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Cis to Trans Photoisomerization of $[CoCl_2\{(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2\}_2]^+$, $[CoCl(H_2O)\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_2]^{2+}$ and Related Complexes

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(Received August 22, 1988)

Synopsis. Ligand field irradiation of *cis*-$[CoCl_2\{(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2\}_2]^+$ in methanol and *cis*-$[CoCl(H_2O)\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_2]^{2+}$ in acetonitrile at 5 °C led to isomerization to the trans isomer with quantum yields of 0.010 and 0.070, respectively. The same cis to trans photoisomerization of $[CoCl_2(R_2PCH_2CH_2PR_2)_2]^+$ ($R=CH_3$, C_4H_9) occurred with much smaller quantum yields (ca. 1×10^{-4}) and *cis*-$[CoCl_2\{(C_6H_5)_2PCHCHP(C_6H_5)_2\}_2]^+$ was reduced to cobalt(II) species on irradiation.

Although photochemistry of cobalt(III) complexes has been studied extensively, reactions with a high quantum yield are limited to a few complexes.[1] Recently, Houlding and Miskowski[2] have reported the photoaquation of $[Co\{(CH_3O)_2PCH_2CH_2P(OCH_3)_2\}_3]^{3+}$ with a high quantum yield of 0.26. In this paper we report photoisomerizations of several *cis*-bis(diphosphine)cobalt(III) complexes to trans isomers in methanol or aceotnitrile solutions. The phosphine ligands are $(CH_3)_2PCH_2CH_2P(CH_3)_2$=dmpe, $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$=dmpp, $(C_4H_9)_2PCH_2CH_2P(C_4H_9)_2$=dbpe, and *cis*-$(C_6H_5)_2PCHCHP(C_6H_5)_2$=dpee.

Experimental

Materials. The complexes were prepared as described peviously.[3] Methanol and acetonitrile used for solvents were purified and dried by standard methods, and purged with dry nitrogen for 10 min prior to use.

Quantum Yield Determinations. Photolyses were carried out with solutions (3.0 cm^3, ca. 3.0×10^{-4} to 3.0×10^{-3} mol dm^{-3}) in a 1.0 cm length spectrophotometer cell which was thermostated at 5±0.5 °C. Solutions in the cell were stirred during irradiation. The light source was a 150 W Xenon short arc lamp of Ushio Co., Ltd. with a mirror to enhance the light intensity on the cell window. Irradiation light was made monochromatic by use of a JASCO CT-10 monochrometer. The incident photon flux on the cell window as measured by trioxalatoferrate(III)[4] and reineckate actinometry[5] ranged from 6.4×10^{-9} to 3.2×10^{-8} einstein cm^{-2} s^{-1}. Absorption spectral changes of a solution were recorded on a JASCO UVIDEC 650 or a HITACHI U-3400 spectrophotometer at appropriate intervals during irradiation. Quantum yields were determined from the spectral data for less than 20% reactions according to the method of Adamson et al.[6] The values were corrected for thermal reactions (isomerization) in the dark, which were, however, negligibly slow under the experimental conditions (5 °C).[3]

Results and Discussion

Figures 1 and 2 show absorption spectra of *cis*- and *trans*-$[CoCl_2(dmpp)_2]^+$ and *cis*- and *trans*-$[CoCl(H_2O)(dmpe)_2]^{2+}$, respectively. In a previous paper,[3] we assigned the band at 16700 cm^{-1} of *trans*-$[CoCl_2(dmpp)_2]^+$ to the split component (Ia) of the first d-d band ($^1T_{1g}\leftarrow{}^1A_{1g}(O_h)$), and the broad band (17000—22000 cm^{-1}) and the shoulder around 25000 cm^{-1} of *cis*-$[CoCl_2(dmpp)_2]^+$ to the first and the second

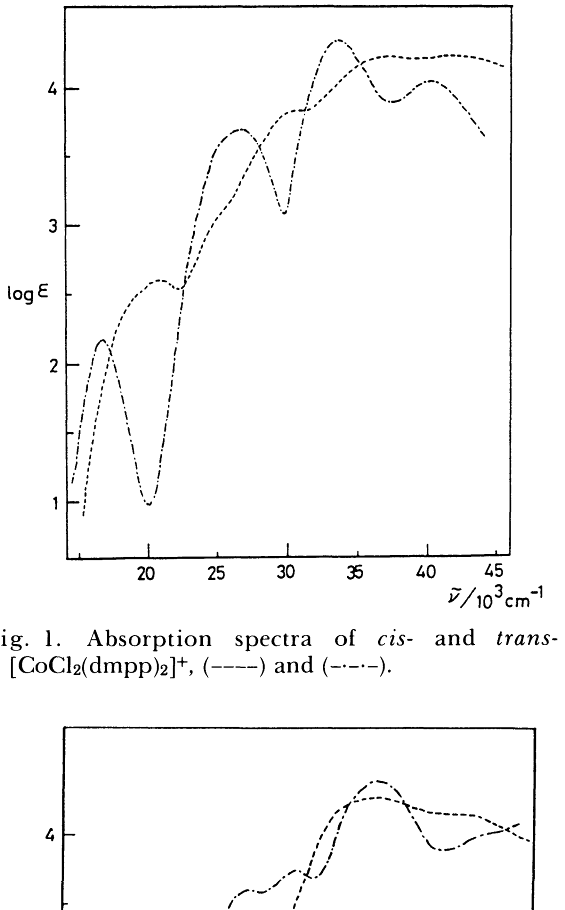

Fig. 1. Absorption spectra of *cis*- and *trans*-$[CoCl_2(dmpp)_2]^+$, (----) and (–·–·–).

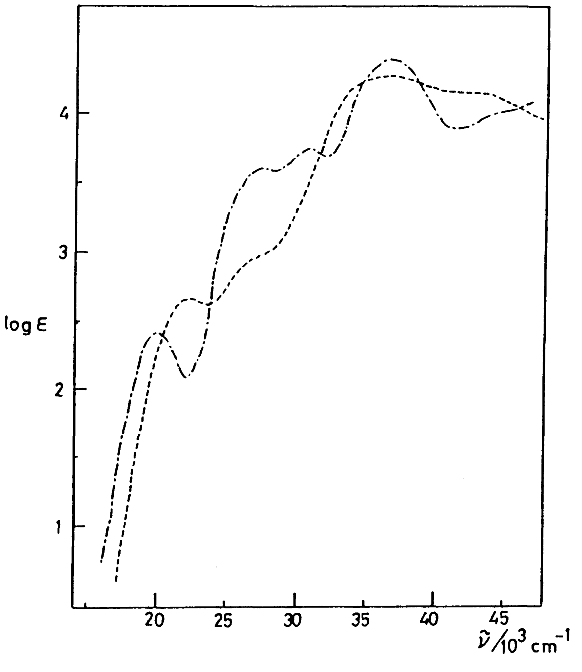

Fig. 2. Absorption spectra of *cis*- and *trans*-$[CoCl(H_2O)(dmpe)_2]^{2+}$, (----) and (–·–·–).

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($^1T_{2g}\leftarrow{}^1A_{1g}(O_h)$) d-d bands, respectively. The ligand field spectra of other $[CoCl_2L_2]^+$ (L=dmpe, dbpe, dpee) are very similar to those of the corresponding isomers of the dmpp complex except that the absorption maxima are slightly shifted to higher energy in the order L=dpee<dbpe<dmpp<dmpe. For $[CoCl(H_2O)(dmpe)_2]^{2+}$, the trans isomer shows the first band at 20100 cm^{-1}, and the cis isomer gives the first band at 22400 cm^{-1} and the second one around 27000 cm^{-1} as a shoulder. Other strong bands in the higher energy region are all attributable to charge-transfer transitions from ligands to cobalt(III).

Figure 3 shows the changes in absorption spectrum at 5 min intervals that occur upon 480 nm irradiation of *cis*-$[CoCl_2(dmpp)_2]^+$ in methanol at 5 °C. Two clear isosbestic points were found at 442 nm and 571 nm. After 3 h irradiation the spectrum almost coincided with that of *trans*-$[CoCl_2(dmpp)_2]^+$. The *trans*-$[CoCl_2(dmpp)_2]^+$ isomer showed no spectral change by the same irradiation even for more than 10 h. Thus the photolysis of *cis*-$[CoCl_2(dmpp)_2]^+$ is concluded to afford only the trans isomer. Photolyses with 545 and 452 nm lights gave similar results. The quantum yields were determined according to the method of Adamson et al.,[6] and are listed in Table 1.

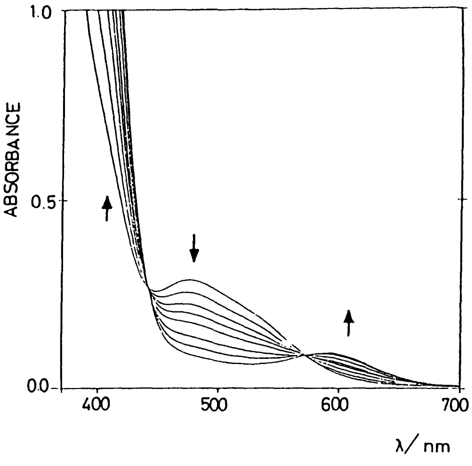

Fig. 3. Sequence of absorption spectra on 480 nm irradiation of *cis*-$[CoCl_2(dmpp)_2]^+$ in methanol at 5 °C (5 min intervals).

Table 1. Quantum Yields of the Complexes at 5°C

Complex	Irradiation wavelength nm	Quantum yield (ϕ)
cis-$[CoCl_2(L)_2]X$[a]		
L=dmpp, X=BF_4	545	0.011±0.003
	480	0.010±0.001
	452	0.010±0.001
	334	0.012±0.001
	254	0.014±0.001
L=dmpe, X=ClO_4	452	ca. 1×10^{-4}
	254	0.0051±0.0004
L=dbpe, X=PF_6	480	ca. 1×10^{-4}
	254	[b]
L=dpee, X=BF_4	504	[b]
	254	[b]
cis-$[CoCl(H_2O)(dmpe)_2](PF_6)_2$[c]	452	0.070±0.007
	254	0.046±0.013

a) Solvent; methanol. b) Reductions to Co(II) species. c) Solvent; acetonitrile.

Ligand field irradiation of *cis*-$[CoCl_2(L)_2]^+$ (L=dmpe and dbpe) caused very small changes in the absorption spectra. The changes have isosbestic points and also indicate the isomerization to the trans isomers. However, the quantum yields were about 1×10^{-4}. In the case of the dpee complex, the spectrum changed with no isosbestic points and the intensity decreased. The changes indicate that the reduction of cobalt(III) to cobalt(II) took place by irradiation, although the photolysis products were not characterized. Thus the *cis*-dichloro complexes of 1,2-diphosphines exhibited different photochemical behavior from that of the 1,3-diphosphine, dmpp complex.

In contrast to rather photoinert *cis*-$[CoCl_2(dmpe)_2]^+$, *cis*-$[CoCl(H_2O)(dmpe)_2]^{2+}$ in acetonitrile yielded the trans isomer on irradiation at 452 nm with a quantum yield of 0.070. This value is about 700 times as large as that of *cis*-$[CoCl_2(dmpe)_2]^+$. The trans isomer was photoinert under the same conditions. Sheridan and Adamson[6] reported similar photoisomerization for an ethylenediamine (en) analog, *cis*-$[CoCl(H_2O)(en)_2]^{2+}$ in 0.2 mol dm^{-3} HCl; the complex undergoes cis to trans isomerization on 488 nm irradiation with a quantum yield of 0.0042, while the trans isomer is photoinert. Thus both chloroaqua complexes of en and dmpe exhibit similar photoreactivity, but the quantum yield of the former is smaller than that of the latter by a factor of about 10.

On irradiation with ultraviolet light (254 and 334 nm) *cis*-$[CoCl_2(L)_2]^+$ (L=dmpe and dmpp) and *cis*-$[CoCl(H_2O)(dmpe)_2]^{2+}$ isomerized to the trans isomers. In the spectral changes, isosbestic points were almost kept until about 45, 50, and 80% reactions of the dichloro complexes of dmpe and dmpp, and the chloroaqua complex of dmpe, respectively. Further photolyses led to apparent deviation from the isosbestic points. The deviations will be attributable to photoreaction of the reaction products, trans isomers, since all of these trans isomers undergo photolyses on 254 nm irradiation at moderate rates. These reactions are supposed to be reduction of cobalt(III) to cobalt(II), since ligand field bands characteristic of cobalt(III) complexes disappear. The quantum yields were obtained from the spectral data for less than 20% reactions. The value of *cis*-$[CoCl_2(dmpp)_2]^+$ was nearly the same as those obtained by ligand field irradiation. The independence on the wavelength of irradiation light suggests a reaction from a low energy excited state, although the mechanism is not clear at present. For most photoreactions of cobalt(III) complexes with strong ligands such as CN^- a ligand field triplet pathway has been postulated.[1] However, the value of *cis*-$[CoCl_2(dmpe)_2]^+$ obtained by 254 nm irradiation is about fifty times as large as that by 452 nm irradiation. No explanation can be given to the difference between the dmpp and dmpe complexes at present. The dbpe and dpee complexes were more susceptible to photoreduction on irradiation at 254 nm and the quantum yields were not determined.

The authors wish to thank the Ministy of Education for Scientific Research Grant-in-Aid No. 61430013.

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