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Preparation and Characterization of Cobalt(III) Complexes Containing 1,1′-Bis(diphenylphosphino)ferrocene (dppf) or 1,1′-Bis(dimethylphosphino)ferrocene (dmpf) as a Bidentate Ligand, and Molecular Structures of $[\mathrm{Co(acac)_2(dmpf)}]\mathrm{B(C_6H_5)_4}$ and $[\mathrm{Co(dtc)_2(dmpf)}]\mathrm{B(C_6H_5)_4}$ (acac=2,4-pentanedionate ion, dtc=dimethyldithiocarbamate ion)

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Four new complexes, [Co(acac or dtc)$_2$(dppf or dmpf)]X (X=$\mathrm{BF_4}$, $\mathrm{B(C_6H_5)_4}$) have been prepared and characterized by absorption and ^{1}H NMR spectra, and electrochemical measurements. The $[\mathrm{Co(acac)_2(dppf)}]^+$ complex exhibits the first d–d band at much lower energy than that of $[\mathrm{Co(acac)_2(dppe)}]^+$ (dppe=1,2-bis(diphenylphosphino)ethane), while the other complexes give the bands at similar energies to those of the corresponding diphosphine complexes. The structures of two dmpf complexes have been determined by the X-ray diffraction method. Crystal data are: $[\mathrm{Co(acac)_2(dmpf)}]\mathrm{B(C_6H_5)_4}$ (**1**), monoclinic, $P2_1/a$, a=20.366(4), b=13.513(2), c=16.860(2) Å, β=108.09(2)°, V=4411(1) Å^3, Z=4, R=0.041 for 5774 reflections. $[\mathrm{Co(dtc)_2(dmpf)}]\mathrm{B(C_6H_5)_4}$ (**2**), monoclinic, $C2/c$, a=33.573(7), b=10.148(1), c=31.039(6) Å, β=123.13(1)°, V=8856(2) Å^3, Z=8, R=0.044 for 6323 reflections. In these complexes dmpf functions as a bidentate chelate ligand with the Co–P bond distances of 2.250(1)—2.257(2) Å and the P–Co–P chelate angles are 101.09(4)° in **1** and 102.3(1)° in **2**. The trans influence of the phosphino donor group is observed on the Co–O (ca. 0.04 Å) and Co–S (ca. 0.03 Å) bond distances.

As an extension of our preparative work for octahedral cobalt(III)-phosphine complexes,[1] we have studied the coordination ability of bulky 1,1'-bis(diphenylphosphino) ferrocene (dppf) and its dimethyl analogue (dmpf) towards a hard cobalt(III) ion. A number of transition metal complexes of dppf have been reported,[2] but little is known for octahedral complexes except several carbonyl complexes of metals with the low oxidation number.[3] On the other hand, $[\mathrm{MCl_2(dmpf)}]$ (M=Ni, Pd)[4] are only known complexes of dmpf to our knowledge, although dmpf is expected to have stronger affinity towards metal ions than dppf, since the $-\mathrm{PMe_2}$ group of dmpf is less bulky and more basic than the $-\mathrm{PPh_2}$ group of dppf. This paper reports the preparation and characterization of bis-acetylacetonato (acac) and dimethyldithiocarbamato (dtc) cobalt(III) complexes of these bulky diphosphine ligands, in addition to the X-ray crystal analysis of $[\mathrm{Co(acac)_2(dmpf)}]\mathrm{B(C_6H_5)_4}$ and $[\mathrm{Co(dtc)_2(dmpf)}]\mathrm{B(C_6H_5)_4}$.

Experimental

The dppf[5] and dmpf[4,5] ligands were prepared by literature methods and handled under an atmosphere of nitrogen until they formed cobalt(III) complexes. All solvents used for the preparation were made oxygen-free by bubbling nitrogen through them for 20 min immediately before use. Absorption, and ^{1}H and ^{13}C NMR spectra were recorded on Hitachi U3400 and R-90H spectrometers, respectively.

Preparation of the Complexes. $[\mathrm{Co(acac)_2(dppf)}]\mathrm{BF_4}$. Acetic acid (0.5 cm^3) and a $\mathrm{CH_2Cl_2}$ solution (8 cm^3) of dppf (582 mg, 1 mmol) were added to a methanol solution (10 cm^3) of $[\mathrm{Co(acac)_2(H_2O)_2}]$[6] (300 mg, 1 mmol) with stirring, yielding a yellow precipitate. The mixture was stirred for 30 min, and then $\mathrm{PbO_2}$ (250 mg, 1 mmol) was added. Stirring was continued for another 30 min, and the mixture was filtered. The filtrate was concentrated to a small volume under reduced pressure. To the concentrate were added a methanol solution of $\mathrm{LiBF_4}$ and then diethyl ether. The yielded green precipitate was collected by filtration, and the product was mixed with $\mathrm{CHCl_3}$ to extract the green complex. The extract obtained by filtration was mixed with diethyl ether, and the mixture was stored in a refrigerator to yield green crystals, which were collected by filtration, washed with diethyl ether, and air-dried. Yield: 450 mg (50%). Found: C, 58.72; H, 4.67%. Calcd for $[\mathrm{Co(acac)_2(dppf)}]\mathrm{BF_4}$=$\mathrm{C_{44}H_{42}O_4BF_4P_2FeCo}$: C, 58.82; H, 4.71%. ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.72(s, 6H), 1.80(s, 6H), 5.02(s, 2H), 4.44—5.26(m, 8H), 7.25—7.80(m, 20H). The complex is soluble in methanol, chloroform, acetone, and dimethyl sulfoxide, but insoluble in water and diethyl ether.

$[\mathrm{Co(acac)_2(dmpf)}]\mathrm{B(C_6H_5)_4}$. A methanol solution (10 cm^3) containing $[\mathrm{Co(acac)_3}]$[7] (178 mg, 0.5 mmol) and dmpf (156 mg, 0.5 mmol) was stirred for 5 h at room temperature. The resulting violet solution was diluted five times with water and applied on a column (ϕ 2.7 cm×30 cm) of SP-Sephadex C-25. The adsorbed products were eluted with an aqueous solution of 0.05 mol dm^{-3} NaCl. The eluate of the major dark violet band was evaporated to dryness under reduced pressure. The residue was extracted with $\mathrm{CH_2Cl_2}$, the extract was evaporated

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again to dryness, and the brown product was dissolved in methanol. On addition of a methanol solution of $NaB(C_6H_5)_4$, the solution yielded a dark brown precipitate, which was collected by filtration and recrystallized from hot methanol to give dark brown crystals. Yield: 208 mg (47%). Found: C, 65.35; H, 6.25%. Calcd for $[Co(acac)_2(dmpf)]B(C_6H_5)_4 = C_{48}H_{54}O_4BP_2FeCo$: C, 65.32; H, 6.18%. ^1H NMR ($CDCl_3$) δ=1.08(m, 6H), 1.40(m, 6H), 1.87(s, 6H), 2.12(s, 6H), 4.38—4.50(m, 8H), 5.43(s, 2H), 6.86—7.55(m, 20H). The complex is soluble in the same solvents as for the above dppf complex, but is less soluble in methanol than the dppf one.

$[Co(dtc)_2(dppf)]BF_4 \cdot 0.5CH_2Cl_2$. Addition of a CH_2Cl_2 solution (8 cm^3) of dppf (582 mg, 1 mmol) to a methanol solution (15 cm^3) of $Co(BF_4)_2 \cdot 6H_2O$ (170 mg, 0.5 mmol) resulted in an immediate precipitation of an orange product. After stirring the mixture for 30 min, a CH_2Cl_2 solution (5 cm^3) of tetramethylthiuram disulfide (60 mg, 0.25 mmol) was added, and the mixture was stirred for 1 h. A dark brown precipitate formed on addition of diethyl ether was collected by filtration, and washed with diethyl ether. The product was dissolved in CH_2Cl_2, filtered, mixed with diethyl ether, and the mixture was stored in a refrigerator to yield dark green-brown crystals. Yield: 83 mg (18%). Found: C, 49.45; H, 4.10; N, 2.79%. Calcd for $[Co(dtc)_2(dppf)]BF_4 \cdot 0.5CH_2Cl_2 = C_{40.5}H_{41}N_2BF_4P_2S_4ClFeCo$: C, 49.48; H, 4.20; N, 2.85%. ^1H NMR ($CDCl_3$) δ=2.72(s, 6H), 2.83(s, 6H), 4.52—4.84(m, 8H), 7.28—7.70(m, 20H). Solubilities of the complex in various solvents are very similar to the corresponding acac complex.

$[Co(dtc)_2(dmpf)]B(C_6H_5)_4$. To a methanol solution (5 cm^3) of $Co(BF_4)_2 \cdot 6H_2O$ (170 mg, 0.5 mmol) were added dmpf (191 mg, 0.62 mmol) and then a CH_2Cl_2 solution (5 cm^3) of tetramethylthiuram disulfide (60 mg, 0.25 mmol). The solution was stirred for 3 h, and then a methanol solution (5 cm^3) of $Na(dtc) \cdot 2H_2O$ (60 mg, 0.5 mmol) was added. The mixture was stirred for another 1 h, and then evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of methanol, and the solution was applied on a column (ϕ 3 cm×20 cm) of Sephadex LH-20. By elution with methanol, a major dark violet band was developed. The eluate of the band was concentrated to a small volume, and a methanol solution of $NaB(C_6H_5)_4$ was added. The dark violet precipitate which formed was collected by filtration, and dissolved in a mixture of CH_2Cl_2 and methanol. Dark brown crystals of the complex were grown by slow evaporation of the solvent. Yield: 154 mg (33%). Found: C, 57.25; H, 5.65; N, 2.97%. Calcd for $[Co(dtc)_2(dmpf)]B(C_6H_5)_4 = C_{44}H_{52}N_2BP_2S_4FeCo$: C, 57.15; H, 5.67; N, 3.03%. ^1H NMR ($CDCl_3$) δ=1.10—1.63(m, 12H), 3.10(s, 3H), 3.14(s, 6H), 4.26—4.54(m, 8H), 6.79—7.54(m, 20H). The complex is soluble in the same solvents as for the corresponding dppf complex.

X-Ray Analyses. Crystal data of $[Co(acac)_2(dmpf)]B(C_6H_5)_4$ (**1**): monoclinic, $P2_1/a$, a=20.366(4), b=13.513(2), c=16.860(2) Å, β=108.09(2)°, V=4411(1) Å^3, Z=4, D_m=1.31(1) g cm^{-3}, D_c=1.329 g cm^{-3}, μ(Mo $K\alpha$)=8.156 cm^{-1}. A brown crystal of approximate dimensions 0.68×0.12×0.15 mm^3 grown from a methanol solution of the complex was used for X-ray analysis. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range $2° < 2\theta < 60°$, 5774 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were obtained. 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.[8] The absorption correction was made by using the DABEX program of the Computer Center Library. The structure was solved by the usual heavy-atom method; the

Table 1. Positional Parameters (×10^4) and Equivalent Temperature Factors (Å^2) of $[Co(acac)_2(dmpf)]B(C_6H_5)_4$

Atom	x	y	z	B_{eq}
Co	2324.2(3)	1938.5(4)	7557.7(4)	2.5
Fe	3402.5(4)	1528.6(5)	10147.4(4)	3.2
P(1)	2426.4(7)	560.9(8)	8337.4(8)	3.2
P(2)	3073.7(6)	2956.8(8)	8454.8(7)	2.7
O(1)	3034(2)	1473(3)	7150(2)	3.5
O(2)	1605(2)	1198(2)	6755(2)	3.3
O(3)	1610(2)	2411(2)	7965(2)	2.8
O(4)	2200(2)	2987(2)	6735(2)	3.0
C(1)	2548(4)	−510(4)	7771(4)	5.4
C(2)	1636(3)	324(5)	8588(5)	5.4
C(3)	3096(3)	415(3)	9319(3)	3.3
C(4)	3812(3)	597(4)	9483(4)	4.2
C(5)	4139(4)	445(5)	10350(4)	5.6
C(6)	3642(4)	179(5)	10719(4)	5.6
C(7)	2994(3)	153(4)	10100(4)	4.4
C(8)	3928(3)	2953(4)	8359(4)	4.1
C(9)	2797(3)	4230(4)	8249(3)	3.9
C(10)	3183(3)	2832(3)	9547(3)	2.9
C(11)	3823(3)	2901(4)	10233(3)	3.9
C(12)	3663(4)	2694(4)	10979(3)	4.5
C(13)	2954(4)	2493(4)	10771(3)	4.4
C(14)	2654(3)	2580(4)	9903(3)	3.4
C(15)	3552(4)	972(6)	6154(5)	6.3
C(16)	2915(3)	1126(4)	6406(4)	4.1
C(17)	2270(3)	881(5)	5877(3)	4.4
C(18)	1659(3)	878(4)	6075(3)	3.6
C(19)	1016(3)	438(5)	5499(4)	5.0
C(20)	525(3)	3073(4)	7865(4)	4.0
C(21)	1115(2)	2974(4)	7530(3)	3.2
C(22)	1110(3)	3479(4)	6814(3)	3.8
C(23)	1659(3)	3505(4)	6477(3)	3.3
C(24)	1633(3)	4203(5)	5778(4)	4.8
C(25)	1887(3)	2121(4)	3085(3)	3.6
C(26)	2377(3)	1773(4)	2724(4)	3.9
C(27)	3075(3)	1940(5)	3053(4)	4.7
C(28)	3317(3)	2518(6)	3750(5)	5.8
C(29)	2866(4)	2916(6)	4113(3)	6.2
C(30)	2163(3)	2707(5)	3785(4)	5.0
C(31)	934(3)	702(4)	3014(3)	3.3
C(32)	265(3)	337(4)	2900(4)	4.4
C(33)	142(3)	−589(4)	3170(4)	4.6
C(34)	681(4)	−1200(4)	3570(4)	4.5
C(35)	1340(3)	−886(4)	3687(4)	4.4
C(36)	1463(3)	53(4)	3418(3)	3.5
C(37)	592(2)	2597(4)	3041(4)	3.7
C(38)	566(3)	2499(5)	3861(4)	4.9
C(39)	204(4)	3137(6)	4215(5)	5.7
C(40)	−145(3)	3930(5)	3768(5)	5.8
C(41)	−146(4)	4038(5)	2972(5)	6.3
C(42)	214(3)	3388(4)	2615(4)	4.8
C(43)	883(3)	1832(4)	1668(3)	3.5
C(44)	978(3)	2689(4)	1250(4)	4.6
C(45)	923(3)	2702(5)	408(4)	5.1
C(46)	751(3)	1844(5)	−51(4)	5.1
C(47)	637(3)	999(5)	325(4)	4.8
C(48)	691(3)	994(4)	1173(3)	3.9
B	1059(3)	1824(4)	2692(4)	3.4

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 all hydrogen atoms were identified in subsequent difference-Fourier maps. The structure was refined by the block-diagonal least squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. The function minimized was $\Sigma||F_o|-|F_c||^2$. Final R was 0.041 for 5774 observed unique reflections, and the atomic parameters of non-hydrogen atoms are listed in Table 1.[9]

Crystal data of [Co(dtc)$_2$(dmpf)]B(C$_6$H$_5$)$_4$ (**2**): Monoclinic, $C2/c$, a=33.573(7), b=10.148(1), c=31.039(6) Å, β=123.13(1)°, V=8856(2) Å^3, Z=8, μ(Mo $K\alpha$)=8.939 cm^{-1}, D_m=1.42(1), D_c=1.39 g cm^{-3}. Crystals of **2** were grown from a dichloromethane-methanol solution of the complex. A prismatic crystal of 0.25×0.40×0.55 mm^3 in dimensions was mounted on a Rigaku AFC-5 diffractometer. Based on the four-circle angles of twenty reflections searched in the range of $2\theta<12°$, a triclinic unit cell was assigned. However, it was corrected to be monoclinic after the refinement as described later. The X-ray intensities were measured using graphite monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å). The θ–2θ scan technique was employed at a scan rate of 6° min^{-1} in θ. Up to 2θ=55°, 20394 reflections were measured, 11546 reflections were observed with $|F_o|>3\sigma(|F_o|)$, and 11508 unique ones were obtained after absorption correction by the Gaussian numerical integration method[10] (transmission factor, $0.68<A<0.82$). The lattice constants were determined from 45 2θ values ($20°<2\theta<30°$). The structure was solved by the direct methods,[11] and non-hydrogen atoms were refined anisotropically to R=0.063 for 11508 reflections. At this stage of the refinement assuming the space group $P\bar{1}$ with Z=4, reduced cell analysis by NBS*AID80[12] indicated that the triclinic unit cell could be transferred to a monoclinic C centered cell. It is worth mentioning that reduced cell analysis shoud be made based on the accurate cell dimensions. After the axis transformation, $2/m$ Laue symmetry of the reflection data appeared (R_{int}=0.021). Systematic absences, $h\,k\,l$, $h+k$ odd; $h0l$, h or l odd indicated the space group Cc or $C2/c$. The structure model of $P\bar{1}$ could be transferred into that of $C2/c$, reducing the number of independent atoms to half, and giving R=0.060 for 6323 unique reflections. R dropped to 0.044 after including all the hydrogen atoms in the refinement. The function, $\Sigma w||F_o|-|F_c||^2$, was minimized with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ by the block-diagonal least-squares method. Complex neutral-atom scattering factors were used.[13] The calculations were carried out on a FACOM M780/10 computer at Keio University using the computation program system UNICS III.[8] The atomic parameters are listed in Table 2.[9]

Electrochemistry. Rotating disk electrode voltammetry (RDE) measurements were carried out on CH$_3$CN solutions ([Co]: ca. 1.0×10^{-3} mol dm^{-3}, 0.1 mol dm^{-3} Bu$_4$NBF$_4$) at 25±1 °C by using a FUSO HECS 321B potential sweep unit and a FUSO HECS 317B potentiostat. A grassy-carbon rotating-disk (1500 rev min^{-1} attached to a Yanako P10-RE Mark II head, a platinum-wire, and a Ag/Ag$^+$ electrode (Ag/0.01 mol dm^{-3} AgNO$_3$) were used as the working, auxiliary, and reference electrodes, respectively. The oxidation wave of ferrocene was observed at +0.08 V vs. Ag/Ag$^+$. Cyclic voltammetry (CV) measurements were performed at a scan rate of 200 mV s^{-1} with a grassy-carbon working electrode. Other experimental conditions were the same as those for RDE measurements. Tetraphenylborate salts of the dmpf complexes were converted to the tetrafluoroborate salts with QAE-Sephadex anion exchange regin, because of lability of tetraphenylborate anions on oxidation.

Table 2. Positional Parameters (×10^4) and Equivalent Temperature Factors (Å^2) of [Co(dtc)$_2$(dmpf)]B(C$_6$H$_5$)$_4$

Atom	x	y	z	B_{eq}
Co	4858.1(2)	2405.2(6)	1102.1(2)	2.3
Fe	3957.9(3)	−486.5(7)	1155.7(3)	2.9
P(1)	4235.7(5)	2700(1)	1183.4(5)	2.7
P(2)	4898.3(4)	196(1)	1076.9(5)	2.5
S(1)	5383.3(4)	2618(1)	1966.2(5)	2.9
S(2)	5588.5(4)	2391(1)	1205.9(5)	3.1
S(3)	4456.7(5)	2506(1)	228.5(5)	3.2
S(4)	4787.1(5)	4636(1)	918.9(5)	3.2
N(1)	6288(1)	2553(4)	2205(2)	3.1
N(2)	4350(2)	5009(4)	−105(2)	3.6
C(1)	5829(2)	2541(5)	1851(2)	2.8
C(2)	6472(2)	2679(6)	2751(2)	4.2
C(3)	6635(2)	2491(6)	2059(2)	4.3
C(4)	4509(2)	4192(5)	291(2)	2.8
C(5)	4129(2)	4552(6)	−633(2)	4.8
C(6)	4396(3)	6436(6)	−13(2)	5.1
C(7)	3693(3)	3266(6)	607(2)	4.6
C(8)	4353(2)	3972(5)	1661(2)	3.9
C(9)	5370(2)	−592(5)	1670(2)	4.3
C(10)	5008(2)	−360(5)	592(2)	4.1
C(11)	4035(2)	1374(5)	1407(2)	2.9
C(12)	3553(2)	946(6)	1188(2)	4.1
C(13)	3562(2)	−146(6)	1467(3)	5.3
C(14)	4042(3)	−421(6)	1864(2)	5.3
C(15)	4334(2)	523(5)	1834(2)	3.8
C(16)	4377(2)	−779(5)	889(2)	2.8
C(17)	4347(2)	−1976(5)	1117(2)	3.5
C(18)	3860(2)	−2342(5)	844(2)	3.8
C(19)	3594(2)	−1417(5)	453(2)	3.7
C(20)	3904(2)	−456(5)	472(2)	3.0
C(21)	7152(2)	9389(5)	6438(2)	2.8
C(22)	6676(2)	9185(5)	6036(2)	3.5
C(23)	6302(2)	9933(6)	5962(2)	4.7
C(24)	6382(2)	10944(6)	6297(2)	4.8
C(25)	6842(2)	11167(6)	6706(3)	5.2
C(26)	7215(2)	10428(5)	6763(2)	4.0
C(27)	7436(2)	7024(5)	6347(2)	2.7
C(28)	7136(2)	6443(5)	5862(2)	3.8
C(29)	6997(2)	5134(6)	5787(2)	4.7
C(30)	7154(2)	4318(6)	6209(3)	5.0
C(31)	7442(2)	4851(6)	6691(3)	5.3
C(32)	7586(2)	6158(5)	6758(2)	3.8
C(33)	7588(2)	9231(4)	5950(2)	2.4
C(34)	7442(2)	10528(5)	5781(2)	3.4
C(35)	7444(2)	11076(5)	5377(2)	3.9
C(36)	7585(2)	10357(5)	5104(2)	3.4
C(37)	7739(2)	9078(5)	5262(2)	2.9
C(38)	7745(2)	8548(5)	5683(2)	2.7
C(39)	8111(2)	8770(5)	6974(2)	3.0
C(40)	8525(2)	8791(5)	6974(2)	3.8
C(41)	8976(2)	8901(6)	7418(2)	5.2
C(42)	9023(2)	8976(6)	7893(2)	5.7
C(43)	8628(2)	8932(6)	7908(2)	5.2
C(44)	8172(2)	8819(6)	7457(2)	4.2
B	7578(2)	8592(6)	6435(2)	2.6

Results and Discussion

Synthesis and Spectroscopic Properties. Synthetic procedures are somewhat different between the dppf and dmpf complexes. The $[Co(acac)_2(dmpf)]^+$ complex was prepared by the reaction of dmpf with $[Co(acac)_3]$ according to a method for the corresponding complexes of 1,2-diphosphines such as $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (dmpe)[14] or $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (dppe).[15] However, dppf did not react with $[Co(acac)_3]$, and the reaction in the presence of active charcoal resulted in the formation of unknown Co(II) species. The $[Co(acac)_2(dppf)]^+$ complex was prepared by oxidation of a methanol solution containing dppf and $[Co(acac)_2(H_2O)_2]$ with PbO_2. The bis-acac complexes with bulky monophosphines such as $P(C_6H_5)_3$ or $P(C_6H_{12})_3$ were prepared by this method.[16] The dtc complexes were obtained by oxidizing Co(II)-dppf or -dmpf complexes with tetramethylthiuram disulfide ($[(CH_3)_2NC(S)S-]_2$). A number of Co(III)-dtc complexes with diphosphine[17] or diamine[18] ligands were prepared by the same oxidation method. In the reaction for the dppf complex, it was necessary to use twice the molar quantity of dppf. The use of a stoichiometric amount of dppf gave only $[Co(dtc)_3]$, no detectable amount of $[Co(dtc)_2(dppf)]^+$ being formed. On the other hand, $[Co(dtc)_2(dmpf)]^+$ was obtained by the reaction with a stoichiometric amount of dmpf in moderate yield. Thus dmpf has a stronger affinity than dppf for Co(III). However, dmpf, as well as dppf are a bulky ligand. Several attempts were all unsuccessful to prepare the bis-type complexes, $[CoX_2(\text{dppf or dmpf})_2]^{n+}$ ($X_2=(Cl)_2$, acac, dtc) or complexes with other chelate ligands such as $[Co(NH_2CH_2CH_2NH_2)_2(\text{dppf or dmpf})]^{3+}$.

In the ^1H NMR spectrum, $[Co(acac)_2(dppf)]^+$ shows the methine proton signal of acac at a fairly high field ($\delta=5.02$) compared with those of $[Co(acac)_2(dmpf)]^+$ ($\delta=5.42$) and $[Co(acac)_3]$ ($\delta=5.51$).[15] The δ value of 5.02 for the dppf complex is similar to that of $[Co(acac)_2(dppe)]^+$($\delta=4.93$), the high field shift of which was attributed to the shielding effect of a phenyl group disposed over the acac chelate ring.[15] The stacking structure between the phenyl and acac rings has been found by X-ray analyses in $[Co(acac)(CN)_2(dppe)]$[19] and $[Co(acac)(RR\text{-chxn})(edpp)]^{2+}$ (RR-chxn=(R,R)-1,2-cyclohexanediamine, edpp=$NH_2CH_2CH_2P(C_6H_5)_2$).[20] The dppf complex would involve a similar stacking structure for the phenyl and acac chelate rings. The $-N(CH_3)_2$ proton signals of $[Co(dtc)_2(dppf)]^+$ are also observed at a high field, $\delta=2.83$ and 2.72, while those of $[Co(dtc)_2(dmpf)]^+$ are at $\delta=3.14$ and 3.10 and that of $[Co(dtc)_3]$ at $\delta=3.23$. The $-N(CH_3)_2$ groups in the dppf complex are also shielded by the phenyl groups.

In Fig. 1 the absorption spectrum of $[Co(acac)_2(dppf)]^+$ is compared with those of the related complexes. The first d-d band of the dppf complex is similar in pattern to that of $[Co(acac)_2(dppe)]^+$, but its band maximum

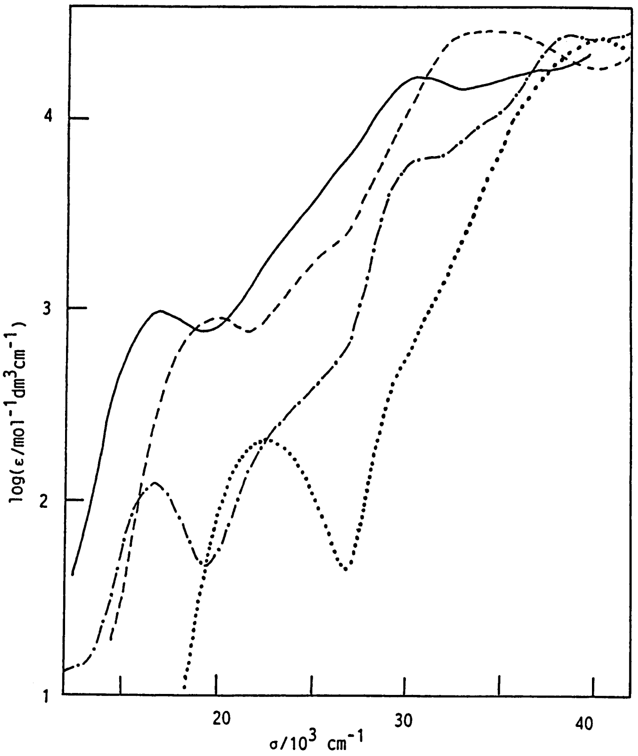

Fig. 1. Absorption spectra of $[Co(acac)_2(dppf)]BF_4$ in CH_2Cl_2 (——), $[Co(acac)_2(dppe)]PF_6$ in ethanol (------), $[Co(acac)_3]$ in CH_2Cl_2 (—·—), and dppf in CH_2Cl_2 solutions (······).

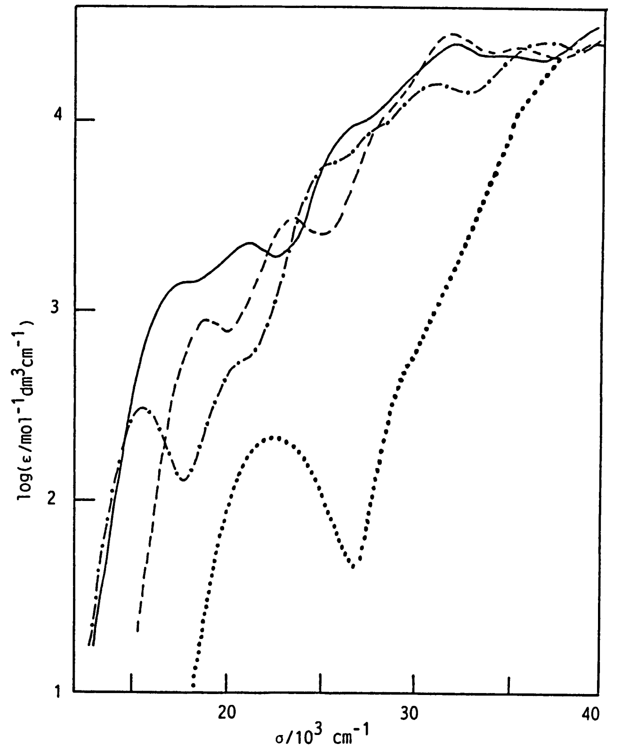

Fig. 2. Absorption spectra of $[Co(dtc)_2(dppf)]BF_4$ in CH_2Cl_2 (——), $[Co(dtc)_2(dppe)]BF_4$ in CH_2Cl_2 (------), and $[Co(dtc)_3]$ in CH_2Cl_2 (—·—), and dppf in CH_2Cl_2 solutions (······).

(17000 cm^{-1}) is largely shifted to the lower energy side from that of the dppe complex (20160 cm^{-1}).[15] The band energy of the dppf complex is nearly the same as that of $[Co(acac)_3]$ (16900 cm^{-1}), indicating that the ligand field strength of dppf is remarkably weak for a diphosphine chelate ligand. A similar, but smaller red shift is observed in the first d–d band of $[Co(dtc)_2(dppf)]^+$ (17500 cm^{-1}) as compared with that of $[Co(dtc)_2(dppe)]^+$ (18800 cm^{-1}) (Fig. 2). The band of $[Co(dtc)_2(dppf)]^+$ is similar both in the shape and position to that of $[Co(dtc)_2(dppb)]^+$ (17600 cm^{-1}, dppb $=(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2$)[17] containing a large seven-membered diphosphine chelate. The reduction of the ligand field strength of dppf is attributable to the bulkiness of this ligand, and extent of the reduction is larger in the six-membered acac complex than in the small four-membered dtc one. The energy differences in d–d bands seem to be small between $[Co(acac\ or\ dtc)_2(dmpf)]^+$ and the corresponding dmpe complexes, although their band positions are not clear (Fig. 3). The less bulky dmpf ligand than dppf may not reduce its ligand field strength appreciably in the present complexes. In conclusion, dppf and dmpf seem to have ligand field strengths similar to dppe and dmpe, respectively, but the strength of dppf is reduced by the steric factor due to its bulkiness.

Electrochemistry. Table 3 lists the half wave potentials, $E_{1/2}$(red) and $E_{1/2}$(ox) of the complexes measured by the RDE method, together with the data of related diphosphine chelate complexes. Irreversible waves were observed for some redox reactions of the complexes as noted in Table 3. The cyclic voltammograms were also obtained, and the representative is shown in Fig. 4. The $E_{1/2}$(red) values are all assigned to reduction potentials of Co(III) to Co(II).[21] In the dtc complexes, the values become more positive as the ring size of $R_2P(CH_2)_nPR_2$ increases. The positive sifts seem to indicate that the complex containing a larger diphosphine chelate is less stable owing to steric repulsions between the ligands, although no detailed discussion can be given for these potential differences at present. The value of $[Co(dtc)_2(dppf)]^+$ is the same as that of $[Co(dtc)_2(dppb)]^+$ (−0.93 V). As stated previously, the ligand field spectra of these two complexes are also very similar. Thus dppf may exert a steric effect similar to dppb on the stability of the present type of complex.

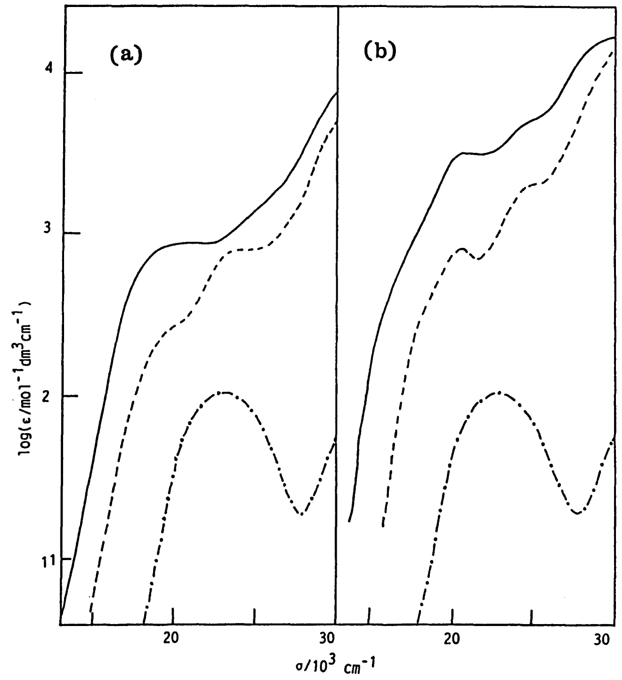

Fig. 3. Absorption spectra of a) $[Co(acac)_2(dmpf)]B(C_6H_5)_4$ in CH_2Cl_2 (——), $[Co(acac)_2(dmpe)]PF_6$ in methanol (------), and ferrocene in CH_2Cl_2 (— • —); b) $[Co(dtc)_2(dmpf)]BF_4$ in CH_2Cl_2 (------) and $[Co(dtc)_2(dmpe)]BF_4$ in CH_2Cl_2 (------), and ferrocene in CH_2Cl_2 solutions (······).

The $E_{1/2}$(red) values of the $[Co(dtc)_2(dmpx)]BF_4$ (x=f, p, e) complexes are more negative than those of the corresponding dppx complexes. The dmpx complexes would be more stable than the dppx ones, since the dimethylphosphino group is more basic and less bulky than the diphenylphosphino one. The potential difference between the dmpx and dppx complexes becomes larger in the order of x=f(0.34 V)>p(0.21 V) >e(0.12 V). With the increasing ring size of diphosphine chelate, the

Table 3. Electrochemical Data by RDE Voltammetry

Complex	$E_{1/2}$(red)/V	$E_{1/2}$(ox)/V
dppf	—	0.28
$[Co(dtc)_2(dppf)]BF_4$	−0.93	0.61
$[Co(dtc)_2(dppb)]BF_4$[a)]	−0.93	1.12
$[Co(dtc)_2(dppp)]BF_4$[a)]	−1.14	1.14
$[Co(dtc)_2(dppe)]BF_4$[a)]	−1.26	1.11
$[Co(dtc)_2(dmpf)]BF_4$	−1.27	0.56[d)]
$[Co(dtc)_2(dmpp)]BF_4$[a)]	−1.35	1.01
$[Co(dtc)_2(dmpe)]BF_4$[a)]	−1.38	0.97
$[Co(acac)_2(dppf)]BF_4$	−0.61[b)]	0.68
$[Co(acac)_2(dmpf)]BF_4$	−1.03[c)]	0.67[d)]

a) Refs. 17 and 21. b) Irreversible, $E_{1/4}-E_{3/4}$=110 mV. c) Irreversible, $E_{1/4}-E_{3/4}$=155 mV. d) Irreversible, $E_{1/4}-E_{3/4}$=130 mV.

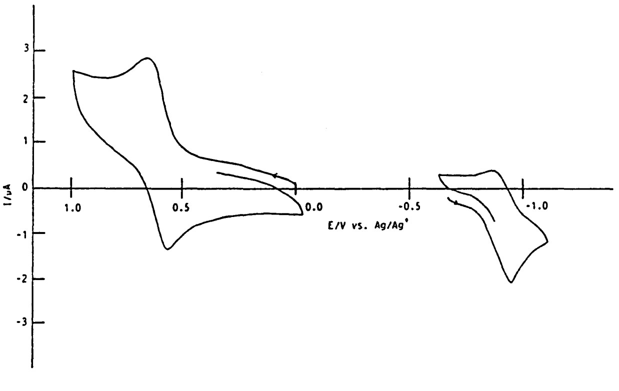

Fig. 4. Cyclic voltammogram of $[Co(dtc)_2(dppf)]BF_4$.

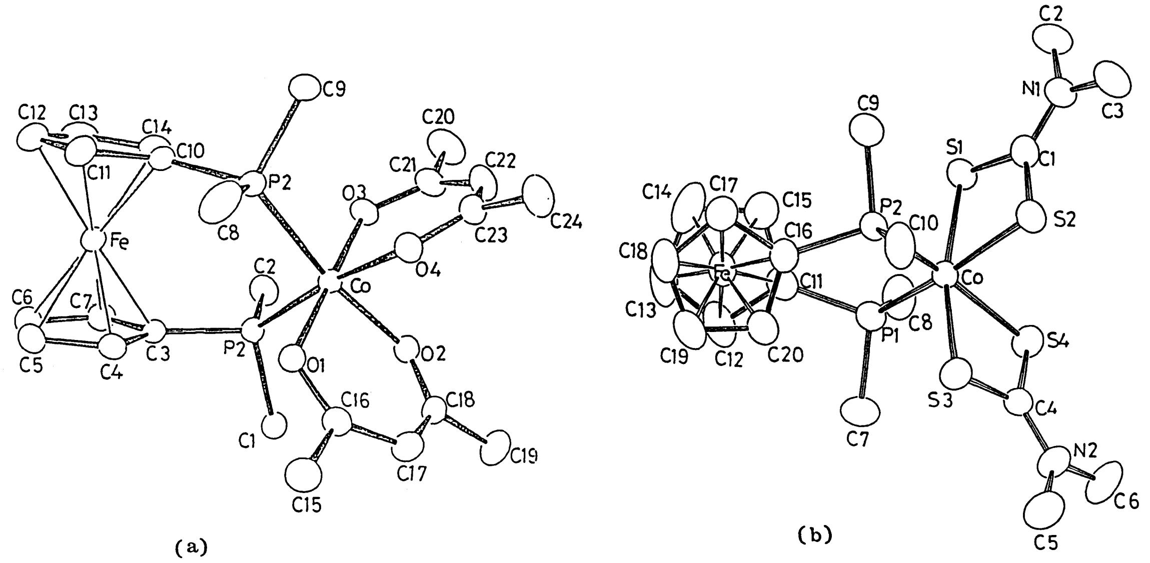

Fig. 5. Perspective views of (a) $[Co(acac)_2(dmpf)]B(C_6H_5)_4$ and (b) $[Co(dtc)_2(dmpf)]B(C_6H_5)_4$.

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°) of $[Co(acac)_2(dmpf)]B(C_6H_5)_4$

Co-P(1)	2.252(1)	Co-P(2)	2.254(1)	C(5)-Fe-C(14)	177.8(2)	C(6)-Fe-C(7)	40.2(2)
Co-O(1)	1.897(3)	Co-O(2)	1.939(2)	C(6)-Fe-C(10)	177.3(2)	C(6)-Fe-C(11)	138.5(2)
Co-O(3)	1.900(3)	Co-O(4)	1.940(2)	C(6)-Fe-C(12)	112.7(2)	C(6)-Fe-C(13)	114.0(2)
Fe-C(3)	2.013(3)	Fe-C(4)	2.023(5)	C(6)-Fe-C(14)	140.8(2)	C(7)-Fe-C(10)	139.8(2)
Fe-C(5)	2.053(5)	Fe-C(6)	2.054(4)	C(7)-Fe-C(11)	178.3(2)	C(7)-Fe-C(12)	137.7(2)
Fe-C(7)	2.037(4)	Fe-C(10)	2.004(3)	C(10)-Fe-C(11)	41.6(1)	C(10)-Fe-C(12)	69.1(1)
Fe-C(11)	2.036(4)	Fe-C(12)	2.066(5)	C(10)-Fe-C(13)	111.4(2)	C(10)-Fe-C(14)	41.6(2)
Fe-C(13)	2.055(5)	Fe-C(14)	2.035(4)	C(11)-Fe-C(12)	40.8(2)	Co-P(1)-C(1)	111.2(2)
P(1)-C(1)	1.803(5)	P(1)-C(2)	1.820(6)	Co-P(1)-C(2)	110.6(2)	Co-P(1)-C(3)	122.4(1)
P(1)-C(3)	1.797(3)	P(2)-C(8)	1.803(5)	C(1)-P(1)-C(2)	105.3(3)	C(1)-P(1)-C(3)	102.3(2)
P(2)-C(9)	1.809(4)	P(2)-C(10)	1.799(4)	C(2)-P(1)-C(3)	103.6(3)	Co-P(2)-C(8)	114.3(1)
O(1)-C(16)	1.292(5)	O(2)-C(18)	1.267(5)	Co-P(2)-C(9)	110.3(1)	Co-P(2)-C(10)	118.5(2)
O(3)-C(21)	1.285(4)	O(4)-C(23)	1.263(4)	C(8)-P(2)-C(9)	103.8(2)	C(8)-P(2)-C(10)	105.7(2)
C(3)-C(4)	1.422(6)	C(3)-C(7)	1.442(6)	C(9)-P(2)-C(10)	102.8(2)	Co-O(1)-C(16)	122.1(3)
C(4)-C(5)	1.413(6)	C(5)-C(6)	1.398(9)	Co-O(2)-C(18)	123.6(3)	Co-O(3)-C(21)	122.7(3)
C(6)-C(7)	1.405(6)	C(10)-C(11)	1.436(6)	Co-O(4)-C(23)	123.9(3)	Fe-C(3)-P(1)	122.8(2)
C(10)-C(14)	1.433(6)	C(11)-C(12)	1.430(7)	Fe-C(3)-C(4)	69.8(2)	Fe-C(3)-C(7)	126.8(2)
C(12)-C(13)	1.392(7)	C(13)-C(14)	1.407(5)	P(1)-C(3)-C(4)	126.8(3)	P(1)-C(3)-C(7)	126.1(3)
C(15)-C(16)	1.496(8)	C(16)-C(17)	1.373(6)	C(4)-C(3)-C(7)	107.0(3)	Fe-C(4)-C(3)	69.0(3)
C(17)-C(18)	1.388(6)	C(18)-C(19)	1.484(6)	Fe-C(4)-C(5)	70.9(3)	C(3)-C(4)-C(5)	108.1(4)
C(20)-C(21)	1.491(7)	C(21)-C(22)	1.388(6)	Fe-C(5)-C(4)	68.6(3)	Fe-C(5)-C(6)	70.1(3)
C(22)-C(23)	1.400(6)	C(23)-C(24)	1.497(6)	C(4)-C(5)-C(6)	108.4(4)	Fe-C(6)-C(5)	70.1(3)
				Fe-C(6)-C(7)	69.3(2)	C(5)-C(6)-C(7)	109.0(4)
P(1)-Co-P(2)	101.09(4)	P(1)-Co-O(1)	89.75(9)	Fe-C(7)-C(3)	68.3(2)	Fe-C(7)-C(6)	70.6(3)
P(1)-Co-O(2)	83.97(8)	P(1)-Co-O(3)	90.61(8)	C(3)-C(7)-C(6)	107.4(5)	Fe-C(10)-P(2)	122.6(2)
P(1)-Co-O(4)	170.81(8)	P(2)-Co-O(1)	90.55(8)	Fe-C(10)-C(11)	70.4(2)	Fe-C(10)-C(14)	70.4(2)
P(2)-Co-O(2)	172.98(8)	P(2)-Co-O(3)	89.14(8)	P(2)-C(10)-C(11)	127.7(3)	P(2)-C(10)-C(14)	125.0(3)
P(2)-Co-O(4)	87.02(7)	O(1)-Co-O(2)	94.4(1)	C(11)-C(10)-C(14)	107.3(3)	Fe-C(11)-C(10)	68.0(2)
O(1)-Co-O(3)	179.6(1)	O(1)-Co-O(4)	85.8(1)	Fe-C(11)-C(12)	70.7(2)	C(10)-C(11)-C(12)	107.4(4)
O(2)-Co-O(3)	85.9(1)	O(2)-Co-O(4)	88.3(1)	Fe-C(12)-C(11)	68.5(2)	Fe-C(12)-C(13)	69.8(2)
O(3)-Co-O(4)	93.9(1)	C(3)-Fe-C(4)	41.3(2)	C(11)-C(12)-C(13)	108.0(3)	Fe-C(13)-C(12)	70.7(3)
C(3)-Fe-C(5)	68.7(2)	C(3)-Fe-C(6)	68.7(2)	Fe-C(13)-C(14)	69.1(3)	C(12)-C(13)-C(14)	109.7(4)
C(3)-Fe-C(7)	41.7(2)	C(3)-Fe-C(10)	109.6(1)	Fe-C(14)-C(10)	68.1(2)	Fe-C(14)-C(13)	70.7(3)
C(3)-Fe-C(11)	139.9(2)	C(3)-Fe-C(12)	177.0(2)	C(10)-C(14)-C(13)	107.6(4)	O(1)-C(16)-C(15)	113.8(4)
C(3)-Fe-C(13)	137.6(2)	C(3)-Fe-C(14)	109.3(1)	O(1)-C(16)-C(17)	125.5(5)	C(15)-C(16)-C(17)	120.7(4)
C(4)-Fe-C(5)	40.6(2)	C(4)-Fe-C(6)	68.0(2)	C(16)-C(17)-C(18)	126.2(4)	O(2)-C(18)-C(17)	123.6(3)
C(4)-Fe-C(7)	69.1(2)	C(4)-Fe-C(10)	109.3(2)	O(2)-C(18)-C(19)	114.9(4)	C(17)-C(18)-C(19)	121.5(4)
C(4)-Fe-C(11)	111.7(2)	C(4)-Fe-C(12)	141.6(2)	O(3)-C(21)-C(20)	115.0(3)	O(3)-C(21)-C(22)	125.6(4)
C(4)-Fe-C(13)	177.6(2)	C(4)-Fe-C(14)	137.3(2)	C(20)-C(21)-C(22)	119.4(3)	C(21)-C(22)-C(23)	124.7(4)
C(5)-Fe-C(6)	39.8(2)	C(5)-Fe-C(7)	67.8(2)	O(4)-C(23)-C(22)	124.5(3)	O(4)-C(23)-C(24)	115.8(4)
C(5)-Fe-C(10)	137.8(2)	C(5)-Fe-C(11)	111.7(2)	C(22)-C(23)-C(24)	119.7(3)		
C(5)-Fe-C(12)	114.2(2)	C(5)-Fe-C(13)	141.9(2)				

Table 5. Selected Bond Distances (l/Å) and Angles (ϕ/°) of [Co(dtc)$_2$(dmpf)]B(C$_6$H$_5$)$_4$

Co-P(1)	2.257(2)	Co-P(2)	2.250(1)	C(14)-Fe-C(16)	136.7(3)	C(14)-Fe-C(17)	111.6(3)
Co-S(1)	2.276(1)	Co-S(2)	2.292(2)	C(14)-Fe-C(18)	115.1(3)	C(14)-Fe-C(19)	143.4(3)
Co-S(3)	2.277(2)	Co-S(4)	2.314(1)	C(14)-Fe-C(20)	176.4(3)	C(15)-Fe-C(16)	108.8(3)
Fe-C(11)	2.005(5)	Fe-C(12)	2.030(7)	C(15)-Fe-C(17)	112.1(2)	C(15)-Fe-C(18)	142.5(2)
Fe-C(13)	2.055(10)	Fe-C(14)	2.059(8)	C(15)-Fe-C(19)	176.4(2)	C(15)-Fe-C(20)	136.2(2)
Fe-C(15)	2.042(5)	Fe-C(16)	2.007(8)	C(16)-Fe-C(17)	41.5(3)	C(16)-Fe-C(18)	68.8(3)
Fe-C(17)	2.044(6)	Fe-C(18)	2.060(5)	C(16)-Fe-C(19)	68.8(3)	C(16)-Fe-C(20)	41.6(3)
Fe-C(19)	2.056(5)	Fe-C(20)	2.029(4)	C(17)-Fe-C(18)	40.5(2)	C(17)-Fe-C(19)	68.1(2)
P(1)-C(7)	1.813(5)	P(1)-C(8)	1.839(6)	C(17)-Fe-C(20)	69.2(3)	C(18)-Fe-C(19)	39.8(2)
P(1)-C(11)	1.805(7)	P(2)-C(9)	1.830(5)	C(18)-Fe-C(20)	67.8(2)	C(19)-Fe-C(20)	40.2(2)
P(2)-C(10)	1.823(8)	P(2)-C(16)	1.807(6)	Co-P(1)-C(7)	115.1(2)	Co-P(1)-C(8)	112.3(2)
S(1)-C(1)	1.720(8)	S(2)-C(1)	1.708(6)	Co-P(1)-C(11)	120.5(2)	C(7)-P(1)-C(8)	103.3(2)
S(3)-C(4)	1.720(5)	S(4)-C(4)	1.698(6)	C(7)-P(1)-C(11)	103.3(3)	C(8)-P(1)-C(11)	100.0(3)
N(1)-C(1)	1.316(6)	N(1)-C(2)	1.458(8)	Co-P(2)-C(9)	115.8(2)	Co-P(2)-C(10)	112.3(2)
N(1)-C(3)	1.464(10)	N(2)-C(4)	1.329(7)	Co-P(2)-C(16)	119.4(2)	C(9)-P(2)-C(10)	103.9(3)
N(2)-C(5)	1.457(8)	N(2)-C(6)	1.468(7)	C(9)-P(2)-C(16)	103.8(3)	C(10)-P(2)-C(16)	99.3(3)
C(11)-C(12)	1.438(9)	C(11)-C(15)	1.434(7)	Co-S(1)-C(1)	87.3(3)	Co-S(2)-C(1)	87.0(2)
C(12)-C(13)	1.397(10)	C(13)-C(14)	1.422(9)	Co-S(3)-C(4)	87.3(2)	Co-S(4)-C(4)	86.6(2)
C(14)-C(15)	1.410(11)	C(16)-C(17)	1.437(8)	Fe-C(11)-P(1)	123.3(4)	Fe-C(11)-C(12)	70.1(3)
C(16)-C(20)	1.434(7)	C(17)-C(18)	1.419(8)	Fe-C(11)-C(15)	70.7(3)	P(1)-C(11)-C(12)	127.1(4)
C(18)-C(19)	1.402(7)	C(19)-C(20)	1.404(9)	P(1)-C(11)-C(15)	125.8(4)	C(12)-C(11)-C(15)	107.1(5)
				Fe-C(12)-C(11)	68.2(4)	Fe-C(12)-C(13)	71.0(4)
P(1)-Co-P(2)	102.3(1)	P(1)-Co-S(1)	91.4(1)	C(11)-C(12)-C(13)	108.0(5)	Fe-C(13)-C(12)	69.0(5)
P(1)-Co-S(2)	165.9(1)	P(1)-Co-S(3)	98.4(1)	Fe-C(13)-C(14)	69.9(4)	C(12)-C(13)-C(14)	108.9(6)
P(1)-Co-S(4)	85.4(1)	P(2)-Co-S(1)	96.5(1)	Fe-C(14)-C(13)	69.6(3)	Fe-C(14)-C(15)	69.3(5)
P(2)-Co-S(2)	85.3(1)	P(2)-Co-S(3)	90.6(1)	C(13)-C(14)-C(15)	108.0(5)	Fe-C(15)-C(11)	67.9(3)
P(2)-Co-S(4)	165.1(1)	S(1)-Co-S(2)	75.8(1)	Fe-C(15)-C(14)	70.5(4)	C(11)-C(15)-C(14)	108.0(5)
S(1)-Co-S(3)	166.4(1)	S(1)-Co-S(4)	96.1(1)	Fe-C(16)-P(2)	124.0(3)	Fe-C(16)-C(17)	70.6(4)
S(2)-Co-S(3)	93.4(1)	S(2)-Co-S(4)	89.9(1)	Fe-C(16)-C(20)	70.0(3)	P(2)-C(16)-C(17)	128.3(4)
S(3)-Co-S(4)	75.5(1)	C(11)-Fe-C(12)	41.7(2)	P(2)-C(16)-C(20)	124.4(4)	C(17)-C(16)-C(20)	107.3(5)
C(11)-Fe-C(13)	68.8(3)	C(11)-Fe-C(14)	69.0(3)	Fe-C(17)-C(16)	67.8(3)	Fe-C(17)-C(18)	70.4(4)
C(11)-Fe-C(15)	41.5(2)	C(11)-Fe-C(16)	109.2(3)	C(16)-C(17)-C(18)	107.2(4)	Fe-C(18)-C(17)	69.2(3)
C(11)-Fe-C(17)	140.2(2)	C(11)-Fe-C(18)	175.7(2)	Fe-C(18)-C(19)	70.0(3)	C(17)-C(18)-C(19)	108.8(5)
C(11)-Fe-C(19)	136.1(2)	C(11)-Fe-C(20)	108.1(3)	Fe-C(19)-C(18)	70.2(3)	Fe-C(19)-C(20)	68.9(3)
C(12)-Fe-C(13)	40.0(3)	C(12)-Fe-C(14)	68.2(3)	C(18)-C(19)-C(20)	108.8(5)	Fe-C(20)-C(16)	68.3(3)
C(12)-Fe-C(15)	69.1(2)	C(12)-Fe-C(16)	140.0(3)	Fe-C(20)-C(19)	71.0(4)	C(16)-C(20)-C(19)	108.0(5)
C(12)-Fe-C(17)	178.0(3)	C(12)-Fe-C(18)	137.6(2)	S(1)-C(1)-S(2)	109.9(3)	S(1)-C(1)-N(1)	125.5(5)
C(12)-Fe-C(19)	110.8(2)	C(12)-Fe-C(20)	111.2(3)	S(2)-C(1)-N(1)	124.6(6)	S(3)-C(4)-S(4)	110.6(3)
C(13)-Fe-C(14)	40.4(3)	C(13)-Fe-C(15)	68.0(3)	S(3)-C(4)-N(2)	123.5(4)	S(4)-C(4)-N(2)	125.9(4)
C(13)-Fe-C(16)	176.7(4)	C(13)-Fe-C(17)	138.6(3)	C(1)-N(1)-C(2)	122.0(5)	C(1)-N(1)-C(3)	120.5(6)
C(13)-Fe-C(18)	113.4(3)	C(13)-Fe-C(19)	114.4(3)	C(2)-N(1)-C(3)	117.4(4)	C(4)-N(2)-C(5)	122.8(4)
C(13)-Fe-C(20)	141.1(3)	C(14)-Fe-C(15)	40.2(3)	C(4)-N(2)-C(6)	119.3(5)	C(5)-N(2)-C(6)	117.9(5)

dppx complex seems to decrease its stability more largely than the dmpx complex.

The acac complexes of dppf and dmpf show more positive $E_{1/2}$(red) values by 0.2—0.3 V than those of the corresponding dtc complexes. The acac complexes are reduced more easily to Co(II) than the dtc complexes are. Our previous studies indicate that mixed-ligand Co(III)-phosphine complexes are formed more easily and are more stable with dtc than with acac.[15,17)]

The $E_{1/2}$(ox) values of the dppf and dmpf complexes are in the range of 0.56—0.68 V, while those of the $R_2P(CH_2)_nPR_2$ complexes are 0.97—1.14 V. The former values can be assigned to the oxidation potential of Fe(II) to Fe(III), and the latter ones to that of Co(III) to Co(IV). The value of dppf (0.28 V) shifts to the positive side by 0.3—0.4 V upon coordination to Co(III), indicating a decrease in electron density of Fe(II) by donation of the phosphino groups. The oxidation potential of dmpf was not measured, because pure dmpf was not obtained. The Co(III) ions in the dppf and dmpf complexes were not oxidized to Co(IV) within the voltage limit of solvent, acetonitrile (ca. +1.8 V). The electron-withdrawing effect of the oxidized dppf and dmpf ligands raises the oxidation potential of the Co(III) center to a large extent.

Crystal Structures. No X-ray structure analysis has been reported for dmpf complexes, although those of a large number of dppf complexes have been done.[2,22)] Perspective views of [Co(acac)$_2$(dmpf)]$^+$ (**1**) and [Co(dtc)$_2$(dmpf)]$^+$ (**2**) are shown in Fig. 5, together with the numbering schemes. The selected bond distances and angles are listed in Tables 4 and 5. Both Co atoms in **1** and **2** form a distorted octahedron. The dmpf ligand functions as a large bidentate chelate. The Co-P bond lengths of **1** (2.252(1), 2.254(1) Å) and **2** (2.257(2), 2.250(1) Å) are fairly longer than those found in related mixed-ligand phosphine complexes with oxygen or sulfur donor atoms such as [Co(acac)$_2${NH$_2$CH$_2$CH$_2$P-

$(CH_3)_2\}]^+$ (2.192(4) Å)[23] or $[Co(S_2COC_2H_5)_2(dmpe)]^+$ (2.205(1) Å).[24] The P–Co–P chelate angles are widened largely from the octahedral angle, 101.09(4)° in **1** and 102.3(1)° in **2**. The Co–P–C (Cp ring) angles in **1** (122.4(1), 118.5(2)°) and in **2** (120.5(2), 119.4(2)°) are also much larger than the tetrahedral angle. The P–Co–P angles found in this study are appreciably larger than those of octahedral complexes of dppf, 93.58(4)° in $[ReCl(CO)_3(dppf)]$,[22] 95.28(1)° in $[Mo(CO)_4(dppf)]$,[25] and 98.2(1)° in [Mn(MeCp)(CO)(dppf)],[26] and are rather similar to those of 4-coordinate [Rh(dppf) (norbornadien)]ClO_4 (103.71(5)°)[27] and $[(dppf)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(dppf)]BF_4\cdot 0.5H_2O$ (103.66(6)°).[28] Two cyclopentadienyl rings of the ferrocene moiety are staggered with the angle of 37.7(2)° in **1** and of 37.6(2)° in **2**, and are slightly tilted towards the Co atom with the angle of 4.4(2)° in **1** and 5.0(3)° in **2**. The chelate ring formed by dmpf and the Co atom is twisted to take the *ob* in **1** and *lel* in **2** conformations[29] with respect to the pseudo-threefold axis of the tris(chelate) complex. Other geometries of the cyclopentadienyl moiety are similar to those of dppf and other substituted ferrocenes.[25]

The Co–O bond lengths trans to P (av. 1.940(2) Å) in **1** are longer than those trans to O (av. 1.899(2) Å) by 0.041(3) Å. Similarly the Co–S bond lengths trans to P (av. 2.303(2) Å) are longer than those trans to S (av. 2.277(2) Å) by 0.026(2) Å. The elongations of the Co–O and Co–S bonds trans to P are attributable to the trans influence of the dimethylphosphino donor group. However, the extents of elongation are small compared with 0.076(7) Å in $[Co(acac)_2\{NH_2CH_2CH_2P(CH_3)_2\}]^+$[23] and 0.035(2) Å in $[Co(S_2COC_2H_5)_2(dmpe)]^+$.[24] The weak trans influence of dmpf in **1** and **2** may be the results from the longer Co–P bond lengths than those in these two related complexes. Other structural parameters for the acac and dtc chelates are similar to those, respectively found in related complexes.

Attempts to prepare crystals of the dppf complexes suitable for X-ray crystal analysis were unsuccessful in the present study.

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