CHEMISTRY LETTERS, pp. 575-576, 1981.

PREPARATION AND SPECTROSCOPIC PROPERTIES OF A PAIR OF GEOMETRICAL ISOMERS, *cis*- AND *trans*-BIS(ACETYLACETONATO)BIS(DIMETHYLPHENYLPHOSPHINE)COBALT(III) COMPLEXES

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A pair of geometrical isomers, *cis*- and *trans*-bis(acetylacetonato)bis(dimethylphenylphosphine)cobalt(III) complexes were prepared, and the structures were assigned on the basis of the ^{1}H and ^{13}C NMR spectra. The trans isomer shows a strong absorption band in the first absorption band region, its intensity being 40 times as large as that of the cis isomer.

A few cobalt(III) complexes containing monophosphines have been prepared,[1)] and no set of geometrical isomers of such cobalt(III) complexes seems to be reported. This letter deals with the first isolation of a pair of geometrical isomers of $[Co(acac)_2(PMe_2Ph)_2]^+$ (acac = acetylacetonate ion, PMe_2Ph = dimethylphenylphosphine).

The free phosphine ligand was handled under nitrogen atmosphere until it formed air-stable cobalt(III) complexes. A mixture of $[Co(acac)_3]$ (1.2 g, 3.4 mmol), PMe_2Ph (0.94 g, 6.8 mmol), and active charcoal in a mixture (50 cm^3) of ethanol and tetrahydrofuran (2:1) was stirred at room temperature for 12 h, and filtered. The filtrate was diluted with water to 3 dm^3 and column-chromatographed with SP-Sephadex C-25 and an eluent of 0.02 mol/dm^3 NaCl. The first blue-violet eluate was concentrated under reduced pressure. On addition of $NaPF_6$ the concentrate gave a blue-violet precipitate, which was purified by rechromatography using Sephadex LH-20 and a mixture of ethanol and hexane (1:1). Yield, 15%. Found: C, 38.14; H, 4.99%. Calcd for $[Co(acac)_2(H_2O)(PMe_2Ph)]PF_6 \cdot 0.5H_2O$: C, 38.11; H, 4.99%. The complex can be assigned to the trans configuration, since the ^{1}H NMR spectrum in CD_2Cl_2 shows only one kind of the methyl signal of acac. The second red brown eluate gave a red brown precipitate by a method similar to that for the first eluate. The precipitate was purified by recrystallization from a mixture of methanol and water (5:1). Yield, 50%. Found: C, 45.75; H, 5.03%. Calcd for $[Co(acac)_2(PMe_2Ph)_2]PF_6$: C, 46.03; H, 5.33%. The ^{1}H and ^{13}C NMR spectra show two kinds of the methyl signals of acac and the complex is assigned to the cis isomer. The corresponding trans isomer was obtained by mixing the blue-violet complex and a slight excess PMe_2Ph in ethanol in the absence of active charcoal, red orange crystals being deposited in ca. 15 min. Yield, 80%. Found: C, 46.03; H, 5.22%. Calcd for $[Co(acac)_2(PMe_2Ph)_2]PF_6$: C, 46.03; H, 5.35%. The trans structure of the complex is also supported by the NMR spectra. The blue-violet and cis complexes are

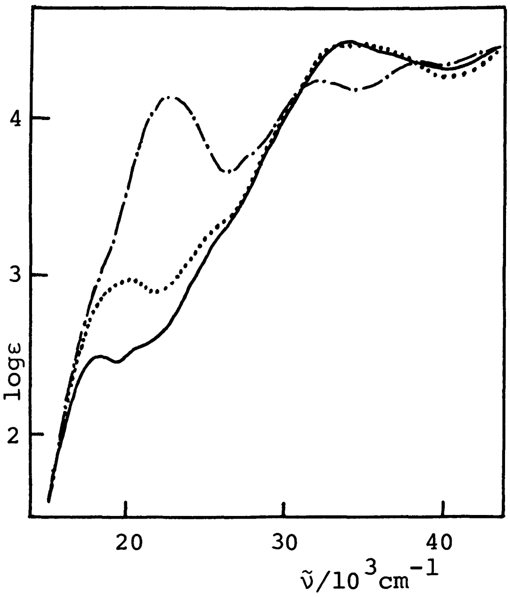

Figure. Absorption spectra of the cis isomer in CH_3OH (————), the trans isomer in CH_2Cl_2 (—·—·—), and $[Co(acac)_2(Ph_2PCH_2CH_2PPh_2)]^+$ in C_2H_5OH (······).

stable in ethanol and CH_2Cl_2. The trans isomer is stable in CH_2Cl_2, but slowly liberates one phosphine ligand in ethanol. It isomerizes to the cis isomer in ethanol in the presence of active charcoal.

Absorption spectra of the isomers differ remarkably from each other as seen in the Figure. The spectrum of the cis isomer resembles that of $[Co(acac)_2(Ph_2PCH_2CH_2PPh_2)]^+$,[2)] but shows two peaks around 20000 cm^{-1}, both of which can be assigned to split components of the first absorption band.[3)] On the other hand, the trans isomer gives a very strong absorption band in this region. This band might comprise charge transfer transitions between the Co(III) ion and the phosphine ligand. The remarkable red shift of the charge transfer band seems to be characteristic of a cobalt(III) complex with two phosphorus donor atoms in the trans positions. The *trans*-$[Co(acac)_2(H_2O)(PMe_2Ph)]^+$ complex shows the first absorption band with similar intensity to that of the cis isomer.

The P-CH_3 groups of the cis isomer show two kinds of triplet signals in the ^1H and ^{13}C NMR spectra at 1.35 ppm(J = 13.4 Hz) and 1.41 ppm(J = 14.1 Hz), and at 9.62 ppm (J = 29.0 Hz) and 10.64 ppm(J = 29.3 Hz), respectively (J refers to the interval between the two outer peaks; $|J_{AX} + J_{BX}|$). The appearance of the two kinds of methyl signals indicates that the phosphine ligands are in chiral environment. For the trans isomer, the P-CH_3 groups show single triplet signals at 1.71 ppm(J = 8.3 Hz) and 9.13 ppm(J = 24.4 Hz) in the ^1H and ^{13}C NMR spectra, respectively. The P-CH_3 groups of both isomers exhibit triplet signals with J values of similar magnitudes. Thus the $^2J(P,P)_{cis}$ is presumed to have a value similar to that of the $^2J(P,P)_{trans}$. For some octahedral complexes, $^2J(P,P)_{cis}$ values have been reported to be fairly large,[1)] although they are generally very small in planar complexes.[4)]

This work was partly supported by The Kurata Research Grant of the Kurata Foundation and by the Joint Studies Program (1980 ∿ 1981) of the Institute for Molecular Science.

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(Received February 23, 1981)