H_{37}NClCoF_{12}OP_6$: C, 22.61; H, 4.84; N, 2.04%. The complex is soluble in acetonitrile. The perchlorate of the complex can be obtained by use of $NaClO_4$ instead of NH_4PF_6, but tends to explode by mechanical shock.

***trans*-[CoCl(H$_2$O)(dmpe)$_2$](PF$_6$)$_2$·CH$_3$CN.** An acetonitrile solution (50 cm^3) of *cis*-$[CoCl(H_2O)(dmpe)_2](PF_6)_2 \cdot CH_3CN$ (50 mg, 0.067 mmol) was allowed to stand at room temperature. The color of the solution changed very slowly from yellow to red-orange in the dark, but the change was remarkably accelerated by sunlight. With slow evaporation of acetonitrile red-orange crystals were precipitated, filtered, and air-dried. Yield: 45 mg (90%). Found: C, 23.18; H, 4.92; N, 2.02%. Calcd for $C_{14}H_{37}NClCoF_{12}OP_6$: C, 22.61; H, 4.84; N, 2.04%. The complex is soluble in acetonitrile.

Kinetic Measurements. Isomerization reactions of *cis*-[CoCl$_2$(L)$_2$]$^+$ (L=dmpe, dmpp, dbpe, and dpee) and *cis*-[CoBr$_2$(dmpe)$_2$]$^+$ to the trans isomers in methanol or ethanol solution were monitored spectrophotometrically with a Jasco UNIDEC 610 spectrophotometer equipped with a thermostated cell compartment. The solvents of spectroscopic grade methanol and ethanol were dried over Molecular Sieves, and the complex concentrations were ca. 4×10^{-4}—1×10^{-3} mol dm^{-3}. The temperature of the solutions was in the range of 39.0—65.0 °C and kept constant within ±0.3 °C by use of a temperature-controlled circulating bath, Yamato-Komatsu CET-24W. Suitable wavelengths for following the isomerization reactions were in the range of 485—556 nm where the complexes show the first absorption band. In each kinetic run, the plot of $\ln(D_t - D_\infty)$ vs. time gave a straight line until at least five half-lives, where D_t and D_∞ denote the absorbance at time t and at infinite time, respectively. The slope gave the first-order rate constant of isomerization k, and Eyring treatment of $\log(k/T)$ vs. T^{-1} yielded the activation parameter. All the experiments should be carried out in the dark, because the isomerization reactions were accelerated by sunlight.

Results and Discussion

Preparation and Characterization of the Complexes. All the *trans*-[CoX$_2$(diphosphine)$_2$]$^+$ (X=Cl$^-$, Br$^-$, or I$^-$) complexes in this study can be easily prepared by oxidation of the cobalt(II)-diphosphine species in methanol or ethanol with air in moderate yields, although the yield of the dbpe complex was rather poor because of its high solubility. For *cis*-[CoX$_2$(diphosphine)$_2$]$^+$ (X=Cl$^-$ or Br$^-$), the dmpe, dmpp, and dbpe complexes were prepared by treating the corresponding carbonato complexes with concd HX, while *cis*-[CoCl$_2$(dpee)$_2$]$^+$ was obtained by the reaction of [Co(O$_2$)(dpee)$_2$]$^+$ with concd HCl, the reaction with [Co(CO$_3$)(dpee)$_2$]$^+$ giving only the trans isomer. The former three complexes can also be prepared from the corresponding peroxo complexes.[10] The reactions with concd HX should be carried out at a low temperature, since the trans isomer is formed in larger amounts with an increasing reaction temperature. The [Co(O$_2$)(dpee)$_2$]$^+$ complex afforded a mixture of the cis and trans isomers by the reaction even at a low temperature. The formation of the trans isomer will be attributable to the following properties of the dpee complex; the [Co(O$_2$)(dpee)$_2$]$^+$ complex has less reactivity toward HX compared with other diphosphine-peroxo complexes,[10] and *cis*-[CoCl$_2$(dpee)$_2$]$^+$ isomerizes to the trans isomer much faster than other *cis*-[CoCl$_2$(diphosphine)$_2$]$^+$ do (vide infra). The reaction of [CoCO$_3$(dmpe)$_2$]$^+$ with concd HI yielded only the *trans*-diiodo complex. The cis isomer in which two large I$^-$ ions are in the cis positions will be sterically unstable.

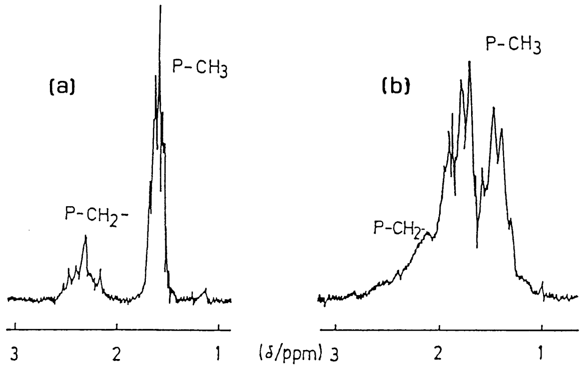

Fig. 1. ^{1}H NMR spectra of (a) *trans*-[CoCl$_2$(dmpe)$_2$]$^+$ and (b) *cis*-[CoCl$_2$(dmpe)$_2$]$^+$ (in CD$_3$CN, TMS reference).

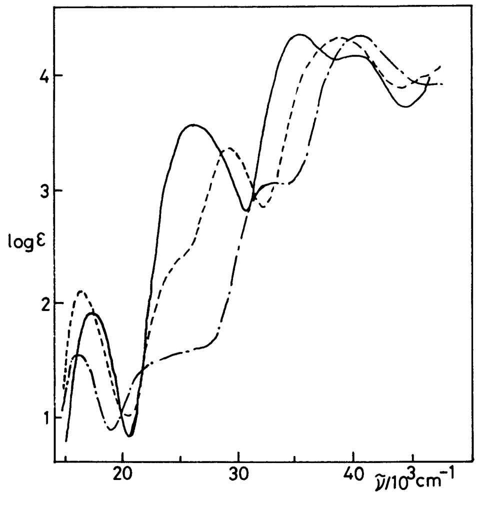

Fig. 2. Absorption spectra of *trans*-[CoCl$_2$(dmpe)$_2$]$^+$ (——), *trans*-[CoCl$_2$(edmp)$_2$]$^+$ (----), and *trans*-[CoCl$_2$(en)$_2$]$^+$ (–·–·–).

All the *cis*-[CoX$_2$(diphosphine)$_2$]$^+$ complexes in nonaqueous solvents are fairly stable in the dark, but easily isomerize to the trans isomer on exposure of ultraviolet light. The *cis*-[CoCl$_2$(dmpe)$_2$]$^+$ complex in acetonitrile afforded *cis*-[CoCl(H$_2$O)(dmpe)$_2$]$^+$ by the addition of water. The aqua complex in acetonitrile was stable in the dark, but isomerized to the trans aqua complex on exposure of ultraviolet light. Both cis and trans aqua complexes were isolated as the hexafluorophosphate. Detailed studies on these photochemical reactions are in progress.

Geometrical structures of the complexes were assigned from the ^{1}H NMR spectra, and from comparisons of the absorption spectra with those of other phosphine and ethylenediamine complexes. In the ^{1}H NMR spectrum, for example, *trans*-[CoCl$_2$(dmpe)$_2$]$^+$ shows a multiplet methyl signal at δ ca. 1.6, while the cis isomer gives many signals in the region of δ 1.5—2.0 (Fig. 1). The spectral pattern of the cis isomer is quite similar to those of [CoCO$_3$(dmpe)$_2$]$^+$ and

$[CoC_2O_4(dmpe)_2]^+$,[11] which have necessarily a cis geometry.

Figure 2 compares the absorption spectra of *trans*-$[CoCl_2(L)_2]^+$ (L= dmpe, edmp, and en), where edmp denotes $NH_2CH_2CH_2P(CH_3)_2$. For *trans*(Cl, Cl), *cis*(P, P)-$[CoCl_2(edmp)_2]^+$, we have assigned the peak at 16600 cm^{-1} to the Ia component of the first absorption band, the shoulder at ca. 23800 cm^{-1} to the second absorption band overlapped the Ib component of the first absorption band, the bands at 29500 and 39700 cm^{-1} to the Co-Cl charge-transfer band, and the shoulder at ca. 36500 cm^{-1} to the Co-P charge-transfer band, by comparing the spectrum with that of the en complex.[12] The spectrum of *trans*-$[CoCl_2(dmpe)_2]^+$ may be assigned in a similar manner; the band at 17300 cm^{-1} can be assigned to the Ia component of the first absorption band, the broad band at 26100 cm^{-1} to that involving three components, the second absorption band, the Ib component of the first absorption band, and the Co-Cl charge-transfer band, the band at 35400 cm^{-1} to the Co-P charge-transfer band, and the band at 40500 cm^{-1} to the Co-Cl charge-transfer band. In Fig. 3 the spectra of *trans*-$[CoX_2(dmpe)_2]^+$ (X=Br^- and I^-) are compared with that of *trans*-$[CoCl_2(dmpe)_2]^+$. The spectrum of the dibromo complex is similar to that of the dichloro complex, but that of the diiodo complex differs from those of other halogeno complexes. For *trans*-$[CoX_2(en)_2]^+$, the spectra of the dichloro and dibromo complexes are similar, but that of the diiodo complex also differs from others.[13] Other phosphine complexes, *trans*-$[CoCl_2(L)_2]^+$ (L=dmpp and dbpe), give spectra similar to that of the dmpe complex (Fig. 4(a)). The Ia band shifts to higher energy in the order L=dpee<dbpe<dmpp<dmpe (Table 1). This order coincides with the decreasing order in cone angle of

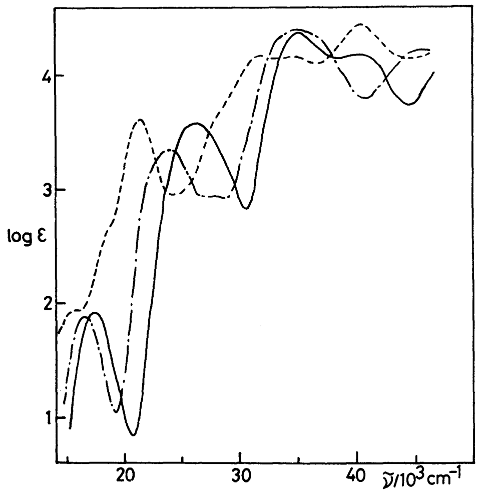

Fig. 3. Absorption spectra of *trans*-$[CoCl_2(dmpe)_2]^+$ in CH_3OH (——), *trans*-$[CoBr_2(dmpe)_2]^+$ in CH_3OH (—·—), and *trans*-$[CoI_2(dmpe)_2]^+$ in CH_3CN (----).

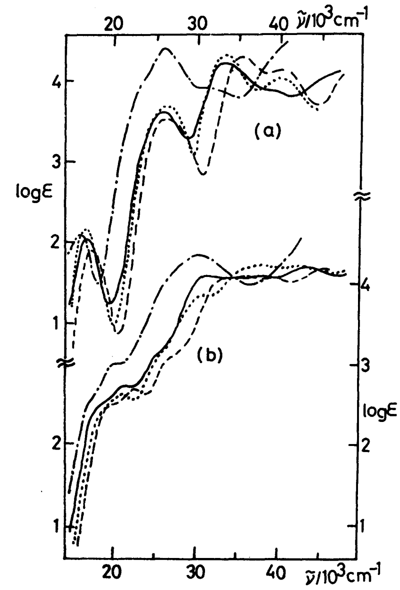

Fig. 4. Absorption spectra of (a) *trans*-$[CoCl_2(dmpe)_2]^+$ (----), *trans*-$[CoCl_2(dmpp)_2]^+$ (······), *trans*-$[CoCl_2(dbpe)_2]^+$ (——), and *trans*-$[CoCl_2(dpee)_2]^+$ (—·—), and (b) *cis*-$[CoCl_2(dmpe)_2]^+$ (----), *cis*-$[CoCl_2(dmpp)_2]^+$ (······), *cis*-$[CoCl_2(dbpe)_2]^+$ (——), and *cis*-$[CoCl_2(dpee)_2]^+$ (—·—). Solvent: CH_3OH except for the dpee complexes (CH_2Cl_2).

Table 1. Absorption Spectral Data[a)]

Complex	$\tilde{\nu}/10^3\,cm^{-1}(\log\varepsilon)$			
trans-$[CoCl_2(dmpe)_2]^+$	17.30(1.92)	26.10(3.70)	35.40(4.35)	40.50(4.16)
cis-$[CoCl_2(dmpe)_2]^+$	19.7 (2.5)[b)]	22.30(2.69)	26.60(3.06)	
trans-$[CoCl_2(dmpp)_2]^+$	16.66(2.19)	26.50(3.50)	33.50(4.34)	40.30(4.06)
cis-$[CoCl_2(dmpp)_2]^+$	19.5 (2.5)[b)]	21.01(2.62)	25.0 (3.1)[b)]	
trans-$[CoCl_2(dbpe)_2]^+$	16.61(2.05)	26.00(3.64)	33.20(4.26)	39.20(3.88)
cis-$[CoCl_2(dbpe)_2]^+$	18.2 (2.5)[b)]	21.14(2.74)	24.80(3.08)	
trans-$[CoCl_2(dpee)_2]^+$	15.87(2.11)	22.7 (3.9)[b)]	25.80(4.40)	31.00(3.94)
cis-$[CoCl_2(dpee)_2]^+$	17.0 (2.5)[b)]	20.00(3.00)	26.0 (4.0)[b)]	
trans-$[CoBr_2(dmpe)_2]^+$	16.39(1.89)	24.00(3.35)	35.09(4.39)	45.0(4.2)
trans-$[CoBrI(dmpe)_2]^+$	16.13(1.90)	22.47(3.38)	33.80(4.27)	
trans-$[CoI_2(dmpe)_2]^+$	15.38(1.94)	18.2 (2.6)[b)]	22.30(3.60)	27.2(3.5)[b)]
	31.70(4.15)	34.50(4.14)	40.40(4.43)	

a) Solvent: CH_3OH except for *trans*- and *cis*-$[CoCl_2(dpee)_2]^+$ (CH_2Cl_2) and *trans*-$[CoI_2(dmpe)_2]^+$ (CH_3CN).
b) Shoulder.

phosphine ligands.[14]

Figure 4(b) shows absorption spectra of *cis*-$[CoCl_2(L)_2]^+$ (L=dmpe, dmpp, dbpe, and dpee). The spectra in the region of 15000—25000 cm^{-1} are similar among the four complexes and have three bands or shoulders. These absorptions can be assigned to the first and second bands from a comparison with the spectrum of *cis*-$[CoCl_2(en)_2]^+$. This complex shows the first absorption band at 18600 cm^{-1} with a shoulder at ca. 17000 cm^{-1} and the second absorption band at 25500 cm^{-1}.[15] In a previous paper,[16] we reported that the first absorption band of the $[Co(N)_n(P)_{6-n}]^{3+}$-type complexes shifts to higher energy by replacing N with P, while the energy of the second absorption band remains almost unchanged. Thus the bands and shoulders in the region of 17000—22000 cm^{-1} of *cis*-$[CoCl_2(diphosphine)_2]^+$ are assigned to the first absorption band split into two components,[17] and the shoulders in the region of 25000—26000 cm^{-1} to the second absorption band. The higher energy first absorption band shifts to higher energy in the order diphosphine=dpee<dbpe<dmpp<dmpe. This order is the same as that observed for the corresponding trans isomer. The spectral patterns in the ligand field absorption band region of these *trans*- and *cis*-$[CoCl_2(diphosphine)_2]^+$ complexes are very similar to those of *trans*- and *cis*-$[CoCl_2(diarsine)_2]^+$, respectively, to which similar band assignments have been made.[18,19]

The chloride ions in *trans*-$[CoCl_2(diphosphine)_2]^+$ are quite inert to aquation compared with those in *trans*-$[CoCl_2(en)_2]^+$. For example, *trans*-$[CoCl_2(dmpe)_2]^+$ is stable in neutral water at room temperature for at least several days, while *trans*-$[CoCl_2(en)_2]^+$ liberates one chloride ion to aquate with the half-life time of 361 min (25 °C, pH 1).[20] The *trans*-$[CoCl_2\{NH_2CH_2CH_2P(CH_3)_2\}_2]^+$ complex is also stable to aquation.[12] The reactivity of *trans*-$[CoCl_2(diphosphine)_2]^+$ to the substitution reaction of CO_3^{2-} for the two chloride ions depends on the kind of phosphines. The reaction of the dmpe complex with K_2CO_3 occurs instantly at room temperature to yield $[CoCO_3(dmpe)_2]^+$, whereas those of the dmpp and dbpe complexes proceed at a higher temperature or the addition of active charcoal. Miskowski et al.[7] used Ag_2CO_3 to prepare $[CoCO_3(dpee)_2]^+$, from *trans*-$[CoCl_2(dpee)_2]^+$, the breaking of the Co-Cl bond being assisted by Ag^+. The *trans*-dichloro complexes containing bulky phosphine ligands seem to have less reactivity to substitution reactions for the chloride ions.

In contrast to *trans*-$[CoCl_2(diphosphine)_2]^+$, the corresponding cis isomers liberate rapidly one chloride ion in aqueous solution to yield *cis*-$[CoCl(H_2O)(diphosphine)_2]^{2+}$. The reaction of *cis*-$[CoCl_2(dmpe)_2]^+$ is complete within 15 min in neutral water at 25 °C, which is much faster than that of *cis*-$[CoCl_2(en)_2]^+$ ($t_{1/2}$=ca. 46 min, 25 °C, pH 1).[20] The lability of Cl^- in *cis*-$[CoCl_2(dmpe)_2]^+$ may be brought about by the strong trans effect of the phosphine ligand.[21] However, the subsequent reaction to liberate the second chloride ion is so slow that *cis*-$[CoCl(H_2O)(dmpe)_2]^{2+}$ can be isolated. A similar aquation reaction has been reported for *cis*-$[RuCl_2\{(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2\}_2]$.[22]

The *trans*-$[CoI_2(dmpe)_2]^+$ complex, which was prepared from $[CoCO_3(dmpe)_2]^+$ and concd HI, can also be obtained by metathesis of *trans*-$[CoX_2(dmpe)_2]ClO_4$ ($X=Cl^-$, Br^-) and NaI. The mixed halogeno complexes, *trans*-$[CoXI(dmpe)_2]^+$ ($X=Cl^-$, Br^-), were isolated by similar reactions, although the pure chloroiodo complex was not obtained. Reverse reactions yielding the chloro and bromo complexes from the diiodo complex do not take place. These results indicate that the cobalt(III) ion in the dmpe complex has stronger affinity to I^- than to Cl^- and Br^-. The cobalt(III) ion which belongs to a hard acid may be softened by coordination of phosphine ligands, and may have stronger affinity to a more soft base I^- than Cl^- and Br^- as predicted by the principle of "Hard and Soft Acids and Bases."[23]

Isomerization Reactions. All the *cis*-$[CoX_2(diphosphine)_2]^+$ complexes prepared in this study isomerize in methanol or ethanol to the trans isomer. Figure 5 shows the change in absorption spectrum at intervals during the isomerization of *cis*-$[CoCl_2(dpee)_2]^+$ in methanol at 50 °C. Three isosbestic points were found at 363, 488, and 634 nm and the final spectrum was identical with that of a freshly prepared solution of *trans*-$[CoCl_2(dpee)_2]^+$. These results indicate that the cis isomer isomerizes to the trans isomer, and no reverse reaction occurs. The cis isomers of other phosphine complexes gave similar results. The rates of the isomerization were followed by measuring the change in absorbance at a given wavelength, and from

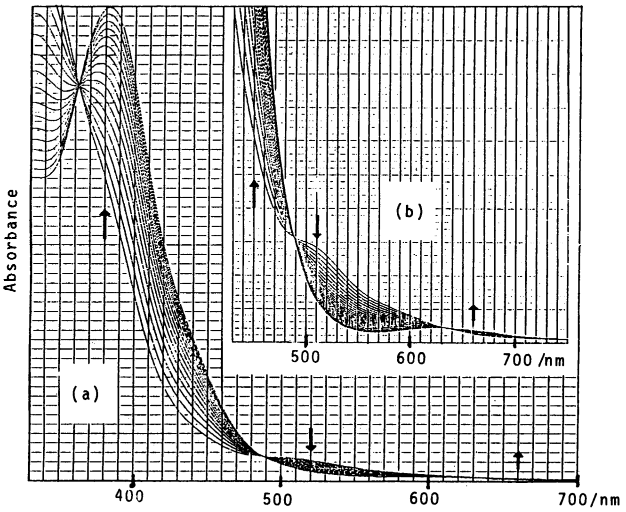

Fig. 5. Change in absorption spectrum of *cis*-$[CoCl_2(dpee)_2]BF_4$ in methanol at 50°C (recorded intervals: 30 min). Trends of spectral changes with time are shown by arrows.. In (b), the scale of absorbance is expanded.

the data the first-order rate constants were obtained (Experimental, Fig. 6, and Table 2). For *cis*-$[CoCl_2(dbpe)_2]^+$, the isomerization was also studied at 39 °C in the presence of 200 times as many moles of LiCl, but the rate was the same within the experimental error.

The mechanism for isomerization of the present complexes is not clear at present. However, the fact that the rate of isomerization of *cis*-$[CoCl_2(dbpe)_2]^+$ is not affected by the addition of LiCl suggests that the complex isomerizes by an intramolecular mechanism. Peloso and Tobe[24] proposed an intramolecular mechanism for the isomerization of *cis*-$[CoCl_2(diars)_2]^+$ (diars=*o*-phenylenebis(dimethylarsine)). This complex isomerizes to the trans isomer in methanol with a similar rate ($1.67\times10^{-6}\,s^{-1}$, 55 °C) to that of *cis*-$[CoCl_2(dmpe)_2]^+$, and the rate increases only a little by the addition of LiCl. The *cis*-$[CoCl_2\{(CH_3)_2AsCH_2CH_2CH_2As(CH_3)_2\}_2]^+$ complex gives similar results in the isomerization to the trans isomer.[19] The *cis*-$[CoX_2(L)_2]^+$-type complexes (L=diphosphine and diarsine) in methanol seem to isomerize to the trans isomer intramolecularly by a similar mechanism. The *cis*-$[CoCl_2(en)_2]^+$ complex in methanol isomerizes to the trans isomer faster ($t_{1/2}$=3.6 h, 35 °C) than do the diphosphine and diarsine complexes, and the rate is dependent upon the LiCl concentration, for which a unimolecular mechanism involving a five-coordinate intermediate was proposed.[25]

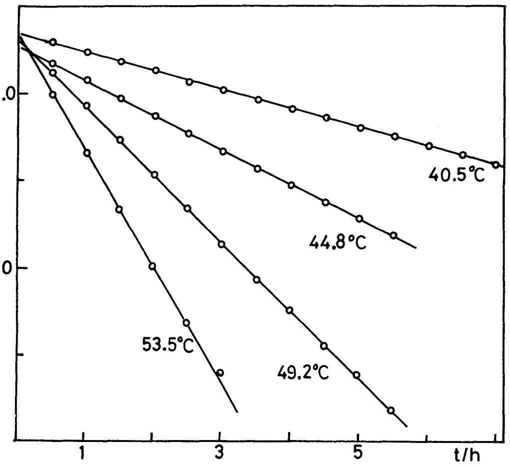

Fig. 6. Plots of $\ln(D_t-D_\infty)$ against time at 40.5, 44.8, 49.2, and 53.5°C for *cis*-$[CoCl_2(dpee)_2]BF_4$.

Table 2. Rate Constants for Isomerization of the Complexes

Complex	*t*	*k*
	°C	$s^{-1}\times10^{-5}$
cis-$[CoCl_2(dpee)_2]BF_4$	40.5	2.91±0.01
	44.8	5.38±0.02
	49.2	10.72±0.02
	53.5	18.03±0.02
cis-$[CoCl_2(dbpe)_2]PF_6$	39.0	1.10±0.02
	43.3	2.06±0.03
	49.3	4.65±0.03
	52.3	7.29±0.05
cis-$[CoCl_2(dmpp)_2]BF_4$	46.4	3.27±0.02
	49.1	4.60±0.02
	51.7	6.48±0.02
	54.0	8.47±0.03
cis-$[CoCl_2(dmpe)_2]ClO_4$	55.0	0.13±0.02
	60.0	0.25±0.02
	62.3	0.28±0.04
	65.0	0.40±0.03
cis-$[CoBr_2(dmpe)_2]ClO_4$	50.0	1.15±0.03

Solvent: CH_3OH except for *cis*-$[CoCl_2(dmpe)_2]ClO_4$ (C_2H_5OH).

Table 3 lists the activation parameters for the isomerization. The $\Delta H^{\ddagger}$ values increase in the order, the dmpe<dmpp<dbpe<dpee complexes. However, the $\Delta G^{\ddagger}$ (25 °C) values are similar because of the positive $\Delta S^{\ddagger}$ values increasing in the same order as for the $\Delta H^{\ddagger}$ values. The orders in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values coincide with the increasing order in cone angle of phosphine ligands, and suggest that the difference in rates among the complexes comes from a steric factor. If the isomerization is assumed to proceed intramolecularly , the increasing $\Delta H^{\ddagger}$ values with increasing bulkiness of a phosphine ligand may be conceivable, since the complex with a bulky phosphine ligand would require larger energy to reach a transition state by twisting the octahedral structure of the complex. For the change in $\Delta S^{\ddagger}$, however, no appropriate explanation can be given at present, although there are fairly large differences among the complexes. More data are needed to discuss in detail.

The rate constant $1.15\times10^{-5}\,s^{-1}$ at 50 °C of *cis*-$[CoBr_2(dmpe)_2]^+$ is larger by a factor of about 10 than that of *cis*-$[CoCl_2(dmpe)_2]^+$ at the same temperature. As stated previously, $[CoI_2(dmpe)_2]^+$ formed only the trans isomer by the reaction of $[CoCO_3(dmpe)_2]^+$ with HI. The cis isomer may isomerize very rapidly to the trans isomer during the reaction. The stability of *cis*-$[CoX_2(dmpe)_2]^+$ depends largely on the kind of halide ions and becomes low rapidly on going from a small Cl^- to a large I^- ion.

Table 3. Thermodynamic Parameters for Isomerization of the Complexes

Complex	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}_{25\,°C}$
	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
cis-$[CoCl_2(dpee)_2]BF_4$	118.2±1.8	45.0±5.6	104.8±3.5
cis-$[CoCl_2(dbpe)_2]PF_6$	116.5±0.8	33.4±2.4	106.6±1.5
cis-$[CoCl_2(dmpp)_2]BF_4$	106.4±0.9	2.1±2.9	105.8±1.7
cis-$[CoCl_2(dmpe)_2]ClO_4$	95.6±3.4	−66.3±10	115.4±6.4

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