Molecular Structures of *cis*-[Co(CN)$_2$(acac)(dppe)] and *trans*(*C*,*N*)-[Co(CN)$_2$(acac)(edpp)]·H$_2$O and Trans Influence of Phosphine and Cyanide Ligands

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Molecular structures of *cis*-[Co(CN)$_2$(acac)(dppe)] (**a**) and *trans*(*C*,*N*)-[Co(CN)$_2$(acac)(edpp)]·H$_2$O (**b**) have been determined by X-ray analysis, where acac, dppe, and edpp denote an acetylacetonate ion, 1,2-bis(diphenylphosphino)ethane and (2-aminoethyl)diphenylphosphine, respectively. Crystal data for **a**: monoclinic, $P2_1/a$, a=13.975(2), b=19.709(2), c=11.575(2) Å, β=109.71(1)°, V=3001.5(6) Å^3, Z=4, and R=0.049. Crystal data for **b**: monoclinic, $P2_1/c$, a=17.870(3), b=7.354(2), c=16.709(3) Å, β=105.45(2)°, V=2116.5(5) Å^3, Z=4, and R=0.056. The Co–O bonds trans to the phosphine and the cyanide ligands are longer, respectively, by ca. 0.06—0.08 Å and ca. 0.03—0.05 Å than those usually found in Co(III)–acac complexes such as [Co(acac)$_3$], indicating stronger trans influence of the former than the latter.

X-Ray structural studies of non-organocobalt(III)–phosphine complexes have been reported for [Co(O$_2$)-{(C$_6$H$_5$)$_2$PCHCHP(C$_6$H$_5$)$_2$}$_2$]$^+$,[1] [{P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$(CN)-(O$_2$)Co(μ-CN)Co(CN)$_2${P(CH$_3$)$_2$(C$_6$H$_5$)}$_3$],[2] [Co(NCS)$_3$-{P(CH$_3$)$_3$}$_3$],[3] a number of bis(dimethylglyoximato)-cobalt(III) complexes containing unidentate phosphine ligands,[4] and a number of diphosphine–[5–8] and aminoalkylphosphine–cobalt(III) complexes[9–14] prepared in our laboratory. In this paper we have determined crystal structures of two cyanide–phosphine mixed ligand complexes of cobalt(III), [Co-(CN)$_2$(acac)(dppe)] and [Co(CN)$_2$(acac)(edpp)]. The complexes contain cyanide and phosphine ligands both of which give trans influence to many metal ions,[15] although the influence of the cyanide ligand in a cobalt(III) complex is not made clear.[15–21] The complexes studied here are suitable for examining trans influence of cyanide and phosphine ligands, since the magnitudes of influence can be compared within one complex molecule.

Experimental

X-Ray Analysis. *cis*-[Co(CN)$_2$(acac)(dppe)]. The complex was prepared in a previous work.[22] Crystal data: monoclinic, $P2_1/a$, a=13.975(2), b=14.709(2), c=11.575(2) Å, β=109.71(1)°, V=3001.5(6) Å^3, Z=4, D_x=1.35 g cm^{-3}, D_m=1.36 g cm^{-3}, μ(Mo $K\alpha$)=7.055 cm^{-1}. An orange crystal of approximate dimensions 0.45×0.25×0.175 mm^3 was wrapped up in thin wax to protect it from moisture and used for X-ray work. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range $2\theta<60°$, 4006 independent reflections with $|F_o|>3\sigma(|F_o|)$ were obtained. No absorption correction was applied.

Calculations for the structure analysis were performed on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS III.[23] Atomic scattering factors of neutral atoms were used.[24] The structure was solved by the usual heavy-atom method: The position of the cobalt atom was picked up by means of the

Table 1. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors (Å^2) of [Co(CN)$_2$(acac)(dppe)] (**a**)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Co	1707.2(4)	1573.0(3)	9530.8(5)	2.8	C(124)	1925(4)	3689(3)	6325(5)	5.8
P(1)	2287(1)	1838(1)	8031(1)	2.8	C(125)	2344(4)	3146(2)	7113(4)	4.4
P(2)	3224(1)	1917(1)	10867(1)	2.9	C(21)	4062(3)	1223(2)	11605(4)	3.4
O(1)	1139(2)	1346(1)	10811(3)	3.5	C(22)	3263(3)	2466(2)	12149(4)	3.5
O(2)	2246(2)	669(1)	9515(3)	3.3	C(23)	3847(3)	2384(2)	9948(4)	3.4
N(1)	−364(3)	1202(2)	7659(4)	5.2	C(211)	3754(4)	813(2)	12378(4)	4.3
N(2)	1081(3)	3033(2)	9598(4)	4.3	C(212)	4318(4)	254(3)	12928(5)	5.8
C(1)	412(3)	1348(2)	8335(4)	3.5	C(213)	5188(5)	80(3)	12716(5)	6.8
C(2)	1299(3)	2482(2)	9557(4)	3.0	C(214)	5513(5)	493(4)	11973(6)	8.4
C(11)	2198(3)	1213(2)	6839(4)	3.6	C(215)	4952(4)	1062(3)	11398(5)	6.1
C(12)	1748(3)	2586(2)	7120(4)	3.1	C(221)	4120(4)	2843(3)	12722(4)	4.9
C(13)	3663(3)	1991(2)	8735(4)	3.5	C(222)	4180(5)	3243(3)	13738(5)	6.3
C(111)	1636(4)	618(3)	6729(5)	5.5	C(223)	3393(5)	3258(3)	14176(5)	6.0
C(112)	1576(5)	187(3)	5732(6)	7.7	C(224)	2539(4)	2884(3)	13623(5)	6.0
C(113)	2063(5)	345(3)	4925(5)	7.6	C(225)	2467(4)	2491(3)	12599(4)	5.2
C(114)	2622(5)	928(3)	5060(6)	7.7	C(31)	2517(4)	−498(2)	9891(5)	5.3
C(115)	2702(4)	1378(3)	6020(5)	5.9	C(32)	2018(3)	153(2)	10038(4)	3.6
C(121)	730(3)	2562(3)	6381(4)	4.6	C(33)	1374(3)	150(2)	10750(4)	3.7
C(122)	326(4)	3109(3)	5606(5)	5.7	C(34)	992(3)	735(2)	11092(4)	3.3
C(123)	920(5)	3656(3)	5581(5)	5.8	C(35)	360(4)	681(2)	11912(5)	4.7

Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors(Å^2) of $[Co(CN)_2(acac)(dppe)]\cdot H_2O$ (**b**)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Co	8130.9(2)	2235.0(5)	4320.1(2)	2.3	C(16)	8483(2)	248(5)	5922(2)	3.4
P(2)	7158.9(4)	1325.8(9)	4805.6(4)	2.1	C(17)	7656(2)	−373(4)	5560(2)	3.1
O(3)	9041(1)	3073(3)	3973(1)	3.3	C(18)	6329(1)	162(4)	4130(2)	2.4
O(4)	8029(1)	95(3)	3633(1)	2.8	C(19)	6458(2)	−1331(4)	3668(2)	2.9
O(5)	386(2)	2325(4)	412(2)	6.0	C(20)	5835(2)	−2256(4)	3160(2)	3.5
N(6)	8436(2)	5510(4)	5451(2)	4.4	C(21)	5087(2)	−1728(5)	3118(2)	4.0
N(7)	7038(2)	4352(4)	2943(2)	4.0	C(22)	4952(2)	−295(4)	3591(2)	4.1
N(8)	8819(1)	741(4)	5229(2)	3.4	C(23)	5572(2)	665(3)	4102(2)	3.3
C(9)	8281(2)	4260(4)	5020(2)	2.8	C(24)	6754(1)	3055(4)	5335(2)	2.3
C(10)	7448(2)	3558(4)	3470(2)	2.6	C(25)	6377(2)	4536(4)	4886(2)	3.1
C(11)	9784(2)	3676(5)	3039(2)	3.9	C(26)	6036(2)	5851(5)	5266(2)	3.6
C(12)	9171(2)	2592(4)	3287(2)	2.8	C(27)	6094(2)	5719(5)	6105(2)	3.9
C(13)	8820(2)	1149(4)	2800(2)	3.1	C(28)	6483(2)	4285(4)	6558(2)	3.6
C(14)	8323(2)	−93(4)	3028(2)	2.7	C(29)	6809(2)	2946(4)	6180(2)	2.9
C(15)	8132(2)	−1826(5)	2542(3)	4.2					

Patterson synthesis, and all the non-hydrogen atoms were located by the subsequent Fourier synthesis. The positions of 22 among 31 hydrogen atoms were identified in the subsequent difference-Fourier maps and others were not located. The structure was refined by a block-diagonal least squares method with anisotropic thermal parameters for nonhydrogen atoms and isotropic for hydrogens. The function minimized was $\sum w||F_o|-|F_c||^2$. Final R was 0.049 and R_w 0.055 for 4006 observed unique reflections. The atomic parameters of the non-hydrogen atoms are listed in Table 1. Complete lists of observed and calculated structure factors, hydrogen atomic parameters, and anisotropic thermal parameters for non-hydrogen atoms are preserved by the Chemical Society of Japan (Document No. 8829).

***trans*(*C*,*N*)-[Co(CN)$_2$(acac)(edpp)]·H$_2$O.** The complex was prepared in a previous work.[25] An orange rhombic crystal of approximate dimensions 0.37×0.40×0.55 mm^3 was used for X-ray work. Crystal data: monoclinic, $P2_1/c$, a=17.870(3), b=7.354(2), c=16.709(3) Å, β=105.45(2)°, V=2116.5(5) Å^3, Z=4, D_x=1.396 g cm^{-3}, D_m=1.39 g cm^{-3}, μ(Mo $K\alpha$)=9.368 cm^{-1}. Diffraction data were collected on a Rigaku AFC-5A diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range $2\theta<55°$, 3525 reflections were measured. No absorption correction was applied.

Calculations for the structure analysis were performed on a FACOM M-382 computer at the Computer Center, Nagoya University. Atomic scattering factors of neutral atoms were used.[24] The structure was solved by the Monte Carlo direct method[26] with the aid of MULTAN 78[27] using 3464 non-zero unique reflections with $|F_o|>3\sigma(|F_o|)$, and refined on F^2 by the full-matrix least-squares program. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from a difference Fourier synthesis and refined with isotropic temperature factors. Final R and R_w were 0.056 and 0.039, respectively. The atomic parameters of the non-hydrogen atoms are listed in Table 2. Complete lists of observed and calculated structure factors, hydrogen atomic parameters, and anisotropic thermal parameters for non-hydrogen atoms are preserved by the Chemical Society of Japan (Document No. 8829).

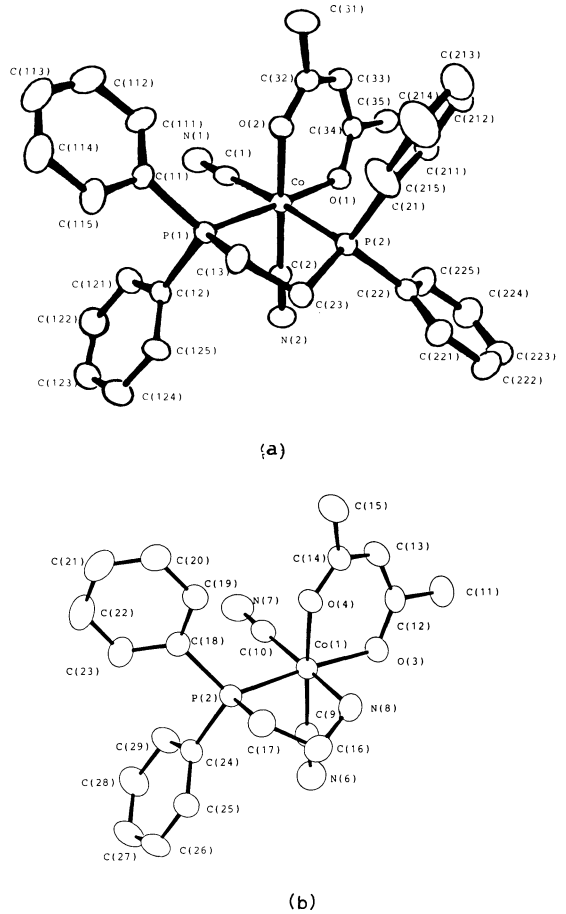

Fig. 1. ORTEP drawings[28] of **a** [Co(CN)$_2$(acac)(dppe)] and **b** [Co(CN)$_2$(acac)(edpp)].

Results and Discussion

Perspective drawings[28] of [Co(CN)$_2$(acac)(dppe)] and [Co(CN)$_2$(acac)(edpp)] with numbering schemes of the atoms are shown in Fig. 1. Selected bond distances and bond angles are listed in Tables 3 and 4. The cobalt atoms in both complexes are coordinated

Table 3. Selected Bond Distances (l/Å) and Angles (ϕ/°) for [Co(CN)2(acac)(dppe)] (**a**)

Co-P(1)	2.212(2)	Co-P(2)	2.265(1)
Co-O(1)	1.955(4)	Co-O(2)	1.937(3)
Co-C(1)	1.924(4)	Co-C(2)	1.884(4)
P(1)-C(11)	1.823(5)	P(1)-C(12)	1.820(4)
P(1)-C(13)	1.843(4)	P(2)-C(21)	1.816(4)
P(2)-C(22)	1.823(5)	P(2)-C(23)	1.834(5)
O(1)-C(34)	1.282(5)	O(2)-C(32)	1.278(6)
N(1)-C(1)	1.139(5)	N(2)-C(2)	1.133(6)
C(13)-C(23)	1.548(6)	C(31)-C(32)	1.496(7)
C(32)-C(33)	1.411(8)	C(33)-C(34)	1.382(7)
C(34)-C(35)	1.502(8)	C(11)-C(111)	1.393(7)
C(11)-C(115)	1.397(8)	C(111)-C(112)	1.414(9)
C(112)-C(113)	1.364(11)	C(113)-C(114)	1.369(10)
C(114)-C(115)	1.397(9)	C(12)-C(121)	1.391(6)
C(12)-C(125)	1.384(7)	C(121)-C(122)	1.394(7)
C(122)-C(123)	1.367(8)	C(123)-C(124)	1.380(8)
C(124)-C(125)	1.401(7)	C(21)-C(211)	1.379(7)
C(21)-C(215)	1.381(8)	C(211)-C(212)	1.378(7)
C(212)-C(213)	1.362(10)	C(213)-C(214)	1.369(10)
C(214)-C(215)	1.402(9)	C(22)-C(221)	1.375(6)
C(22)-C(225)	1.379(8)	C(221)-C(222)	1.395(8)
C(222)-C(223)	1.357(10)	C(223)-C(224)	1.365(8)
C(224)-C(225)	1.391(8)		
P(1)-Co-P(2)	87.66(5)	P(1)-Co-O(1)	177.67(8)
P(1)-Co-O(2)	87.9(1)	P(1)-Co-C(1)	89.7(2)
P(1)-Co-C(2)	88.9(2)	P(2)-Co-O(1)	94.39(8)
P(2)-Co-O(2)	90.24(8)	P(2)-Co-C(1)	175.6(1)
P(2)-Co-C(2)	85.6(1)	O(1)-Co-O(2)	93.2(1)
O(1)-Co-C(1)	88.2(2)	O(1)-Co-C(2)	90.1(2)
O(2)-Co-C(1)	93.2(2)	O(2)-Co-C(2)	174.9(2)
C(1)-Co-C(2)	90.8(2)	Co-P(1)-C(11)	119.0(2)
Co-P(1)-C(12)	117.1(2)	Co-P(1)-C(13)	107.2(2)
Co-P(2)-C(21)	113.7(1)	Co-P(2)-C(22)	119.9(2)
Co-P(2)-C(23)	105.8(1)	Co-O(1)-C(34)	123.2(3)
Co-O(2)-C(32)	124.6(3)	Co-C(1)-N(1)	177.6(5)
Co-C(2)-N(2)	178.0(3)	C(11)-P(1)-C(12)	101.5(2)
C(11)-P(1)-C(13)	103.9(2)	C(12)-P(1)-C(13)	106.9(2)
C(21)-P(2)-C(22)	103.1(2)	C(21)-P(2)-C(23)	107.1(2)
C(22)-P(2)-C(23)	106.5(2)	P(1)-C(11)-C(111)	122.0(4)
P(1)-C(11)-C(115)	115.8(4)	C(111)-C(11)-C(115)	122.2(5)
C(11)-C(111)-C(112)	117.2(6)	C(111)-C(112)-C(113)	121.0(6)
C(112)-C(113)-C(114)	120.8(6)	C(113)-C(114)-C(115)	120.9(7)
C(114)-C(115)-C(11)	117.9(6)	P(1)-C(12)-C(121)	117.8(3)
P(1)-C(12)-C(125)	121.1(3)	C(12)-C(121)-C(122)	118.6(5)
C(121)-C(122)-C(123)	120.4(5)	C(122)-C(123)-C(124)	121.5(5)
C(123)-C(124)-C(125)	118.9(5)	C(124)-C(125)-C(12)	119.6(4)
P(2)-C(21))-C(211)	117.0(4)	P(2)-C(21)-C(215)	124.6(4)
C(21)-C(211)-C(212)	120.8(5)	C(211)-C(212)-C(213)	121.7(6)
C(212)-C(213)-C(214)	118.0(6)	C(213)-C(214)-C(215)	121.6(6)
C(214)-C(215)-C(21)	119.6(6)	P(2)-C(22)-C(221)	119.7(4)
P(2)-C(22)-C(225)	121.4(3)	C(22)-C(221)-C(222)	120.4(6)
C(221)-C(222)-C(223)	120.5(5)	C(222)-C(223)-C(224)	120.2(6)
C(223)-C(224)-C(225)	120.0(6)	C(224)-C(225)-C(22)	120.4(5)
P(1)-C(13)-C(23)	108.2(3)	P(2)-C(23)-C(13)	108.0(3)
O(1)-C(34)-C(35)	113.9(4)	O(1)-C(34)-C(33)	126.9(5)
O(2)-C(32)-C(31)	115.3(5)	O(2)-C(32)-C(33)	126.2(4)
C(31)-C(32)-C(33)	118.5(4)	C(32)-C(33)-C(34)	123.3(4)
C(33)-C(34)-C(35)	119.2(4)		

nearly octahedrally. The dppe complex has a cis and the edpp one a trans(C,N) geometrical structure, as we have suggested by ^{1}H and ^{13}C NMR studies.[22,25] Other geometrical isomers were not yielded in the syntheses.[22,25]

Figure 2 shows schematic structures around the cobalt atoms of the dppe (**a**) and edpp (**b**) complexes, and a related complex, [Co(acac)(RR-chxn)(edpp)]$^{2+}$ (RR-chxn=(1*R*,2*R*)-1,2-cyclohexanediamine) (**c**)[13] with their bond distances. It is seen that both phosphine and cyanide ligands give remarkable trans influence to the cobalt-ligand bond. The Co-O bond distances of 1.955(3) Å in **a** and 1.968(2) Å in **b** both of which are trans to the phosphorus donor atom are longer by ca.

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°) for $[Co(CN)_2(acac)(edpp)]\cdot H_2O$ (**b**)

Co-P(2)	2.211(1)	Co-O(3)	1.968(2)
Co-O(4)	1.933(2)	Co-N(8)	2.011(3)
Co-C(9)	1.874(3)	Co-C(10)	1.881(2)
P(2)-C(17)	1.832(3)	P(2)-C(18)	1.823(2)
P(2)-C(24)	1.811(3)	O(3)-C(12)	1.281(4)
O(4)-C(14)	1.266(4)	N(6)-C(9)	1.158(4)
N(7)-C(10)	1.147(3)	N(8)-C(16)	1.486(4)
C(11)-C(12)	1.503(5)	C(12)-C(13)	1.399(4)
C(14)-C(15)	1.505(5)	C(16)-C(17)	1.513(4)
C(18)-C(23)	1.394(4)	C(19)-C(20)	1.387(4)
C(20)-C(21)	1.378(5)	C(21)-C(22)	1.380(5)
C(22)-C(23)	1.398(4)	C(24)-C(25)	1.394(4)
C(24)-C(29)	1.391(4)	C(25)-C(26)	1.386(5)
C(26)-C(27)	1.383(5)	C(27)-C(28)	1.378(4)
P(2)-Co-N(8)	86.51(8)	P(2)-Co-O(3)	175.77(6)
P(2)-Co-O(4)	90.65(6)	P(2)-Co-C(9)	90.49(9)
P(2)-Co-C(10)	91.07(10)	O(3)-Co-O(4)	92.07(9)
O(3)-Co-N(8)	90.41(10)	O(3)-Co-C(9)	86.6(1)
O(4)-Co-N(8)	86.73(10)	O(4)-Co-C(9)	176.92(9)
O(4)-Co-C(10)	92.05(10)	C(9)-Co-C(10)	90.8(1)
Co-P(2)-C(17)	100.1(1)	Co-P(2)-C(18)	120.40(9)
Co-P(2)-C(24)	114.96(9)	C(17)-P(2)-C(18)	105.6(1)
C(17)-P(2)-C(24)	109.2(1)	C(18)-P(2)-C(24)	105.6(1)
Co-O(3)-C(12)	122.6(2)	Co-O(4)-C(14)	124.8(2)
Co-N(8)-C(16)	115.5(2)	Co-C(9)-N(6)	174.4(3)
Co-C(10)-N(7)	178.8(3)	O(3)-C(12)-C(11)	114.8(3)
O(3)-C(12)-C(13)	125.3(3)	C(11)-C(12)-C(13)	119.8(3)
C(12)-C(13)-C(14)	124.4(3)	O(4)-C(14)-C(13)	125.1(3)
O(4)-C(14)-C(15)	116.2(3)	C(13)-C(14)-C(15)	118.6(3)
N(8)-C(16)-C(17)	108.5(2)	P(2)-C(17)-C(16)	108.2(2)
P(2)-C(18)-C(19)	119.5(2)	P(2)-C(18)-C(23)	119.2(2)
C(19)-C(18)-C(23)	119.5(2)	C(18)-C(19)-C(20)	120.2(3)
C(19)-C(20)-C(21)	120.2(3)	C(20)-C(21)-C(22)	120.2(3)
C(21)-C(22)-C(23)	120.6(3)	C(22)-C(23)-C(18)	119.4(3)
P(2)-C(24)-C(25)	119.2(2)	P(2)-C(24)-C(29)	121.8(2)
C(25)-C(24)-C(29)	119.0(3)	C(24)-C(25)-C(26)	120.8(3)
C(25)-C(26)-C(27)	119.5(3)	C(26)-C(27)-C(28)	120.1(3)
C(27)-C(28)-C(29)	120.7(3)	C(24)-C(29)-C(28)	119.9(3)

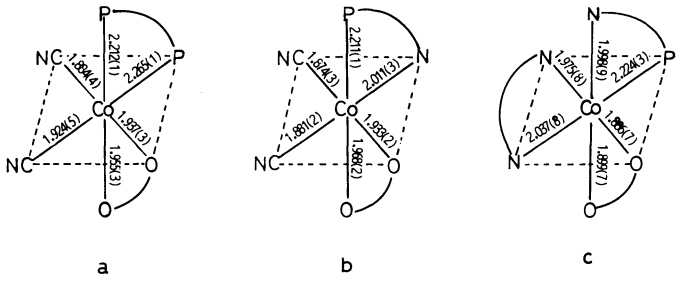

Fig. 2. Bond distances around the cobalt atom in the complexes, **a** $[Co(CN)_2(acac)(dppe)]$, **b** $[Co(CN)_2(acac)(edpp)]$, and **c** [Co(acac)(RR-chxn)-(edpp)]$^{2+}$.[11]

0.06—0.08 Å than those in **c** (1.886(7) and 1.899(7) Å) and in $[Co(acac)_3]$ (1.883(4)—1.892(4) Å).[29] A similar elongation due to trans influence of phosphine ligands has been reported for Co–N bonds in a number of cobalt(III) phosphine–amine mixed ligand complexes.[5,6,9–14] The Co–O bond distances trans to the cyanide ligand in **a** (1.937(3) Å) and **b** (1.933(2) Å) are also longer by ca. 0.03—0.05 Å than those in **c** and $[Co(acac)_3]$, indicating trans influence of the cyanide ligand. However, the extent of elongation is somewhat small compared with that due to the phosphine ligand. The Co–N bond trans to the phosphine ligand in **c** (2.037(8) Å) is also longer than that trans to the cyanide ligand in **b** (2.011(3) Å). Although structural data are rather limited at present, a phosphine ligand seems to give stronger trans influence to cobalt(III)–ligand bonds than a cyanide ligand.

In complex **a** the Co–P bond distance of 2.265(1) Å and the Co–C bond distance of 1.924(5) Å, which are trans to each other, are fairly longer than the other Co–P and Co–C bond distances, respectively. The Co–C bond distances (1.927(2) and 1.930(2) Å) in *trans*-$[Co(CN)_2(tn)_2]^+$ (tn=trimethylenediamine)[30] are also longer than those (1.85(3) and 1.88(3) Å) in *cis*-$[Co(CN)_2(en)_2]^+$.[18] These results indicate that the two coordination bonds trans to each other are weakened by mutual trans influence of the phosphine and cyanide ligands. The results may also be related to the fact that the mixed cyano and

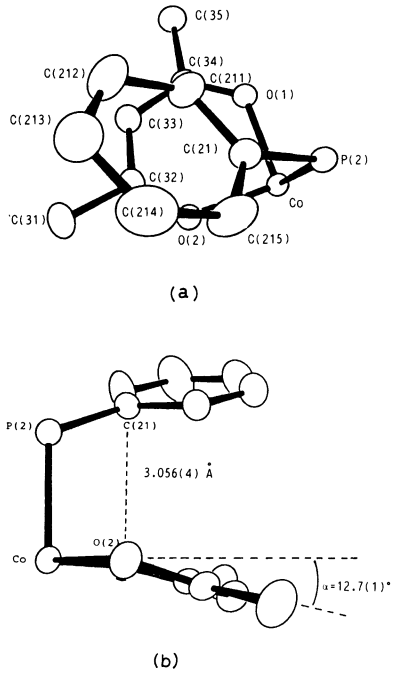

Fig. 3. A stacking structure of the acac and phenyl rings of [Co(CN)2(acac)(dppe)].

phosphine cobalt(III) complexes tend to form cis isomers for these ligands. The [Co(CN)2(acac)(edpp)] complex yielded selectively isomer **b**, in which two carbon and one phosphorus donor atoms are coordinated in a facial configuration. Two other possible isomers have these three donor atoms in a meridional configuration.

In complex **a** one of two phenyl groups is forced to be disposed over the acac chelate ring (Figs. 1(a) and 3). The O(2)···C(21) distance of 3.056(4) Å between two rings is shorter than the sum of their van der Waals radii (3.22 Å). A bent structure of the acac chelate ring with α=12.7(1)° as shown in Fig. 3(b) is probably attributable to such a stacking structure of these two rings. A similar bent structure has been observed in complex **c**.[13] On the other hand, complex **b** has no stacking structure of the phenyl and acac rings, and the acac chelate ring is nearly planar (α=4.1(5)°). All of the acac chelate rings in [Co(acac)3] are also nearly planar (α=1.6, 4.5, and 5.5°).[29] These results suggest that the interaction caused by stacking of the pseudo aromatic acac chelate and the phenyl rings is repulsive rather than attractive.

The dppe and edpp chelate rings in complexes **a** and **b** take a typical gauche conformation, and the tortion angle is 52.4(1)° (P(1)-C(13)-C(23)-P(2)) for the former and 49.9(1)° (P(2)-C(17)-C(16)-N(8)) for the latter.

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References

1) N. W. Terry, E. L. Amma, and L. Vaska, *J. Am. Chem. Soc.*, **94**, 653 (1972).
2) J. Halpern, B. L. Goodall, G. P. Kahre, H. S. Lim, and J. J. Pluth, *J. Am. Chem. Soc.*, **97**, 2301 (1975).
3) O. Alnaji, Y. Peres, F. Dahan, M. Dartiguenave, and Y. Dartiguenave, *Inorg. Chem.*, **25**, 1383 (1986).
4) N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers, and P. J. Toscano, *Coord. Chem. Rev.*, **63**, 1 (1985).
5) S. Ohba, Y. Saito, T. Ohishi, K. Kashiwabara, and J. Fujita, *Acta Crystallogr., Sect. C*, **39**, 49 (1983).
6) T. Ohishi, S. Ohba, K. Kashiwabara, Y. Saito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 877 (1984).
7) T. Ohishi, K. Kashiwabara, J. Fujita, S. Ohba, T. Ishii, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **59**, 385 (1986).
8) S. Ohba, M. Ito, Y. Saito, and T. Ishii, *Acta Crystallogr., Sect. C*, **39**, 997 (1983).
9) I. Kinoshita, K. Kashiwabara, J. Fujita, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **54**, 2683 (1981).
10) I. Kinoshita, Y. Yokota, K. Matsumoto, S. Ooi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1067 (1983).
11) T. Ohishi, K. Kashiwabara, H. Ito, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1551 (1983).
12) M. Atoh, K. Kashiwabara, H. Ito, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 3139 (1984).
13) M. Takata, K. Kashiwabara, H. Ito, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **58**, 2247 (1985). In Table 2 of this paper the numbering of the following atoms should be exchanged as follows: N(1)↔N(2), C(1)↔C(2), C(3)↔C(6), C(4)↔C(5).
14) M. Atoh, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **58**, 3492 (1985).
15) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
16) R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, **1970**, 1601.
17) R. Mason and D. R. Russell, *Chem. Commun.*, **1965**, 182.
18) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **44**, 2721 (1971).
19) M. Iwata and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 822 (1973).
20) K. Toriumi, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **33**, 1378 (1977).
21) S. Alvarez and C. Lopez, *Inorg. Chim. Acta*, **64**, L99 (1982).
22) K. Kashiwabara, K. Katoh, T. Ohishi, J. Fujita, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **55**, 149 (1982).
23) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).
24) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham(1974), Vol. IV.

25) T. Ohishi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1553 (1983).
26) A. Furusaki, *Acta Crystallogr., Sect. A*, **35**, 220 (1979).
27) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson (1978), MULTAN 78. "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univs. of York, England, and Louvain, Belgium.
28) C. K. Johnson, "ORTEP-II: A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-5138, March 1976," Oak Ridge National Laboratory.
29) G. J. Kruger and E. C. Reynhardt, *Acta Crystallogr., Sect. B*, **30**, 822 (1974).
30) H. Kupka, J. Degen, A. Urushiyama, K. Angermund, and C. Kruger, *Inorg. Chem.*, **25**, 3294 (1986).