Preparation and Spectroscopic Characteristics of Geometrical Isomers of Bis[1,2-bis(dimethylphosphino)ethane]cobalt(III) Complexes with Thiolate Ligands

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(Received June 5, 1989)

The thiolato cobalt(III) complexes, $[Co(SR)_2(dmpe)_2]^+$, where R denotes CH_3, C_2H_5, or $CH_2C_6H_5$ and dmpe denotes 1,2-bis(dimethylphosphino)ethane, were newly prepared from *trans*-$[CoCl_2(dmpe)_2]^+$ and monothiolate ligands. The cis and trans isomers were formed for R=CH_3 and $CH_2C_6H_5$, while only the trans isomer was formed for R=C_2H_5. These isomers were assigned on the basis of the ^1H NMR (500 MHz) and absorption spectra in comparison with those of the newly prepared $[Co(SCH_2CH_2S)(dmpe)_2]^+$ complex. The trans isomer showed the sulfur-to-cobalt charge-transfer band at lower energy than that of the cis isomer.

Cobalt(III) complexes with two or three thiolato donor atoms prefer to take the cis(S) geometry,[1-3] and no trans isomer has been obtained for $[Co(SR)_2(amine)_4]^+$ (R=CH_3, C_2H_5, $CH_2C_6H_5$, and C_6H_5).[4] On the other hand, chelating diphosphine ligands, such as dmpe (1,2-bis(dimethylphosphino)ethane) and depe (1,2-bis(diethylphosphino)ethane), tend to favor the formation of *trans*-$[CoX_2(diphosphine)_2]^+$ (X=Cl, Br, and I).[5-8] This trend reveals that the trans(S) geometry is possibly formed in the $[Co(SR)_2(diphosphine)_2]$-type complex. The present work is concerned with the preparation of $[Co(SR)_2(dmpe)_2]^+$ (R=CH_3, C_2H_5, and $CH_2C_6H_5$), and the trans(S) isomers are presented. The isomers obtained were characterized on the basis of the ^1H NMR (500 MHz) and absorption spectra in comparison with those of the newly prepared $[Co(SCH_2CH_2S)(dmpe)_2]^+$. This is the first example of cobalt(III) complexes containing both diphosphine and monothiolate ligands.

Experimental

A) Preparation of Complexes. (1) The starting complex, *trans*-$[CoCl_2(dmpe)_2]ClO_4$, was prepared by the method of Ohishi et al.[6] Found: C, 26.91; H, 6.13%. Calcd for $[CoCl_2(dmpe)_2]ClO_4 \cdot 0.5H_2O = C_{12}H_{33}O_{4.5}Cl_3P_4Co$: C, 26.76; H, 6.18%.

(2) *cis*- and *trans*-$[Co(SCH_3)_2(dmpe)_2]X$ (X=PF_6 and $B(C_6H_5)_4$). To a solution containing 0.1 g of *trans*-$[CoCl_2(dmpe)_2]ClO_4 \cdot 0.5H_2O$ (0.19 mmol) in 20 cm³ of degassed methanol was added 0.06 g of $NaSCH_3$ (0.86 mmol) in 1 cm³ of methanol. The mixture was stirred at 50 °C for 30 min under a nitrogen atmosphere, whereupon the solution became deep brown. To this was added 1 g of $NaPF_6$ in 10 cm³ of water and the solution was allowed to stand in a refrigerator overnight. The resulting brown crystals of *trans*-$[Co(SCH_3)_2(dmpe)_2]PF_6$ (**A-1**) were collected by filtration. The filtrate was kept in a freezer overnight and the resulting **A-1** precipitate was again filtered off. To this filtrate was added 0.1 g of $NaB(C_6H_5)_4$ in 2 cm³ of methanol. After the mixture was allowed to stand in a refrigerator for 1 h, the resulting greenish-brown precipitate of *cis*-$[Co(SCH_3)_2(dmpe)_2]B(C_6H_5)_4$ (**A-2**) was collected by filtration. The **A-2** isomer was recrystallized from acetone by adding a small amount of $NaB(C_6H_5)_4$ in methanol. **A-1** isomer: Yield: 0.05 g, 45%. Found: C, 28.17; H, 6.47%. Calcd for $[Co(SCH_3)_2(dmpe)_2]PF_6 = C_{14}H_{38}F_6P_5S_2Co$: C, 28.10; H, 6.40%. **A-2** isomer: Yield: 0.03 g, 20%. Found: C, 59.04; H, 7.66%. Calcd for $[Co(SCH_3)_2(dmpe)_2]B(C_6H_5)_4$: C, 59.07; H, 7.57%.

The trans (**A-1**) and cis (**A-2**) isomers of $[Co(SCH_3)_2(dmpe)_2]^+$ were also formed in nearly the same ratio as that observed above, using $[Co(CO_3)(dmpe)_2]ClO_4 \cdot 2.5H_2O \cdot NaClO_4$[9] as the starting complex instead of *trans*-$[CoCl_2(dmpe)_2]ClO_4 \cdot 0.5H_2O$.

(3) *trans*-$[Co(SC_2H_5)_2(dmpe)_2]PF_6$. This complex (**B-1**) was prepared by a method similar to that described above for *trans*-$[Co(SCH_3)_2(dmpe)_2]PF_6$ (**A-1**), using 0.06 cm³ of neat HSC_2H_5 (0.81 mmol) and 0.3 cm³ of 1 mol dm⁻³ NaOH (0.30 mmol) instead of $NaSCH_3$. No significant formation of the cis isomer was noticed in this reaction or in a reaction where $[Co(CO_3)(dmpe)_2]ClO_4 \cdot 2.5H_2O \cdot NaClO_4$ was used as the starting complex instead of *trans*-$[CoCl_2(dmpe)_2]ClO_4 \cdot 0.5H_2O$. Yield: 0.04 g, 34%. Found: C, 30.55; H, 6.68%. Calcd for $[Co(SC_2H_5)_2(dmpe)_2]PF_6 = C_{16}H_{42}F_6P_5S_2Co$: C, 30.68; H, 6.76%.

(4) *cis*- and *trans*-$[Co(SCH_2C_6H_5)_2(dmpe)_2]X$ (X=ClO_4 and $B(C_6H_5)_4$). The two isomers, trans (**C-1**) and cis (**C-2**), of $[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$ were prepared and separated by a method similar to that described above for $[Co(SCH_3)_2(dmpe)_2]^+$, using 0.1 cm³ of neat $HSCH_2C_6H_5$ (0.85 mmol) and 0.3 cm³ of 1 mol dm⁻³ NaOH (0.30 mmol) instead of $NaSCH_3$. The trans (**C-1**) isomer was obtained as the perchlorate salt using a small amount of a saturated $NaClO_4$ solution instead of $NaPF_6$. It was found from the absorption and ^1H NMR (500 MHz) spectral measurements that the tetraphenylborate salt is the cis (**C-2**) isomer containing a small amount of the trans (**C-1**) isomer. **C-1** isomer: Yield: 0.045 g, 34%. Found: C, 44.12; H, 6.72%. Calcd for $[Co(SCH_2C_6H_5)_2(dmpe)_2]ClO_4 = C_{26}H_{46}O_4P_4S_2ClCo$: C, 44.29; H, 6.58%. $B(C_6H_5)_4$ salt: Yield: 0.03 g, 17%. Found: C, 63.98; H, 7.06%. Calcd for $[Co(SCH_2C_6H_5)_2(dmpe)_2]B(C_6H_5)_4 \cdot H_2O = C_{50}H_{64}BP_4S_2Co \cdot H_2O$: C, 63.83; H, 7.07%.

(5) $[Co(SCH_2CH_2S)(dmpe)_2]PF_6$. This complex was prepared by a method similar to that described for $[Co(SCH_3)_2(dmpe)_2]PF_6$, using 0.05 cm³ of neat $HSCH_2CH_2SH$ (0.60 mmol) and 0.3 cm³ of 1 mol dm⁻³ NaOH (0.30 mmol) instead of $NaSCH_3$. The reaction was conducted at room temperature for 30 min. Yield: 0.04 g, 35%. Found: C, 28.60; H, 6.02%. Calcd for $[Co(SCH_2CH_2S)(dmpe)_2]PF_6 = C_{14}H_{36}F_6P_5S_2Co$: C, 28.20; H, 6.08%.

B) Measurements. The electronic absorption spectra were recorded in CH_3CN with JASCO UVIDEC-505 and UVIDEC-610 spectrophotometers at ambient temperatures. The 500 MHz ^1H NMR spectra were recorded with a BRUKER-AM-500 NMR spectrometer in CD_3CN at the probe temperature. Tetramethylsilane (TMS) was used at the internal reference.

Results and Discussion

Two geometrical isomers, cis and trans, are possible for $[Co(SR)_2(dmpe)_2]^+$ ($R=CH_3$, C_2H_5, and $CH_2C_6H_5$), while only one isomer having the cis(*S*) configuration is possible for $[Co(SCH_2CH_2S)(dmpe)_2]^+$ (Fig. 1). In the 500 MHz ^1H NMR spectrum (Fig. 2), $[Co(SCH_2CH_2S)(dmpe)_2]^+$ exhibits characteristic P-methyl signals in the region of δ 1.4—1.6 (from TMS). That is, four sets of signals due to the eight $P-CH_3$ groups in the complex are observed (Fig. 2a), reflecting the C_2 symmetry of the complex. A quite similar ^1H NMR spectral pattern is observed for the **A-2** isomer of $[Co(SCH_3)_2(dmpe)_2]^+$, though two signals due to the two $S-CH_3$ groups appear (δ 1.589 and 1.594) besides four sets of signals due to the eight $P-CH_3$ groups in the region of δ 1.4—1.6 (Fig. 2b). On the other hand, the **A-1** isomer of $[Co(SCH_3)_2(dmpe)_2]^+$ shows one set of P-methyl signals which appears as a quintet at δ 1.629 (J=2.2 Hz) and one singlet S-methyl signal at δ 1.304 (Fig. 2c). The starting *trans*-$[CoCl_2(dmpe)_2]^+$ complex also gave one set of quintet P-methyl signals at δ 1.572 (J=2.4 Hz). These ^1H NMR spectral behavior indicate that the **A-1** and **A-2** isomers are *trans*- and *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$, respectively. The ^1H NMR spectral behavior of the **B-1** isomer of $[Co(SC_2H_5)_2(dmpe)_2]^+$ and the **C-1** isomer of $[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$ are similar to that of *trans*-$[Co(SCH_3)_2(dmpe)_2]^+$ (**A-1**), showing one set of quintet signals due to the eight $P-CH_3$ groups in the complex (δ 1.623 (J=2.2 Hz) for **B-1** and δ 1.718 (J=2.1 Hz) for **C-1**). Furthermore, the **B-1** isomer shows one set of triplet signals (δ 1.061, J=7.3 Hz) and one set of quartet signals (δ 1.718, J=7.3 Hz) due to the two SC_2H_5 groups, and the **C-1** isomer shows one singlet signal due to the two $S-CH_2-$ groups at δ 2.931. Accordingly, the **B-1** and **C-1** isomers can be assigned to the trans(*S*) configuration. In the ^1H NMR spectrum of the tetraphenylborate salt of $[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$, four sets of P-methyl signals are observed (centered at δ 1.486, 1.566, 1.629, and 1.775) as in the case of *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$ (**A-2**), in addition to one set of quintet P-methyl signals which corresponds to the signals arising from *trans*-$[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$ (**C-1**). The ^1H NMR spectrum suggests that the tetraphenylborate salt is the cis isomer containing a small amount of the trans one. This is supported by the fact that absorption spectral behavior of this salt agrees with that of *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$ (Fig. 3).

As shown in Fig. 3 and Table 1, the absorption spectrum of *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$ is quite similar to that of $[Co(SCH_2CH_2S)(dmpe)_2]^+$ in the whole

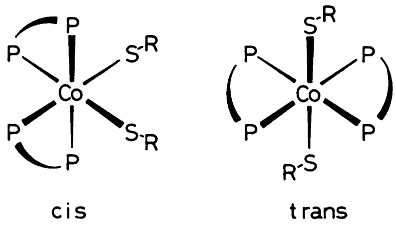

Fig. 1. Two geometrical isomers of $[Co(SR)_2(dmpe)_2]^+$.

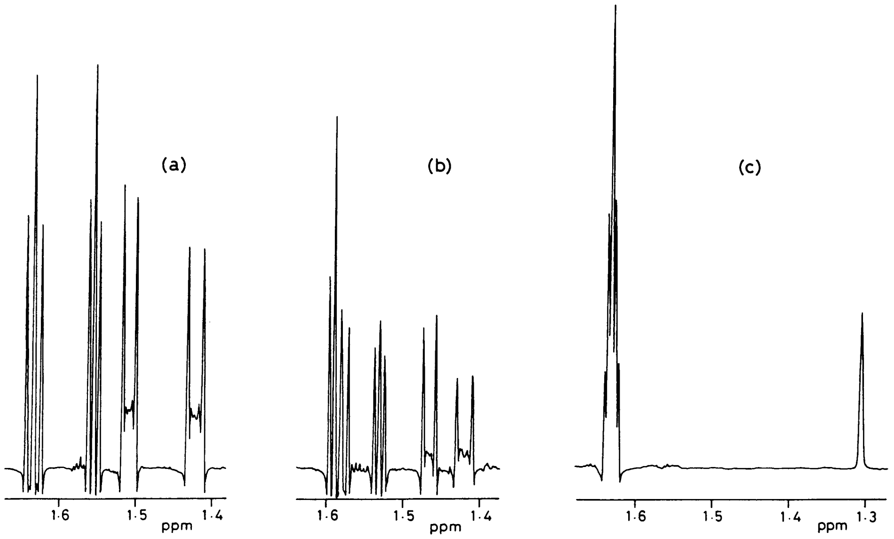

Fig. 2. ^1H NMR (500 MHz) spectra of $[Co(SCH_2CH_2S)(dmpe)_2]^+$ (a), *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$ (b), and *trans*-$[Co(SCH_3)_2(dmpe)_2]^+$ (c) in CD_3CN (TMS reference).

Table 1. Absorption Spectral Data of the Complexes in CH_3CN

Complex	$\sigma/10^3\ cm^{-1}$ (log $\varepsilon/mol^{-1}\ dm^3\ cm^{-1}$)				
$[Co(SCH_2CH_2S)(dmpe)_2]^+$	19.4(2.7sh)	22.12(3.02)	28.9(3.4sh)	33.17(4.16)	43.48(4.25)
cis-$[Co(SCH_3)_2(dmpe)_2]^+$	17.50(2.61)	21.7(3.0sh)	26.32(3.38)	32.15(4.16)	42.55(4.50)
trans-$[Co(SCH_3)_2(dmpe)_2]^+$	18.73(2.39)	28.53(4.05)	41.15(4.26)		
trans-$[Co(SC_2H_5)_2(dmpe)_2]^+$	18.87(2.35)	28.65(4.06)	41.32(4.26)		
trans-$[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$	17.91(2.48)	28.01(4.36)	42.7(4.4sh)		

sh denotes a shoulder.

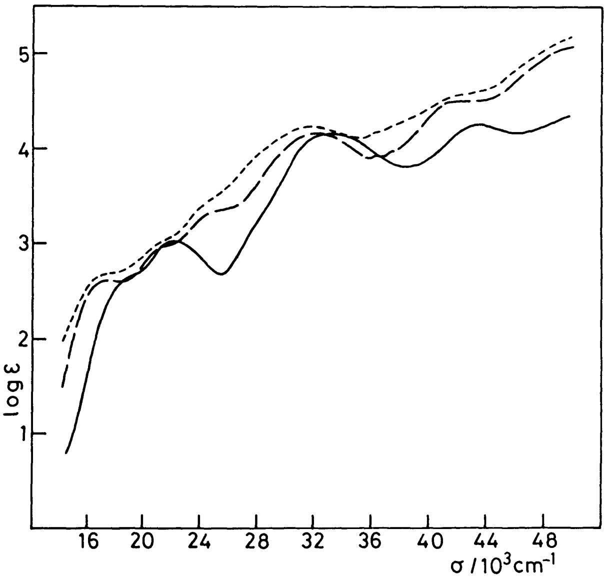

Fig. 3. Absorption spectra of $[Co(SCH_2CH_2S)(dmpe)_2]^+$ (——), *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$ (– – –), and $[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$ (-----) in CH_3CN.

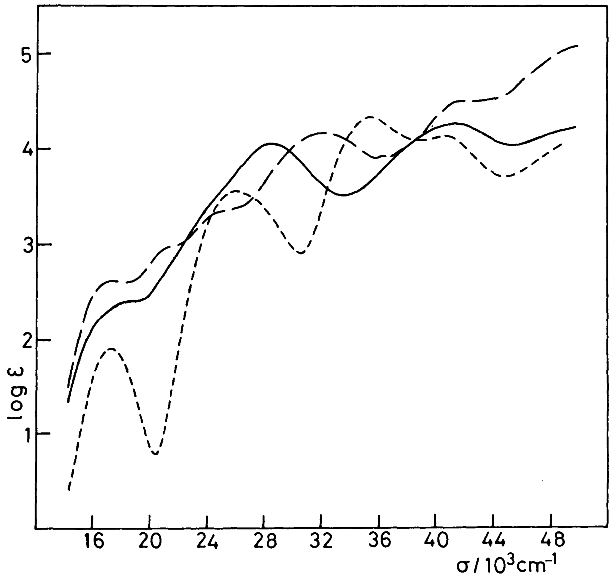

Fig. 4. Absorption spectra of *trans*-$[Co(SCH_3)_2(dmpe)_2]^+$ (——), *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$ (– – –), and *trans*-$[CoCl_2(dmpe)_2]^+$ (-----) in CH_3CN.

region, though the absorption components of the former complex shift to a somewhat lower energy than those of the latter. On the other hand, the absorption spectral behavior of *trans*-$[Co(SCH_3)_2(dmpe)_2]^+$ differs significantly from those of $[Co(SCH_2CH_2S)(dmpe)_2]^+$ and *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$, especially in the near-UV region (Fig. 4). Namely, the trans SCH_3 isomer exhibits an intense absorption band at $28.53\times10^3\ cm^{-1}$, while the cis SCH_3 isomer exhibits a broad intense band at $32.15\times10^3\ cm^{-1}$. The corresponding broad intense band of $[Co(SCH_2CH_2S)(dmpe)_2]^+$ appears at $33.17\times10^3\ cm^{-1}$ (Fig. 3). Quite similar intense absorption bands, which have been assigned to the S-to-Co charge-transfer (SCCT) bands, were observed for the trans(*S*) and cis(*S*) isomers of [Co(quadridentate-SNNS)(diamine)]$^+$:[10] a sharp band at ca. $30\times10^3\ cm^{-1}$ for the trans(*S*) isomer and a broad band at ca. $34\times10^3\ cm^{-1}$ for the cis(*S*) isomer. For the present $[Co(thiolato)_2(diphosphine)_2]^+$-type complexes, it may be considered that the coordinated diphosphine ligand contributes to the absorption spectral behavior in this region. As shown in Fig. 4, however, *trans*-$[CoCl_2(dmpe)_2]^+$ exhibits an intense band at $35.46\times10^3\ cm^{-1}$, which has been assigned as arising from the P-to-Co charge-transfer (PCCT) transition.[8] Taking this fact into consideration, it is probable that the intense bands for the present isomers are due to the SCCT transition rather than to the PCCT transition. In order to confirm the absorption spectral behavior of the trans and cis isomers, $[Co(SC_2H_5)_2(dmpe)_2]^+$ and $[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$ were also newly prepared. The absorption spectra of the trans SC_2H_5 and $SCH_2C_6H_5$ isomers coincide well with that of *trans*-$[Co(SCH_3)_2(dmpe)_2]^+$ over the whole region (Fig. 5 and Table 1), showing the SCCT band at ca. $28.5\times10^3\ cm^{-1}$. The tetraphenylborate salt of $[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$, which is the cis isomer containing a small amount of the trans one (vide supra), gives a broad SCCT band at ca. $32\times10^3\ cm^{-1}$ (Fig. 3), as in the case of *cis*-$[Co(SCH_3)_2(dmpe)_2]^+$. Thus, it is also valid for the present dmpe complexes that the cis(*S*)- and trans(*S*)-type isomers are discriminated on the basis of the relative position of the SCCT bands.[10–13] The cis and trans isomers of $[Co(SCH_3)_2(dmpe)_2]^+$ also show noticeable absorption spectral difference in the visible region (Fig. 4 and Table 1). It has been reported that the cis(*S*) and trans(*S*) isomers of [Co(quadridentate-SNNS)(diamine)]$^+$ can be assigned by the splitting pattern of the first d–d absorption bands.[10] However, it is difficult for the

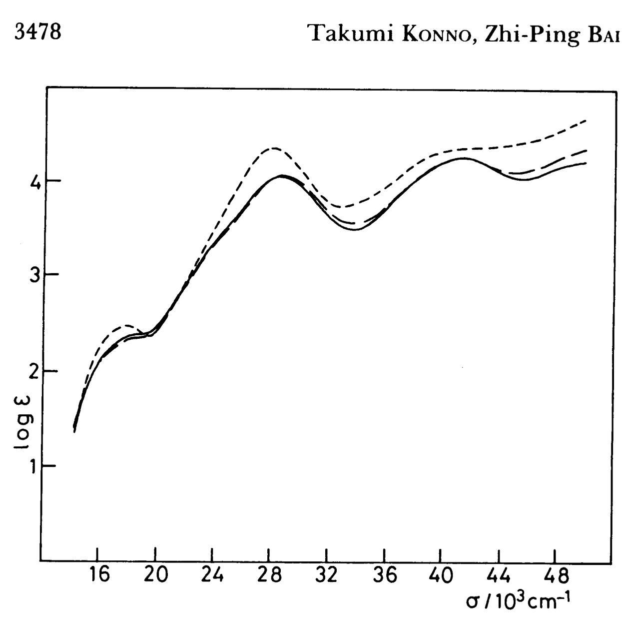

Fig. 5. Absorption spectra of *trans*-$[Co(SCH_3)_2(dmpe)_2]^+$ (——), *trans*-$[Co(SC_2H_5)_2(dmpe)_2]^+$ (— — —), and *trans*-$[Co(SCH_2C_6H_5)_2(dmpe)_2]^+$ (- - - - -) in CH_3CN.

present dmpe complexes to assign the two isomers on the basis of the absorption spectral difference in the visible region.

In this study, a direct treatment of *trans*-$[CoCl_2(dmpe)_2]^+$ with monothiolate ligands produced the $[Co(SR)_2(dmpe)_2]^+$ (R=CH_3, C_2H_5, and $CH_2C_6H_5$) complexes. The trans isomer was formed for all three complexes, while the cis isomer was formed for two complexes (R=CH_3 and $CH_2C_6H_5$). Furthermore, each of the two cis isomers was formed in small amount compared with the corresponding trans isomer. A quite similar preparative result was also obtained by a method in which $[Co(CO_3)(dmpe)_2]^+$ was used as the starting complex instead of *trans*-$[CoCl_2(dmpe)_2]^+$. These results are in contrast to the cis(*S*) selective formation as found in [Co(L-cysteinato-*N*,*S*)$_3$]$^{3-}$,[1,2] [Co(D-penicillaminato-*N*,*O*,*S*)$_2$]$^-$,[3] and $[Co(SR)_2(amine)_4]^+$ (R=CH_3, C_2H_5, $CH_2C_6H_5$, and C_6H_5),[4] and indicate that the trans(*S*) geometry is dominant for $[Co(SR)_2(dmpe)_2]^+$ complexes. Namely, the dmpe ligand functions dominantly in forming *trans*-$[Co(SR)_2(dmpe)_2]^+$. It has been reported that the *cis*-$[CoX_2(dmpe)_2]^+$ (X=Cl, Br, and I) complexes isomerized to the trans isomer and the isomerization reaction was accelerated by ultraviolet light.[8] In contrast to *cis*-$[CoX_2(dmpe)_2]^+$, the present cis and trans isomers of $[Co(SR)_2(dmpe)_2]^+$ in solution are fairly stable in the dark; the intensities of their SCCT bands in CH_3CN or CH_3CN–H_2O (4:1) decreased slightly with time at room temperature (ca. 1.5% in 60 min). No isomerization occurred for the present isomers, even when the solution was exposed to ultraviolet light, though decomposition was promoted. These facts suggest that the cis(*S*) preference of the thiolate ligand prevents the isomerization to the trans(*S*) isomer.

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