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Preparation and Characterization of Cobalt(III)-Dimethyldithiocarbamato Complexes Containing $R_2P(CH_2)_nPR_2$ ($R=CH_3$, C_6H_5; $n=1,2,3,4$) and PR_3 ($R=C_2H_5$, C_6H_5). Crystal Structure of $[Co\{(CH_3)_2NCS_2\}\{(CH_3)_2PCH_2P(CH_3)_2\}_2](BF_4)_2$

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Twelve new cobalt(III)-phosphine complexes, $[Co(dtc)_x\{(CH_3)_2P(CH_2)_nP(CH_3)_2\}_{3-x}]^{(3-x)+}$ ($x=1, 2$; $n=1,2,3$), $[Co(dtc)_2\{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\}]^+$ ($n=1,2,3,4$), and *trans*-$[Co(dtc)_2(PR_3)_2]^+$ ($R=C_2H_5$, C_6H_5) were prepared, where dtc denotes dimethyldithiocarbamate(1−). The molecular structure of $[Co(dtc)\{(CH_3)_2PCH_2P(CH_3)_2\}_2](BF_4)_2$ was determined by X-ray analysis. Crystal data are: monoclinic, space group Cc, $a=15.927(4)$, $b=11.726(2)$, $c=14.422(7)$ Å, $\beta=91.38(3)°$, $V=2692.6(15)$ Å^3, $Z=4$, $R=0.058$ for 2251 reflections. The complex ion forms a distorted octahedron with the small P–Co–P (73.1(2) and 75.5(2)°) and S–Co–S (75.97(9)°) chelate angles. The mean Co–P and Co–S distances are 2.238(5) and 2.285(3) Å, respectively. On the basis of the angular overlap model(AOM) treatment, the ligand field bands were assigned and the effect of ring size of diphosphine chelates on these bands were examined. Positive $e_\pi(P)$ values were necessary to satisfy the observed data, and the result indicates that the Co-dπ orbitals are destabilized by coordination of the phosphine ligand.

In contrast to extensive studies on dithiocarbamato-metal complexes,[1] relatively few investigations have been reported on mixed-dithiocarbamato complexes.[2] Recently one of the present authors (M. Kita) prepared mixed dimethyldithiocarbamato (dtc)-Co(III) complexes containing ethylenediamine (en), $[Co(dtc)_x(en)_{3-x}]^{(3-x)+}$ ($x=1,2$), by oxidizing an aqueous solution containing Co(II) ions and en with tetramethylthiuram disulfide.[3] By similar oxidation reactions we have prepared a number of mixed dtc-Co(III) complexes containing phosphine ligands. This paper reports preparation and characterization of $[Co(dtc)_x\{(CH_3)_2P(CH_2)_nP(CH_3)_2\}_{3-x}]^{(3-x)+}$ ($x=1,2$; $n=1,2,3$), $[Co(dtc)_2\{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\}]^+$ ($n=1,2,3,4$), and *trans*-$[Co(dtc)_2(PR_3)_2]^+$ ($R=C_2H_5,C_6H_5$). The paper also reports X-ray structure analysis of $[Co(dtc)\{(CH_3)_2PCH_2P(CH_3)_2\}_2](BF_4)_2$ which contains a four-membered diphosphine chelate ligand.

The following abbreviations are used for the diphosphine ligands: $(CH_3)_2P(CH_2)_nP(CH_3)_2$; $n=1$ (dmpm), $n=2$ (dmpe), $n=3$ (dmpp), and $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$; $n=1$ (dppm), $n=2$ (dppe), $n=3$ (dppp), and $n=4$ (dppb).

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 JASCO UVIDEC spectrometer and a Hitachi R-90HS spectrometer, respectively.

Phosphine ligands. Phosphine ligands, dppm, dppe, dppp, and PPh_3, and $(CH_3)_2P(S)P(S)(CH_3)_2$ were obtained from Strem Chemicals, Inc. and dppb from Kanto Chemicals, Inc. The dmpe[4] and dmpp[5] ligands were prepared according to literature methods, and dmpm was prepared by a method similar to that for dmpe, the method being more convenient than the literature method.[6] To liquid ammonia (300 cm^3) in a three-necked 500 cm^3 flask at −78 °C was added 1.15 g of sodium. After stirring for 1 h, 2.60 g of $(CH_3)_2PP(CH_3)_2$[4] was added dropwise. The color of the solution gradually changed from blue to orange. Stirring was continued for 30 min, and then 2.12 g of dichloromethane was added dropwise. After 1 h, liquid ammonia was allowed to evaporate, and the product was extracted with diethyl ether (200 cm^3). The extract was evaporated under reduced pressure to give colorless oily dmpm, which was used for preparing complexes without further purification. Yield: ca. 1.3 g (45%). The ^{1}H NMR spectrum of dmpm in $CDCl_3$ ($\delta=1.40$ (t) and 1.08 (t)) was identical with the literature data.[5]

Preparation of Complexes. $[Co(dtc)_x(dmpm)_{3-x}]^{(3-x)+}$ ($x=1$ and 2). To a stirred solution of $Co(BF_4)_2\cdot 6H_2O$ (0.82 g, 2.4 mmol) in methanol (5 cm^3) was added a solution of dmpm (0.65 g, 4.8 mmol) in methanol (5 cm^3). A lemon yellow precipitate was deposited. To this was added a solution of tetramethylthiuram disulfide (0.25 g, 1.04 mmol) in methanol (80 cm^3) and the mixture was stirred at room temperature for 2 days. The resulting yellow-green precipitate was filtered (the filtrate was treated as described below), and washed with diethyl ether (100 cm^3×3) to remove green $[Co(dtc)_3]$. The yellow product remained was recrystallized from water (70 °C) to give yellow needle crystals of $[Co(dtc)(dmpm)_2](BF_4)_2$. Yield: 0.2 g (13%). Found: C, 24.99; H, 5.36; N, 2.25%. Calcd for $[Co(dtc)(dmpm)_2](BF_4)_2=C_{13}H_{34}NP_4S_2B_2F_8Co$: C, 24.98; H, 5.48; N, 2.24%. ^{1}H NMR (D_2O, DSS): $\delta=3.35(N(CH_3)_2)$.

The filtrate obtained above was evaporated to dryness under reduced pressure and the residue was dissolved in a small amount of water. The solution was applied on a column (ϕ3 cm×100 cm) of SP-Sephadex C-25 (Na^+ form) and the adsorbed product was eluted with 0.2 mol dm^{-3} $NaBF_4$. The eluate of the main red band gave red needle crystals of $[Co(dtc)_2(dmpm)]BF_4$ on cooling. Yield: 0.7 g (55%). Found: C, 25.15; H, 5.22; N, 5.51%. Calcd for $[Co(dtc)_2(dmpm)]BF_4=C_{11}H_{26}N_2P_2S_4BF_4Co$: C, 25.30; H, 5.02; N, 5.36%. ^{1}H NMR ($CDCl_3$, TMS): $\delta=3.29$, $3.31(N(CH_3)_2)$.

$[Co(dtc)_x(dmpe)_{3-x}]^{(3-x)+}$($x=1$ and 2). These complexes were prepared by a method similar to that for the dmpm complexes. A mixture of $\mathrm{Co(BF_4)_2\cdot 6H_2O}$ (0.2 g, 0.59 mmol), dmpe (0.18 g, 1.2 mmol), and tetramethylthiuram disulfide (72 mg, 0.30 mmol) in methanol (70 $\mathrm{cm^3}$) was stirred for a day at room temperature. The resulting yellow precipitate was filtered, washed with diethyl ether (100 $\mathrm{cm^3}$×3), and recrystallized from methanol to give yellow needle crystals of $\mathrm{[Co(dtc)(dmpe)_2](BF_4)_2}$. Yield: 65 mg (17%). Found: C, 26.87; H, 5.71; N, 2.10%. Calcd for $\mathrm{[Co(dtc)(dmpe)_2](BF_4)_2{=}C_{15}H_{38}NB_2F_8P_4S_2Co}$: C, 27.59; H, 5.87; N, 2.15%. ^{1}H NMR ($\mathrm{D_2O}$, DSS): δ=3.28($\mathrm{N(CH_3)_2}$). The mother liquor from which the above complex was filtered off was diluted with 20 $\mathrm{cm^3}$ of water. On evaporation of methanol under reduced pressure the solution gave a red precipitate. Red columnar crystals of $\mathrm{[Co(dtc)_2(dmpe)]BF_4}$ were obtained by recrystallization from methanol (ca. 60 °C). Yield: 45 mg (14%). Found: C, 27.27; H, 5.27; N, 5.32%. Calcd for $\mathrm{[Co(dtc)_2(dmpe)]BF_4{=}C_{12}H_{28}N_2BF_4P_2S_4}$: C, 26.87; H, 5.26; N, 5.22%. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ=3.17, 3.26($\mathrm{N((CH_3)_2}$).

$[\mathrm{Co(dtc)_\mathit{x}(dmpp)_{3-\mathit{x}}}]^{(3-x)+}$($x$=1 and 2). Yellow $\mathrm{[Co(dtc)(dmpp)_2](BF_4)_2}$ (0.72 g, 20%) and red $\mathrm{[Co(dtc)_2(dmpp)]BF_4}$ (0.32 g, 11%) crystals were obtained from $\mathrm{Co(BF_4)\cdot 6H_2O}$ (1.8 g, 5.25 mmol), dmpp (1.72 g, 10.5 mmol), and tetramethylthiuram disulfide (0.63 g, 2.6 mmol) by a method similar to that for the dmpm complexes. Found for yellow crystals: C, 29.83; H, 6.26; N, 2.08%. Calcd for $\mathrm{[Co(dtc)(dmpp)_2](BF_4)_2{=}C_{17}H_{42}NP_4S_2B_2F_8Co}$: C, 29.98; H, 6.22; N, 2.06%. ^{1}H NMR ($\mathrm{D_2O}$, DSS): δ=3.30($\mathrm{N(CH_3)_2}$). Found for red crystals: C, 28.36; H, 5.50; N, 4.89%. Calcd for $\mathrm{[Co(dtc)_2(dmpp)]BF_4{=}C_{13}H_{30}N_2P_2S_4BF_4Co}$: C, 28.37; H, 5.49; N, 5.09%. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ=3.25, 3.31($\mathrm{N(CH_3)_2}$).

$\mathrm{[Co(dtc)_2(dppm)]BF_4}$. An acetone solution (10 $\mathrm{cm^3}$) of tetramethylthiuram disulfide (0.12 g, 0.5 mmol) was added to a mixture of $\mathrm{Co(BF_4)_2\cdot 6H_2O}$ (0.34 g, 1 mmol) and dppm (0.8 g, 2 mmol) in acetone (10 $\mathrm{cm^3}$). The resulting deep-purple solution was stirred for 12 h, to yield purple crystals, which were filtered, washed with benzene (50 $\mathrm{cm^3}$) and then diethyl ether (50 $\mathrm{cm^3}$), and recrystallized by dissolving in dichloromethane (10 $\mathrm{cm^3}$) and by adding diethyl ether (10 $\mathrm{cm^3}$). Yield: 0.39 g (50%). Found: C, 48.29; H, 4.39; N, 3.59%. Calcd for $\mathrm{[Co(dtc)_2(dppm)]BF_4{=}C_{31}H_{34}N_2S_4P_2BF_4Co}$: C, 48.32; H, 4.45; N, 3.64%. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ=2.73, 3.04($\mathrm{N(CH_3)_2}$).

$\mathrm{[Co(dtc)_2(dppe)]BF_4}$. An ethanol solution (100 $\mathrm{cm^3}$) of tetramethylthiuram disulfide (0.15 g, 0.63 mmol) was added to a mixture of $\mathrm{Co(BF_4)_2\cdot 6H_2O}$ (0.44 g, 1.3 mmol) and dppe (1.0 g, 2.5 mmol) in ethanol (100 $\mathrm{cm^3}$). The mixture was stirred for 15 h, at room temperature, and then filtered to remove a small amount of yellow precipitate. On evaporation to a small volume under reduced pressure the filtrate yielded dark red crystals, which were filtered, and recrystallized by dissolving in ethanol–dichloromethane (1:1) and by slow evaporation of dichloromethane. Yield: 0.35 g (35%). Found: C, 49.86; H, 4.88; N, 3.54%. Calcd for $\mathrm{[Co(dtc)_2(dppe)]BF_4{=}C_{32}H_{36}N_2BF_4P_2S_4Co}$: C, 48.99; H, 4.62; N, 3.57%. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ=2.58, 2.78($\mathrm{N(CH_3)_2}$).

$\mathrm{[Co(dtc)_2(dppp)]BF_4}$. To a stirred solution of $\mathrm{Co(BF_4)_2\cdot 6H_2O}$ (0.92 g, 2.7 mmol) in ethanol (10 $\mathrm{cm^3}$) were added a solution of dppp (1.18 g, 2.8 mmol) in benzene–methanol (1:1, 200 $\mathrm{cm^3}$), a solution of tetramethylthiuram disulfide (0.33 g, 1.4 mmol) in benzene–methanol (1:1, 20 $\mathrm{cm^3}$), and a solution of sodium dithiocarbamate dihydrate (0.49 g, 2.7 mmol) in water–methanol (1:1, 20 $\mathrm{cm^3}$) successively. The mixture was stirred for 12 h at room temperature, and evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of methanol and the solution was chromatographed with a Toyopearl TSK-GEL column (ϕ3 cm×40 cm) and methanol as an eluent. Red-brown and then green ($\mathrm{[Co(dtc)_3]}$) bands were eluted. The red-brown eluate was collected and mixed with sodium tetrafluoroborate (1.0 g) to give red-brown crystals, which were filtered and recrystallized from methanol (ca. 60 °C). Yield: 0.30 g (14%). Found: C, 50.29; H, 5.08; N, 3.25%. Calcd for $\mathrm{[Co(dtc)_2(dppp)]BF_4{=}C_{33}H_{38}N_2S_4P_2F_4BCo}$: C, 49.63; H, 4.80; N, 3.51%. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ=2.66, 2.80($\mathrm{N(CH_3)_2}$).

$\mathrm{[Co(dtc)_2(dppb)]BF_4}$. A mixture of $\mathrm{Co(BF_4)_2\cdot 6H_2O}$ (0.43 g, 1.26 mmol) dppb (1.07 g, 2.52 mmol) and tetramethylthiuram disulfide (0.15 g, 0.63 mmol) in methanol (40 $\mathrm{cm^3}$) was stirred for 15 h at room temperature. The resulting brown solution was evaporated to ca. 10 $\mathrm{cm^3}$ under reduced pressure, and green ($\mathrm{[Co(dtc)_3]}$) which deposited was filtered off. The filtrate was chromatographed with a Toyopearl TSK-GEL column (ϕ3 cm×40 cm) using methanol as an eluent. Dark green, brown (main), and bright green ($\mathrm{[Co(dtc)_3]}$) bands were eluted in this order. The brown eluate was collected and evaporated under reduced pressure to yield a brown-red precipitate, which was filtered and recrystallized from methanol (ca. 60 °C). Yield: 0.16 g (20%). Found: C, 50.15; H, 4.99; N, 3.49%. Calcd for $\mathrm{[Co(dtc)_2(dppb)]BF_4{=}C_{34}H_{40}N_2P_2S_4CoBF_4}$: C, 50.25; H, 4.96; N, 3.45%. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ=2.75, 2.91($\mathrm{N(CH_3)_2}$).

***trans*-$\mathrm{[Co(dtc)_2(PPh_3)_2]BF_4}$.** A solution of tetramethylthiuram disulfide (0.66 g, 2.5 mmol) in ethanol (100 $\mathrm{cm^3}$) was added to a mixture of $\mathrm{Co(BF_4)_2\cdot 6H_2O}$(0.44 g, 1.3 mmol) and triphenylphosphine (0.66 g, 2.5 mmol) in ethanol (100 $\mathrm{cm^3}$) with stirring. After 1 h, dark brown crystals were precipitated, filtered and recrystallized by dissolving in dichloromethane–ethanol (1:1) and by slow evaporation of dichloromethane. Yield: 0.25 g (21%). Found: C, 55.24; H, 4.85; N, 3.05%. Calcd for $\mathrm{[Co(dtc)_2(PPh_3)_2]BF_4{=}C_{42}H_{42}N_2\ BF_4P_2S_4Co}$: C, 55.39; H, 4.65; N, 3.08%. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ=2.40 ($\mathrm{N(CH_3)_2}$).

***trans*-$\mathrm{[Co(dtc)_2(PEt_3)_2]BPh_4}$.** A solution of tetramethylthiuram disulfide (0.15 g, 0.63 mmol) in ethanol (100 $\mathrm{cm^3}$) was added to a mixture of $\mathrm{Co(BF_4)_2\cdot 6H_2O}$(0.44 g, 1.3 mmol) and triethylphosphine (0.30 g, 2.5 mmol) in ethanol (100 $\mathrm{cm^3}$) and the mixture was stirred for 15 h. The resulting dark brown solution was evaporated to dryness under reduced pressure. The residue was dissolved in methanol (10 $\mathrm{cm^3}$), and the solution was applied on a column (ϕ2 cm×30 cm) of Toyopearl TSK-GEL. By elution with methanol, brown (main), brown, pink, and green bands developed in this order. The eluate of the main brown band was collected and concentrated to ca. 20 $\mathrm{cm^3}$ under reduced pressure. On addition of a solution of sodium tetraphenylborate (0.40 g) in methanol (10 $\mathrm{cm^3}$) the concentrate yielded a brown precipitate, which was filtrated and recrystallized by dissolving in dichloromethane–ethanol (1:1) and by slow evaporation of dichloromethane. Yield: 0.50 g (45%). Found: C, 60.34; H, 7.19; N, 3.30%. Calcd for $\mathrm{[Co(dtc)_2(PEt_3)_2]BPh_4{=}C_{42}H_{62}N_2BP_2S_4Co}$: C, 59.01; H, 7.31; N, 3.28%. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ=3.02($\mathrm{N(CH_3)_2}$).

X-Ray Analysis. Crystal data of $\mathrm{[Co(dtc)(dmpm)_2](BF_4)_2}$:

monoclinic, Cc, a=15.927(4), b=11.726(2), c=14.422(7) Å, β=91.38(3)°, V=2692.8(15) Å^3, Z=4, D_m=1.56(4) g cm^{-3}, D_c=1.54 g cm^{-3}, μ(Mo $K\alpha$)=10.8 cm^{-1}. A yellow-orange crystal of approximate dimensions 0.50×0.35×0.30 mm^3 was used for X-ray analysis. Diffraction data were collected on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range 24°<2θ<60°, 2251 independent reflections with $|F_o|>3\sigma(|F_o|)$ were obtained. No absorption correction was applied. The calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science with the program system UNICS III.[7] The structure was solved by the usual heavy-atom method; the position of Co was deduced by means of the Patterson synthesis, and all the non-hydrogen atoms were located by the subsequent Fourier synthesis. The positions of hydrogen atoms were identified in subsequent difference-Fourier maps as many as possible. The structure was refined by the block-diagonal least squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogens. The function minimized was $\Sigma w||F_o|-|F_c||^2$. Final R was 0.058 for 2251 observed unique reflections, and the atomic parameters of non-hydrogen atoms are listed in Table 1. Complete lists of the observed and calculated structure factors, the hydrogen atomic parameters, and the thermal parameters for non-hydrogen atoms are preserved by the Chemical Society of Japan (Document No. 8930).

Table 1. Positional Parameters (×10^4) and Equivalent Temperature Factors (Å^2) of [Co(dtc)(dmpm)$_2$](BF$_4$)$_2$

Atom	x	y	z	B_{eqv}
Co	5626(3)	5982(1)	2914(2)	1.9
S1	5224(2)	4449(2)	3771(2)	3.0
S2	5986(2)	4450(2)	2035(2)	2.9
P1	6347(2)	7172(2)	2029(2)	3.2
P2	6881(2)	6099(2)	3608(2)	2.7
P3	4857(2)	7165(2)	3754(2)	3.0
P4	4351(2)	6104(2)	2200(2)	2.6
F11	2003(13)	4588(10)	3811(9)	9.2
F12	2491(14)	6101(10)	4903(12)	11.5
F13	2087(9)	4420(11)	5387(8)	7.3
F14	3054(9)	4383(14)	4501(14)	9.4
F21	4374(9)	10299(12)	5643(8)	7.7
F22	4237(9)	9977(11)	7117(10)	7.9
F23	2997(7)	10250(12)	6347(11)	7.8
F24	3749(14)	8726(13)	6311(15)	11.8
N	5609(24)	2487(6)	2890(21)	4.4
C11	6662(7)	6701(11)	908(8)	3.7
C12	6069(12)	8668(9)	1810(9)	5.0
C13	7292(10)	7142(16)	2765(11)	5.4
C14	7590(8)	4869(12)	3750(10)	4.3
C15	7099(10)	6741(16)	4758(11)	5.6
C21	5045(10)	8647(13)	3865(13)	5.2
C22	4706(9)	6672(12)	4936(8)	4.2
C23	3891(9)	7017(11)	3058(9)	4.1
C24	4340(10)	6815(13)	1092(8)	4.6
C25	3746(9)	4826(14)	2120(11)	5.0
C1	5601(19)	3617(7)	2818(15)	2.6
C2	5312(12)	1848(11)	3582(11)	5.2
C3	6091(12)	1873(11)	2110(10)	5.2
B1	2360(8)	5018(13)	4655(10)	3.9
B2	3841(10)	9895(14)	6286(10)	4.2

The AOM Analysis. The d-d transition energies of the mixed dtc-phosphine cobalt (III) complexes were estimated by the AOM calculations with the program AOM6 coded by Dr. T. Komorita of Department of Chemistry, Faculty of Science, Osaka University.[8] For the ligand field parameters of dtc, e_σ and e_π, 7000 and 1000 cm^{-1} were used, respectively. The values were estimated by the AOM analysis of absorption, CD, and MCD spectral data of [Co(dtc)$_{3-n}$(en)$_n$]$^{n+}$ (n=0—3; en=ethylenediamine),[3] the S-Co-S and N-Co-N bite angles being assumed to 76 and 85°,[8] respectively. The values of the Racah's parameters, B and C were estimated from the CD spectral data of [Co(en)$_2$(dmpe)]$^{3+}$ [9] with the assumption of C=4B, and B=450 cm^{-1} and C=1800 cm^{-1} were assumed. Using these parameter values, the ligand field parameters of phosphine ligands, e_σ(P) and e_π(P) in [Co(dtc)$_{3-x}${R$_2$P(CH$_2$)$_n$PR$_2$}$_x$]$^{x+}$ (R=CH$_3$, C$_6$H$_5$) and *trans*-[Co(dtc)$_2$(PR$_3$)$_2$]$^+$ (R=C$_2$H$_5$, C$_6$H$_5$), were determined as the most appropriate values for assigning observed ligand field spectra of these complexes. The P-Co-P bite angles used in the calculation were estimated from the data of X-ray analysis on related complexes; R$_2$PCH$_2$PR$_2$=72°,[10—13] R$_2$P(CH$_2$)$_2$PR$_2$=82°,[14—17] R$_2$P(CH$_2$)$_3$PR$_2$=94°,[13,18—20] and R$_2$P(CH$_2$)$_4$PR$_2$=90°.[21] The results of calculation are given in Table 4.

Results and Discussion

Preparation and Structure of the Complexes. It is known that oxidation of an aqueous solution containing Co(II) ions and en with tetramethylthiuram disulfide affords [Co(dtc)$_x$(en)$_{3-n}$]$^{(3-x)+}$ (x=1,2, and 3)[3] By similar oxidation reactions using phosphine ligands instead of en, [Co(dtc)$_x$(diphosphine)$_{3-x}$]$^{(3-x)+}$ (x=1 and 2) were obtained for tetramethyldiphosphines (dmpm, dmpe, dmpp), while only [Co(dtc)$_2$(diphosphine)]$^+$ was formed for tetraphenyldiphosphines (dppm, dppe, dppp, dppb). The bis(tetraphenyldiphosphine) complexes will be unstable because of steric crowding due to many bulky phenyl groups. In the case of monophosphines, *trans*-[Co(dtc)$_2$(PR$_3$)$_2$]$^+$ (R=Ph, Et) were obtained. The monophosphine complexes show a single resonance for four N-bonded methyl groups of two dtc ligands in the ^{1}H NMR spectra and can be assigned to the trans isomer. As shown in the Experimental Section, the chemical shift of the N-bonded methyl group of the PEt$_3$ complex (3.02 ppm) is similar to that of [Co(dtc)$_3$] (3.23 ppm), while that of the PPh$_3$ complex is observed at a remarkably high field (2.40 ppm). The high field shift is attributable to the shielding effect of phenyl groups on phosphorus disposed over the dtc ring. The [Co(dtc)$_2$(tetraphenyldiphosphine)]$^+$ complexes also show the methyl signals at a high field compared with those of the tetramethyldiphosphine complexes.

In a previous paper,[22] we reported that *trans*-[Co(acac)$_2$(phosphine)$_2$]$^+$ (acac=acetylacetonate ion) easily liberates one phosphine ligand in wet methanol or ethanol to afford *trans*-[Co(acac)$_2$(H$_2$O)(phosphine)]$^+$. The present *trans*-[Co(dtc)$_2$(PR$_3$)$_2$]$^+$ (R=Ph, Et) complexes, however, are fairly stable in wet ethanol. The

PEt_3 complex is more stable than the PPh_3 complex and its aqueous solution shows no spectral change during the measurement. Since the dtc ligand can be regarded as being more soft than acac, the result indicates that mixed Co(III) phosphine complexes with a soft ligand are more stable than those with a hard ligand.

The dmpm and dppm ligands are known to act as two coordination modes; one is a chelate ligand to form a four-membered chelate ring and the other is a bridging ligand to form a dinuclar complex. The $[Co(dtc)(dmpm)_2]^{2+}$ complex is monomeric as revealed by X-ray analysis. Figure 1 shows a perspective drawing[23] of $[Co(dtc)(dmpm)_2]^{2+}$. The bond distances and angles are listed in Table 2. The Co atom is octahedrally coordinated by four P and two S atoms.

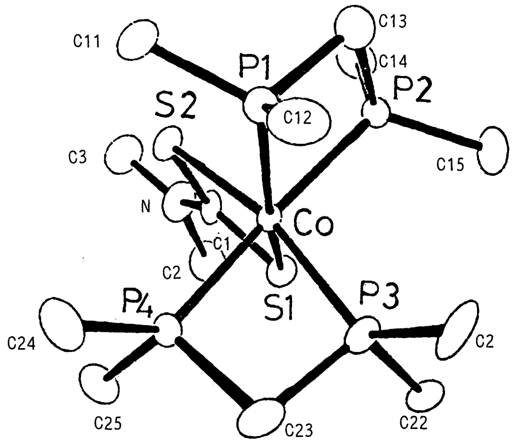

Fig. 1. Perspective view of $[Co(dtc)(dmpm)_2]^{2+}$.

Table 2. Bond Distances (l/Å) and Bond Angles (ϕ/°) of $[Co(dtc)(dmpm)_2](BF_4)_2$

For coordination sphere			
Co-S(1)	2.286(3)	Co-S(2)	2.285(3)
Co-P(1)	2.233(4)	Co-P(2)	2.222(5)
Co-P(3)	2.232(4)	Co-P(4)	2.264(5)
S(1)-Co-S(2)	75.97(9)	S(1)-Co-P(1)	163.5(2)
S(1)-Co-P(2)	93.8(2)	S(1)-Co-P(3)	91.8(2)
S(1)-Co-P(4)	92.1(2)	S(2)-Co-P(1)	92.0(2)
S(2)-Co-P(2)	93.7(2)	S(2)-Co-P(3)	160.4(2)
S(2)-Co-P(4)	91.8(2)	P(1)-Co-P(2)	75.5(2)
P(1)-Co-P(3)	102.6(1)	P(1)-Co-P(4)	99.7(2)
P(2)-Co-P(3)	102.5(2)	P(2)-Co-P(4)	172.8(1)
P(3)-Co-P(4)	73.1(2)		
For dtc ligand			
S(1)-C(1)	1.80(2)	S(2)-C(1)	1.63(2)
C(1)-N	1.33(1)	N-C(2)	1.35(3)
N-C(3)	1.56(3)		
Co-S(1)-C(1)	84.9(5)	Co-S(2)-C(1)	89.0(6)
S(1)-C(1)-S(2)	110.1(5)	S(1)-C(1)-N	119(2)
S(2)-C(1)-N	131(2)	C(1)-N-C(2)	128(2)
C(1)-N-C(3)	114(2)	C(2)-N-C(3)	118(1)
For dmpm ligand			
P(1)-C(11)	1.80(1)	P(1)-C(12)	1.84(1)
P(1)-C(13)	1.82(2)	P(2)-C(13)	1.86(2)
P(2)-C(14)	1.84(1)	P(2)-C(15)	1.85(2)
P(3)-C(21)	1.77(2)	P(3)-C(22)	1.83(1)
P(3)-C(23)	1.81(1)	P(4)-C(23)	1.81(1)
P(4)-C(24)	1.81(1)	P(4)-C(25)	1.79(2)
Co-P(1)-C(11)	118.9(4)	Co-P(1)-C(12)	124.9(6)
Co-P(1)-C(13)	106.0(7)	C(11)-P(1)-C(12)	102.2(6)
C(11)-P(1)-C(13)	106.0(7)	C(12)-P(1)-C(13)	108.2(8)
Co-P(2)-C(13)	94.2(5)	Co-P(2)-C(14)	123.1(4)
Co-P(2)-C(15)	125.4(5)	C(13)-P(2)-C(14)	111.4(7)
C(13)-P(2)-C(15)	104.9(8)	C(14)-P(2)-C(15)	96.8(7)
Co-P(3)-C(21)	124.5(6)	Co-P(3)-C(22)	113.5(5)
Co-P(3)-C(23)	96.2(4)	C(21)-P(3)-C(22)	104.6(8)
C(21)-P(3)-C(23)	106.3(7)	C(22)-P(3)-C(23)	110.9(6)
Co-P(4)-C(23)	95.7(5)	Co-P(4)-C(24)	115.1(6)
Co-P(4)-C(25)	117.0(5)	C(23)-P(4)-C(24)	109.7(6)
C(23)-P(4)-C(25)	108.4(7)	C(24)-P(4)-C(25)	109.7(7)
P(1)-C(13)-P(2)	95.5(8)	P(3)-C(23)-P(4)	94.8(7)

The dmpm ligand forms a four-membered chelate ring with the average P–Co–P angle of 74.3(2)°. The value is larger than that in seven-coordinate $[MoI_2(CO)(dmpm)_2]$ (av. 65.9(2)°), which is only structurally known monomeric dmpm complex,[10] but is similar to those for the dppm chelate complexes ($[Co(C_5H_5)I(dppm)]^+$: 75.1(3)°,[11] $[Rh(dppm)_2(CO)]^+$: 70.45(5)°.[13] The average Co–P–C (98.0(7)°) and P–C–P (95.2(8)°) angles of the dmpm chelate ring in $[Co(dtc)(dmpm)_2]^+$ are also fairly smaller than the tetrahedral angle. Thus, the four-membered dmpm chelate ring involves large strain. The S–Co–S angle of the four-membered dtc chelate ring (75.97(9)°) is similar to those in $[Co(dtc)_3]$ (av. 76.4(1)°)[24] and $[Co(dtc)(en)_2]^{2+}$ (76.90 (9)°).[8] The planes formed by the dmpm chelate ring [Co, P1, P2, C13] and [Co, P3, P4, C23] in $[Co(dtc)(dmpm)_2]^{2+}$ are nearly planar, the deviation from the mean plane of each chelate ring being less than 0.14(2) Å. The Co and dtc ligand atoms [Co, S1, S2, C1, N, C2, C3] also form a plane with the deviation less than 0.11(2) Å from the mean plane.

The average Co–P distance (2.238(5) Å) is a little longer than that of a five-membered dmpe complex containing *O*-ethyldithiocarbonate, $[Co(S_2COC_2H_5)_2(dmpe)]^+$ (2.205(1) Å).[14] The average Co–S distance (2.286(3) Å) is similar to that trans to the P atom in $[Co(S_2COC_2H_5)_2(dmpe)]^+$ (2.290(2) Å), but longer than that trans to the S atom in the same complex (2.255(1) Å). The average Co–S distances of $[Co(dtc)_3]^{24)}$ and $[Co(dtc)(en)_2]^{2+}$ [3] are 2.264(2) Å and 2.263(3) Å, respectively. The longer Co–S distance in the present dtc complex may be attributed to the trans influence of the phosphorus donor atom.

Electronic Spectra. Figures 2, 3, and 4 show absorption spectra of the dtc complexes of $[Co(dtc)(P\text{–}P)_2]^{2+}$, $[Co(dtc)_2(P\text{–}P)]^+$, and *trans*-$[Co(dtc)_2(P)_2]^+$ types, respectively. Table 3 lists the spectral data. The

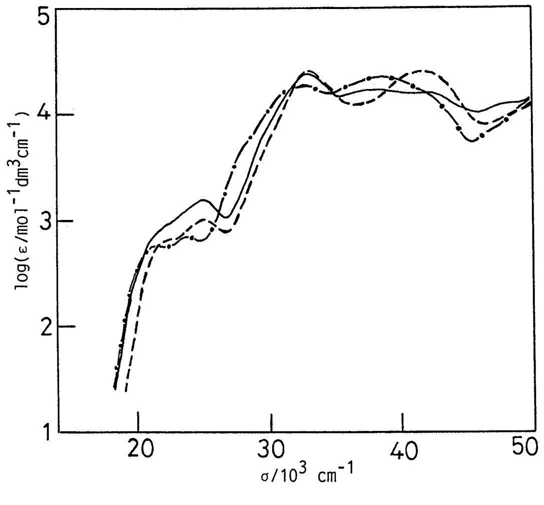

Fig. 2. Absorption spectra of $[Co(dtc)\{Me_2P(CH_2)_nPMe_2\}_2](BF_4)_2$ in H_2O: $n=1$ (dmpm, ——), $n=2$ (dmpe, ----), and $n=3$ (dmpp, -·-·-).

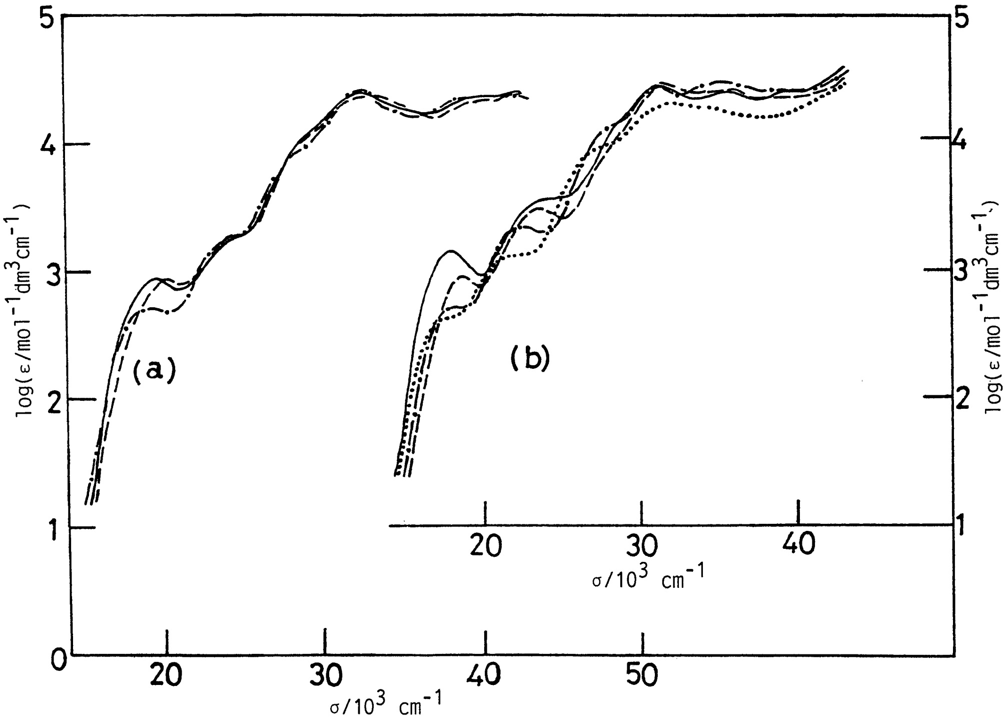

Fig. 3. Absorption spectra of (a) $[Co(dtc)_2\{Me_2P(CH_2)_nPMe_2\}]BF_4$ in CH_2Cl_2: $n=1$ (dmpm, ——), $n=2$ (dmpe, ----), and $n=3$ (dmpp, -·-·-); (b) $[Co(dtc)_2\{Ph_2P(CH_2)_nPPh_2\}]BF_4$ in CH_2Cl_2: $n=1$ (dppm, ——), $n=2$ (dppe, ----), $n=3$ (dppp, -·-·-), and $n=4$ (dppb ·····).

Table 3. Absorption Spectral Data

Complex/Solvent	$\sigma_{\text{LF band}}/10^3\ cm^{-1}$ (log ($\varepsilon/mol^{-1}\ dm^3\ cm^{-1}$))	$\sigma_{\text{CT or Intraligand band}}/10^3\ cm^{-1}$ (log ($\varepsilon/mol^{-1}\ dm^3\ cm^{-1}$))
$[Co(dtc)(dmpm)_2](BF_4)_2/H_2O$	21.8(2.94)^{sh}, 25.2(3.15)	30(3.92)^{sh}, 33.4(4.30), 38.0(4.18), 41.6(4.16)
$[Co(dtc)(dmpe)_2](BF_4)_2/H_2O$	22.7(2.84)^{sh}, 25.2(3.00)	29.5(3.65)^{sh}, 33.4(4.43), 41.7(4.45)
$[Co(dtc)(dmpp)_2](BF_4)_2/H_2O$	21.5(2.82), 23.8(2.90)	28(3.65)^{sh}, 32.5(4.27), 32.5(4.27), 38.2(4.34), 42(4.15)^{sh}
$[Co(dtc)_2(dmpm)]BF_4/CH_2Cl_2$	19.6(2.92), 25(3.20)^{sh}	28.5(4.0)^{sh}, 32.6(4.38), 39(4.27)^{sh}, 42.3(4.39)
$[C(dtc)_2(dmpe)]BF_4/CH_2Cl_2$	20.7(2.92), 25.2(3.30)^{sh}	29.2(4.06)^{sh}, 33.2(4.40), 34.7(4.35)^{sh}, 42.6(4.42)
$[Co(dtc)_2(dmpp)]ClO_4/CH_2Cl_2$	19.3(2.71), 24.5(3.25)^{sh}	29.0(3.97)^{sh}, 32.6(4.41), 39.5(4.33)^{sh}, 42.8(4.36)
$[Co(dtc)_2(dppm)]BF_4/CH_2Cl_2$	18.2(3.15), 24.2(3.56)	31.2(4.45), 35.5(4.39)
$[Co(dtc)_2(dppe)]BF_4/CH_2Cl_2$	18.8(2.96), 23.8(3.49)	31.8(4.47), 28(3.96)^{sh}, 34.4(4.41), 39.0(4.36)
$[Co(dtc)_2(dppp)]ClO_4/CH_2Cl_2$	18.5(2.74), 22.9(3.34)	28(4.08)^{sh}, 31.4(4.44), 35.3(4.46)
$[Co(dtc)_2(dppb)]BF_4/CH_2Cl_2$	17.6(2.62)^{sh}, 22.0(3.24)	27.4(4.00)^{sh}, 31.8(4.33), 34.9(4.27)^{sh}
$[C(dtc)_2(PEt_3)_2]BPh_4/CH_2Cl_2$	17(2.36)^{sh}	25.6(4.10), 29.6(4.48), 36.4(4.45)^{sh}, 41.0(4.63)
$[Co(dtc)_2(PPh_3)_2]BF_4/CH_2Cl_2$	15.9(2.58), 19.1(3.01)^{sh}	23.1(3.95), 28(1.88)^{sh}, 30.3(4.31), 37(4.45)^{sh}

LF denotes spin-allowed ligand field transition. sh denotes shoulder.

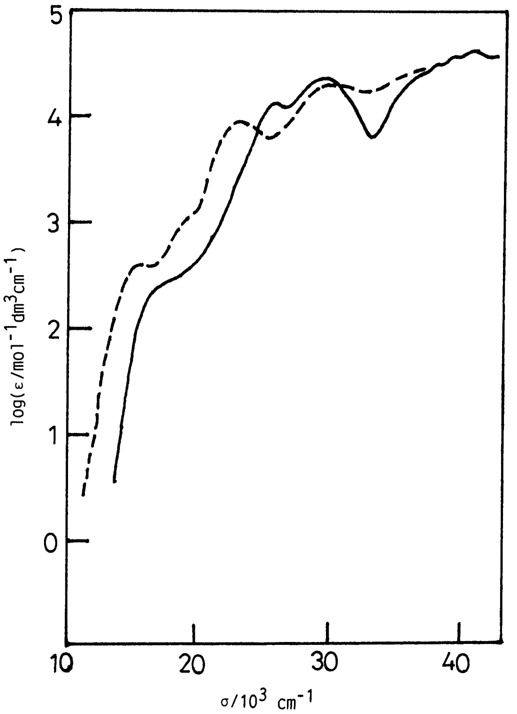

Fig. 4. Absorption spectra of *trans*(P)-$[Co(dtc)_2(PEt_3)_2]BPh_4$ in CH_2Cl_2 (——) and *trans*(P)-$[Co(dtc)_2(PPh_3)_2]BF_4$ in $CHCl_3$ (----).

complexes exhibit two broad bands or shoulders with a small energy separation in the d-d transition region. To assign whether these two absorptions correspond to the 1st and 2nd d-d transitions or split components of the 1st d-d band, the d-d transition energies were evaluated by the AOM treatment described in the Experimental Section. The results shown in Table 4 indicate that the two bands or shoulders of $[Co(dtc)(P-P)_2]^{2+}$ and $[Co(dtc)_2(P-P)]^+$ in the 18000—25000 cm^{-1} region can be assigned to the 1st and 2nd d-d transitions, while the band around 16000 cm^{-1} and the shoulder around 18000 cm^{-1} of *trans*-$[Co(dtc)_2(P)_2]^+$ to two split components of the 1st d-d transition, the second band being hidden by strong bands.

Except the four-membered diphosphine complexes, the d-d bands are shifted to lower energy with an increase in ring member of the diphosphine chelates. The lower 1st d-d transition energy of the four-membered diphosphine complex than those of the five- or six-membered diphosphine complexes will be attributable to the improper overlapping between the Co-d and P donor orbitals due to the small P–Co–P bite angle (73.1(2) and 75.5(2)° in $[Co(dtc)(dmpm)_2]^{2+}$). In the series of $[Co(dtc)_2(dppx)]^+$ (x=m, e, p, b), the 2nd d-d band of the four-membered dppm complex is observed at the highest energy. The results of AOM calculation given in Table 4 show that the weighted average energies of two split components (a and e) of the 2nd d-d band decrease in the order of dppe>dppp>dppm>dppb, but the order of energies of the lower energy components of the 2nd d-d band is dppm>dppe>dppp>dppb. The latter order is the same as that for the observed band positions. Thus the band in the 2nd d-d band region of $[Co(dtc)_2(dppx)]^+$ may correspond to the lower energy component of the 2nd d-d band. As shown in Table 4, the 2nd d-d bands of the other complexes, $[Co(dtc)_n(dmpx)_{3-n}]^{(3-n)+}$ (n=1, 2; x=m, e, p), may also be assigned to the lower energy component of the split 2nd d-d band.

The $e_\sigma(P)$ and $e_\pi(P)$ values satisfying the above spectral features of the mixed diphosphine complexes are given in Table 4. No detailed discussion can be made for these values at present, but it is noticeable that the $e_\pi(P)$ values are all positive and increase with the increasing ring members of diphosphine chelates. The calculation with negative $e_\pi(P)$ values gives no reasonable results. The phosphine donor group can have a filled π-type molecular orbital (e symmetry under C_{3v} approximation) composed of three P–C σ-bond orbitals as shown in Fig. 5.[25] This orbital will interact with the filled $d\pi$ orbital of Co(III) and destabilize it to give a positive e_π (P) value. The energy of Co-$d\pi$ orbital seems to be fairly low compared with that of vacant d orbitals of phosphorus, and no

Table 4. 1st and 2nd d-d Transition Energies ($\sigma/10^3\ \mathrm{cm^{-1}}$) of $[\mathrm{Co(S)}_x\mathrm{(P)}_{6-x}]$-Type Complexes Obtained by the AOM Analysis

P–P (ϕ(P–M–P)/°)		$\sigma_{\mathrm{1st\ d\text{-}d}}/10^3\ \mathrm{cm^{-1}}$	$\sigma_{\mathrm{2nd\ d\text{-}d}}/10^3\ \mathrm{cm^{-1}}$	$e_\sigma(\mathrm{P})/\mathrm{cm^{-1}}$	$e_\pi(\mathrm{P})/\mathrm{cm^{-1}}$
$[\mathrm{Co(dtc)(dmpx)_2}]^{2+}$ (x=m, e, p)					
dmpm	Obsd	$\underline{21.8}^{\mathrm{sh}}$	$\underline{25.2}$		
(72°)	Calcd	20.8^{e}, 21.5 (av. $\underline{21.0}$)	$\underline{26.2}^{\mathrm{e}}$, 30.0 (av. 27.5)	10000	600
dmpe	Obsd	$\underline{22.7}^{\mathrm{sh}}$	$\underline{25.2}$		
(82°)	Calcd	21.8, 22.5^{e} (av. $\underline{22.3}$)	28.2^{e}, 32.1 (av. 29.5)	10600	1000
dmpp	Obsd	$\underline{21.5}$	$\underline{23.8}$		
(94°)	Calcd	20.6, 21.1^{e} (av. $\underline{20.9}$)	$\underline{25.7}^{\mathrm{e}}$, 30.4 (av. 27.3)	10000	1200
$[\mathrm{Co(dtc)_2(P\text{–}P)}]^{+}$ (dmpx or dppx)					
dmpm	Obsd	$\underline{19.6}$	$\underline{25.0}^{\mathrm{sh}}$		
(72°)	Calcd	18.1^{e}, 20.4 (av. $\underline{18.9}$)	$\underline{24.5}$, 25.6^{e} (av. 25.2)	10000	600
dmpe	Obsd	$\underline{20.7}$	$\underline{25.2}^{\mathrm{sh}}$		
(82°)	Calcd	18.1^{e}, 22.4 (av. $\underline{19.6}$)	$\underline{24.8}$, 27.0^{e} (av. 26.3)	10600	1000
dmpp	Obsd	$\underline{19.3}$	$\underline{24.5}^{\mathrm{sh}}$		
(94°)	Calcd	17.5^{e}, 21.5 (av. $\underline{18.8}$)	$\underline{24.1}$, 26.2^{e} (av. 25.5)	10000	1200
dppm	Obsd	$\underline{18.2}$	$\underline{24.2}$		
(72°)	Calcd	17.7^{e}, 19.9 (av. $\underline{18.4}$)	$\underline{24.1}$, 25.2^{e} (av. 24.8)	9800	800
dppe	Obsd	$\underline{18.8}$	$\underline{23.8}$		
(82°)	Calcd	17.6^{e}, 21.6 (av. $\underline{18.9}$)	$\underline{23.8}$, 26.6^{e} (av. 25.7)	10800	1600
dppp	Obsd	$\underline{18.5}$	$\underline{22.9}$		
(94°)	Calcd	17.2^{e}, 20.9 (av. $\underline{18.4}$)	$\underline{23.2}$, 26.0^{e} (av. 25.1)	10400	1800
dppb	Obsd	$\underline{17.6}^{\mathrm{sh}}$	$\underline{22.0}$		
(90°)	Calcd	16.5^{e}, 19.7 (av. $\underline{17.6}$)	$\underline{22.2}$, 25.1^{e} (av. 24.1)	10000	2200
trans-$[\mathrm{Co(dtc)_2(PR_3)_2}]^{+}$					
$\mathrm{PEt_3}$	Obsd	$\underline{17}^{\mathrm{sh}}$, 19^{sh}	hidden by CT bands		
(180°)	Calcd	$\underline{16.8}^{\mathrm{e}}$, $\underline{17.5}$	22.9^{e}, 31.7	10000	1600
$\mathrm{PPh_3}$	Obsd	$\underline{15.9}$, $\underline{19.1}^{\mathrm{sh}}$	hidden by CT bands		
(180°)	Calcd	$\underline{15.6}^{\mathrm{e}}$, $\underline{17.6}$	22.4^{e}, 29.6	10000	2200

Racah's parameters B=450 and C=1800 cm^{-1} and e_σ(S)=7000 and e_π(S)=1000 cm^{-1}, and dtc bite angle=76° were commonly used. e: Doubly degenerate components.

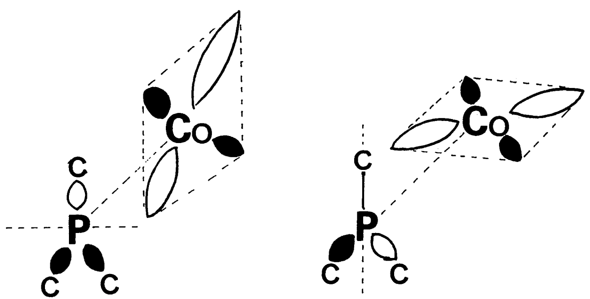

Fig. 5. The filled π-type MOs of a phosphine ligand with e symmetry under C_{3v} approximation and the π-type interaction with the Co-dπ orbital.

effective interaction may occur between them.

The intensity of d-d bands decreases with an increase in ring member of diphosphine chelates. The results may be related to the octahedral distortion of the complex. The reported P–M–P bite angles of $\mathrm{R_2P(CH_2)_{\mathit{n}}PR_2}$ chelates (R=$\mathrm{CH_3}$, $\mathrm{C_6H_5}$) increase in the order of n=1 (70—75°)$^{10-13)}$<n=2 (83—88°)$^{14-17)}$<n=4 (90°)$^{21)}$<n=3 (91—96°).$^{13,18-20)}$ The deviation of these angles from the octahedral angle (90°) becomes large in the order of 4<3<2<1 for n, and the order is in accord with that of increasing band intensity in these complexes.

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