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Crystal Structures of Cobalt(III) Complexes Containing 1,1,1-Tris(dimethylphosphinomethyl)ethane (mmtp), $[CoCl_3(mmtp)]$ and $[Co(CN)_3(mmtp)]\cdot 2H_2O$

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The crystal structures of $[CoCl_3(mmtp)]$ (mmtp=1,1,1-tris(dimethylphosphinomethyl)ethane) (complex **1**) and $[Co(CN)_3(mmtp)]\cdot 2H_2O$ (complex **2**) were determined by the single-crystal X-ray diffraction method. Crystal data and final R values are; for complex **1**, orthorhombic, $P2_1nb$ (c, a, b setting of $Pna2_1$), a=13.545(1), b=13.875(1), c=9.315(1) Å, V=1750.7(3) Å^3, D_x=1.58, D_m=1.57(3) g cm^{-3}, and Z=4, and R=0.046 for 1999 reflections. For complex **2**, orthorhombic, $P2_1nb$, a=14.345(2), b=15.330(2), c=9.229(1) Å, V=2029.4(4) Å^3, D_x=1.39, D_m=1.35(2) g cm^{-3}, and Z=4, and R=0.039 for 2715 reflections. The Co–P bond distances of av 2.203(2) Å for complex **1** and of av 2.228(1) Å for complex **2** are fairly shorter than those (av 2.331(9) Å) in $[Co(mmtp)_2][Co(CN)_6]\cdot 2.25H_2O$, in which the Co–P bonds are mutually in the trans positions, indicating the strong trans influence of the phosphino group.

Previously, we reported the preparation of cobalt(III) complexes of the $[CoX_3(mmtp)]^{n+}$-type (mmtp=1, 1, 1-tris(dimethylphosphinomethyl)ethane), in addition to the crystal structure of $[Co(mmtp)_2][Co(CN)_6]\cdot 2.25H_2O$.[1] An interesting feature in the X-ray study was the long Co(III)–P bond distances of 2.291(9)—2.357(7) Å (av 2.331 Å) compared with those (2.20—2.28 Å) in a large number of Co(III)-phosphine complexes reported in our previous studies. In this paper we have determined the X-ray crystal structures of $[CoCl_3(mmtp)]$ and $[Co(CN)_3(mmtp)]\cdot 2H_2O$ and compared the structural parameters with those of $[Co(mmtp)_2]^{3+}$ and the analogous Cr(III) complex $[CrCl_3(mmtp)]$.[2]

Experimental

Complexes. Complexes **1** and **2** were prepared by the method reported previously.[1] Crystals of **1** and **2** were grown from a nitromethane and a methanol solution, respectively.

Crystal Structure Determination. Crystal data and refinement information for X-ray analyses of **1** and **2** are listed in Table 1. The X-ray intensities were measured using graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å) on a Rigaku four-circle diffractometer AFC-5 at Institute for Molecular Science (Okazaki). The θ–2θ scan technique was employed. Absorption correction was made by the Gauss numerical integration method.[3] For complexes **1** and **2**, Laue group mmm and systematic absences ($h0l$, $h+l$ odd; $hk0$, k odd) indicated the space group $P2_1nb$ (c, a, b setting of $Pna2_1$, No. 33) or $Pmnb$ (b, a, $-c$ setting of $Pnma$, No. 62). Assuming the noncentrosymmetric space group $P2_1nb$, the structures were solved by the direct methods.[4] All non-hydrogen atoms were refined anisotropically. H atoms were included in the structure factor calculations except for those of water of crystallization. The calculations were carried out with the computation program system UNICS-III[5] on a HITAC M680H computer at Institute for Molecular Science or with CRYSTAN-GM software[6] on a SUN-SPARC2 workstation at Keio University. The structure model of $P2_1nb$ cannot be transferred into that of the centrosymmetric space group $Pmnb$, because the number of independent complex molecules is only one, and it has neither the center of symmetry nor the mirror plane (Figs. 1(b) and 2(b)). The atomic parameters for complexes **1** and **2** are listed in Tables 2 and 3, respectively.[7]

Results and Discussion

Perspective drawings[8] of complex molecules **1** and **2** are shown in Figs. 1 and 2, respectively. The selected bond distances and bond angles are listed in Tables 4 and 5. These two complexes form an octahedron with facially coordinated mmtp and three monodentate ligands.

The average Co–P bond distances of 2.203(2) Å for complex **1** and of 2.228(1) Å for complex **2** are shorter by ca. 0.1 Å than that in $[Co(mmtp)_2][Co(CN)_6]\cdot 2.25H_2O$ (av 2.331 Å).[1] The longer Co–P bond distance in $[Co(mmtp)_2]^{3+}$ is attributable to the strong trans influence of the dimethylphosphino group in the mutually trans positions, in addition to the steric effect due to the two bulky mmtp ligands. The average Co–P bond distance in complex **2** is longer by 0.025 Å than that in complex **1**, indicating the stronger trans influence of CN^- than Cl^-. The average Co–P bond distance in complex **1** is shorter by 0.253(2) Å than the Cr–P bond distance (av 2.456(2) Å) in $[CrCl_3(mmtp)]$.[2] The difference, Δl=0.253 Å, is much larger than those between the Co(III)–N and the Cr(III)–N bond distances in the usual amine complexes; e.g. $[Co(en)_3]^{3+}$ (en=1,2-ethanediamine) (av 1.964(2) Å)[9] and $[Cr(en)_3]^{3+}$ (av 2.078(4) Å)[10] (Δl=0.114(4) Å). Since no effective π-back bonding would be involved in these amine and phosphine complexes of Co(III) and

Table 1. Crystal Data and Refinement Information for $[CoX_3(mmtp)]\cdot nH_2O$

Complex	1: $X=Cl^-$ $n=0$	2: $X=CN^-$ $n=2$
Chemical formula	$C_{11}H_{27}P_3Cl_3Co$	$C_{14}H_{31}N_3O_2P_3Co$
Formular weight	417.29	425.27
Color and shape	Red prism	Yellow prism
Space group and Z	$P2_1nb$, 4	$P2_1nb$, 4
Cell dimensions		
a/Å	13.545(1)	14.345(2)
b/Å	13.875(1)	15.330(2)
c/Å	9.315(1)	9.229(1)
V/Å^3	1750.7(3)	2029.4(4)
D_m/g cm^{-3}	1.57(3)	1.35(2)
D_X/g cm^{-3}	1.58	1.39
μ(Mo $K\alpha$)/mm^{-1}	1.69	1.09
Size of specimen/mm^3	0.45×0.38×0.35	0.50×0.60×0.70
$2\theta_{max}$/°	60	60
Transmission factor	0.52—0.63	0.49—0.62
Measured reflections	2236	3066
Observed reflections ($F>3\sigma(F)$)	1999	2715
R value	0.046	0.039

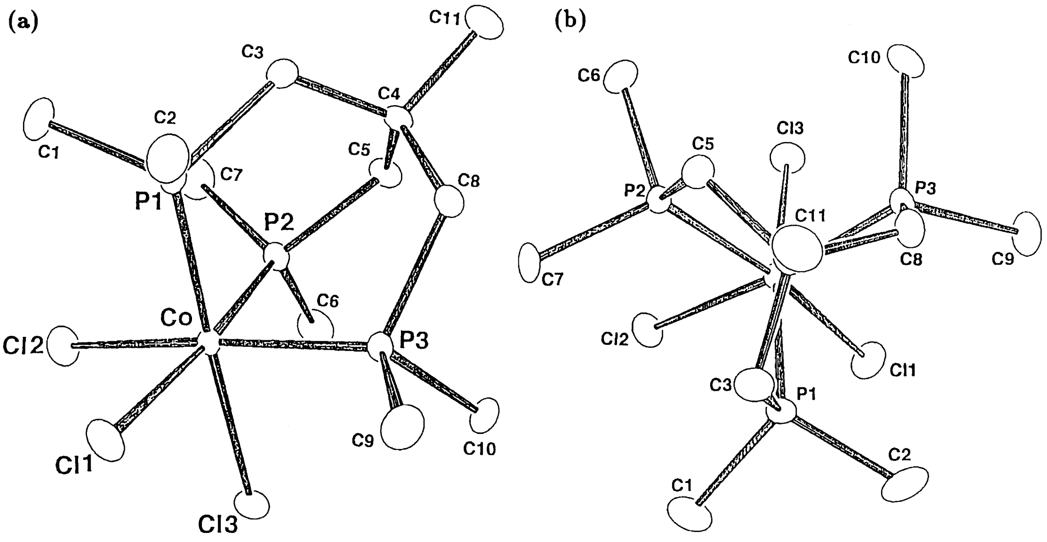

Fig. 1. Perspective views of $[CoCl_3(mmtp)]$.

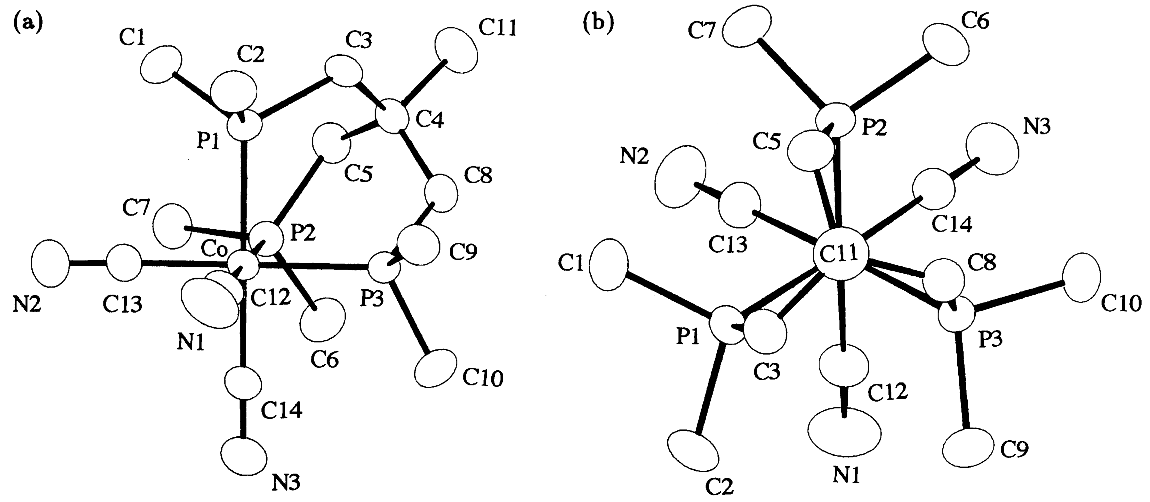

Fig. 2. Perspective views of $[Co(CN)_3(mmtp)]$.

Table 2. Positional Parameters $(\times 10^4)$ and Equivalent Isotropic Temperature Factors for $[CoCl_3(mmtp)]$

Atom	x	y	z	$B_{eq}/Å^2$
Co	2578[a]	8402(1)	9791(1)	1.4
Cl(1)	2489(2)	9791(1)	8445(2)	3.4
Cl(2)	1848(2)	9221(1)	11689(2)	2.8
Cl(3)	995(1)	7991(1)	8978(2)	2.7
P(1)	4014(1)	8717(1)	10797(2)	1.7
P(2)	2566(1)	6986(1)	10864(2)	1.5
P(3)	3370(1)	7770(1)	7955(2)	1.7
C(1)	4062(7)	8725(6)	12755(8)	2.8
C(2)	4555(8)	9871(6)	10377(11)	3.3
C(3)	4962(5)	7818(5)	10376(9)	2.1
C(4)	4588(5)	6798(4)	9997(7)	1.6
C(5)	3806(5)	6472(5)	11103(8)	1.8
C(6)	1908(6)	5998(5)	10010(10)	2.5
C(7)	2024(6)	6957(6)	12642(9)	2.8
C(8)	4176(5)	6761(5)	8460(8)	2.1
C(9)	2613(9)	7306(6)	6500(9)	3.2
C(10)	4203(9)	8562(8)	6951(10)	3.7
C(11)	5450(6)	6088(6)	10093(10)	2.7

a) This parameter was used to define the origin of the unit cell along x and is listed without esd.

Table 3. Positional Parameters $(\times 10^4)$ and Equivalent Isotropic Temperature Factors for $[Co(CN)_3(mmtp)]\cdot 2H_2O$

Atom	x	y	z	$B_{eq}/Å^2$
Co	0[a]	−1574.8(3)	2875.2(5)	2.0
P(1)	769(1)	−427(1)	−1986(1)	2.2
P(2)	450(1)	−1204(1)	−5101(1)	2.2
P(3)	1283(1)	−2378(1)	−2640(1)	2.2
O(1)	−2269(4)	3080(4)	−2079(6)	6.3
O(2)	−2195(3)	1310(3)	−3462(5)	4.9
N(1)	−660(4)	−2085(4)	139(6)	5.1
N(2)	−1790(4)	−509(3)	−3074(6)	4.3
N(3)	−1017(3)	−3126(3)	−4200(6)	3.9
C(1)	340(4)	631(4)	−2572(7)	3.5
C(2)	773(5)	−297(4)	−29(6)	3.6
C(3)	2013(4)	−417(3)	−2476(6)	2.7
C(4)	2268(3)	−921(3)	−3861(5)	2.5
C(5)	1601(4)	−688(4)	−5120(5)	2.8
C(6)	565(5)	−2081(4)	−6416(5)	3.5
C(7)	−324(4)	−471(4)	−6068(6)	3.3
C(8)	2284(3)	−1914(3)	−3583(6)	2.6
C(9)	1662(4)	−2579(4)	−783(6)	3.3
C(10)	1227(5)	−3486(3)	−3321(7)	3.8
C(11)	3262(4)	−636(4)	−4308(7)	3.9
C(12)	−400(3)	−1902(3)	−986(5)	2.9
C(13)	−1108(3)	−898(3)	−3016(5)	2.8
C(14)	−638(3)	−2536(3)	−3691(5)	2.6

a) This parameter was used to define the origin of the unit cell along x and is listed without esd.

Cr(III),[1)] the difference of the above two Δl's would be attributable to the difference in strength of the σ-bonding between the phosphorus and nitrogen donor atoms towards Co(III) and Cr(III) ions. The Cr(III)–P bond seems to be far weak compared with the Co(III)–P bond from the viewpoint of the bond distance. In fact, only a few Cr(III)-phosphine complexes have been known, in contrast to a great number of Co(III)-phosphine ones.[11)]

The average chelate angles of mmtp in complexes **1** and **2** are nearly the right angle, 89.5(1)° and 89.6(1)°, respectively, while the angle in $[Co(mmtp)_2]^{3+}$ is 84.8(3)°.[1)] The smaller chelate angle in $[Co(mmtp)_2]^{3+}$ results from the lenghthening of Co–P bonds, which seems to be due to the steric and electronic reasons de-

Table 4. Bond Distances (l/Å) and Bond Angles (ϕ/°) for [CoCl$_3$(mmtp)]

Co–Cl(1)	2.301(3)	Co–Cl(2)	2.323(3)
Co–Cl(3)	2.345(2)	Co–P(1)	2.202(2)
Co–P(2)	2.205(2)	Co–P(3)	2.201(2)
P(1)–C(1)	1.826(9)	P(1)–C(2)	1.805(11)
P(1)–C(3)	1.833(8)	P(2)–C(5)	1.838(7)
P(2)–C(6)	1.819(9)	P(2)–C(7)	1.812(9)
P(3)–C(8)	1.837(8)	P(3)–C(9)	1.817(12)
P(3)–C(10)	1.833(12)	C(3)–C(4)	1.544(10)
C(4)–C(5)	1.545(10)	C(4)–C(8)	1.537(10)
C(4)–C(11)	1.531(11)		
Cl(1)–Co–Cl(2)	89.0(1)	Cl(1)–Co–Cl(3)	88.9(1)
Cl(1)–Co–P(1)	96.4(1)	Cl(1)–Co–P(2)	173.0(1)
Cl(1)–Co–P(3)	86.3(1)	Cl(2)–Co–Cl(3)	88.6(1)
Cl(2)–Co–P(1)	87.4(1)	Cl(2)–Co–P(2)	95.0(1)
Cl(2)–Co–P(3)	173.7(1)	Cl(3)–Co–P(1)	173.3(1)
Cl(3)–Co–P(2)	85.6(1)	Cl(3)–Co–P(3)	95.6(1)
P(1)–Co–P(2)	89.5(1)	P(1)–Co–P(3)	88.8(1)
P(2)–Co–P(3)	90.1(1)	Co–P(1)–C(1)	117.3(3)
Co–P(1)–C(2)	116.3(4)	Co–P(1)–C(3)	113.1(3)
C(1)–P(1)–C(2)	101.4(5)	C(1)–P(1)–C(3)	101.1(4)
C(2)–P(1)–C(3)	105.9(4)	Co–P(2)–C(5)	113.2(2)
Co–P(2)–C(6)	118.5(3)	Co–P(2)–C(7)	115.9(3)
C(5)–P(2)–C(6)	102.0(4)	C(5)–P(2)–C(7)	104.6(4)
C(6)–P(2)–C(7)	100.6(4)	Co–P(3)–C(8)	113.2(3)
Co–P(3)–C(9)	116.5(4)	Co–P(3)–C(10)	117.2(4)
C(8)–P(3)–C(9)	104.9(5)	C(8)–P(3)–C(10)	102.8(4)
C(9)–P(3)–C(10)	100.3(5)	P(1)–C(3)–C(4)	116.3(5)
C(3)–C(4)–C(5)	109.9(6)	C(3)–C(4)–C(8)	111.3(6)
C(3)–C(4)–C(11)	109.0(6)	C(5)–C(4)–C(8)	111.3(6)
C(5)–C(4)–C(11)	107.2(6)	C(8)–C(4)–C(11)	108.1(6)
P(2)–C(5)–C(4)	115.6(5)	P(3)–C(8)–C(4)	115.4(5)

scribed above. The three arms of mmtp in these complexes are all twisted to the same direction around the C$_3$ axis to yield chirality (Figs. 1(b) and 2(b)). The torsion angles of the Co–P–C–C moieties are 23.6—26.1° (av 24.8°) for complex **1**, 24.1—25.7° (av 24.8°) for complex **2**, and 15.2—51.6° (av 32.5°) for [Co(mmtp)$_2$]$^{3+}$. The angles in [Co(mmtp)$_2$]$^{3+}$, which are largely different from those in complexes **1** and **2** and are spread in a wide range, would also be caused by the crowded structure of [Co(mmtp)$_2$]$^{3+}$ due to the steric repulsions between the methyl groups of two mmtp ligands.[1)]

The *cis* P–Co–Cl angles in complex **1** are classified into two groups, 85.6(1)—87.4(1)° (av 86.4°) and 95.0(1)—96.4(1)° (av 95.7°). The three small and three large angles are arranged alternatively when viewed from the direction of the C$_3$ axis (Fig. 1(b)). Similar alternatively different angles were observed for the *cis* P–Co–P angles in [Co(mmtp)$_2$]$^{3+}$ (av 87.9 and 104.1°).[1)] For complex **2**, the *cis* P–Co–C angles are arranged in a similar manner, but the difference between the small and large angles is very small (av 89.9 and 91.3°). The difference between the small and large angles, which shows magnitude of distortion of an octahedron, increases in the order [Co(CN)$_3$(mmtp)] < [CoCl$_3$(mmtp)] < [Co(mmtp)$_2$]$^{3+}$. This order agrees with an increasing order of bulkiness of the ligands in the facial positions faced to mmtp, CN$^-$ < Cl$^-$ < –P(CH$_3$)$_2$. Since mmtp in the complex is twisted around the C$_3$ axis, two methyl groups on the phosphorus donor atom are not sterically equivalent and would have different repulsion with the ligands in these facial coordination positions. The difference in repulsion between the two methyl groups would increase with an increase in bulkiness of the ligands faced to mmtp to distort an octahedron to a greater extent.

The Co–Cl bond distance of 2.301(3)—2.345(3) Å (av 2.323(3) Å) in complex **1** are fairly longer than those in other phosphine complexes, *trans*(*Cl*,*Cl*)*cis*(*P*,*P*)-[CoCl$_2$(edmp)$_2$]$^+$ (av 2.242(3) Å; edmp=NH$_2$CH$_2$CH$_2$-P(CH$_3$)$_2$)[12)] and *trans*-[CoCl$_2$(dmpe)$_2$]$^+$ (av 2.260(1) Å; dmpe=(CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$),[12)] and those in amine complexes, *trans*-[CoCl$_2$(en)$_2$]$^+$ (2.258(1) Å)[12,13)] and *cis*-[CoCl$_2$(en)$_2$]$^+$ (av 2.27(1) Å).[14)] The elongation of the Co–Cl bonds in complex **1** indicates the strong trans influence of –P(CH$_3$)$_2$ on the Co(III)–Cl$^-$ bond. Complex **1** aquates immediately upon dissolution in water.[1)]

The average Co–C bond distance of 1.898(5) Å in complex **2** is similar to those in *cis*-[Co-(CN)$_2$(en)$_2$]$^+$ (1.85(3) and 1.88(3) Å),[15)] [Co(NH$_3$)$_6$]-[Co(CN)$_6$] (av 1.894(1) Å),[16)] and [Co(mmtp)$_2$][Co-(CN)$_6$] (av 1.886(35) Å).[1)] In a previous paper,[17)]

Table 5. Bond Distances (l/Å) and Bond Angles (ϕ/°) for $[Co(CN)_3(mmtp)]\cdot 2H_2O$

Co–C(12)	1.903(5)	Co–C(13)	1.902(5)
Co–C(14)	1.890(4)	Co–P(1)	2.232(1)
Co–P(2)	2.227(1)	Co–P(3)	2.225(1)
P(1)–C(1)	1.817(6)	P(1)–C(2)	1.817(5)
P(1)–C(3)	1.841(5)	P(2)–C(5)	1.831(5)
P(2)–C(6)	1.819(5)	P(2)–C(7)	1.814(6)
P(3)–C(8)	1.823(5)	P(3)–C(9)	1.825(6)
P(3)–C(10)	1.813(6)	C(3)–C(4)	1.537(7)
C(4)–C(5)	1.547(7)	C(4)–C(8)	1.544(7)
C(4)–C(11)	1.548(7)	N(1)–C(12)	1.138(7)
N(2)–C(13)	1.147(7)	N(3)–C(14)	1.156(7)
C(12)–Co–C(13)	87.4(2)	C(12)–Co–C(14)	90.8(2)
C(12)–Co–P(1)	91.2(2)	C(12)–Co–P(2)	179.1(1)
C(12)–Co–P(3)	90.8(2)	C(13)–Co–C(14)	89.6(2)
C(13)–Co–P(1)	90.5(2)	C(13)–Co–P(2)	92.3(2)
C(13)–Co–P(3)	178.2(2)	C(14)–Co–P(1)	178.1(1)
C(14)–Co–P(2)	88.4(1)	C(14)–Co–P(3)	90.4(1)
P(1)–Co–P(2)	89.68(4)	P(1)–Co–P(3)	89.51(4)
P(2)–Co–P(3)	89.52(4)	Co–P(1)–C(1)	115.3(2)
Co–P(1)–C(2)	117.0(2)	Co–P(1)–C(3)	113.3(2)
C(1)–P(1)–C(2)	101.5(3)	C(1)–P(1)–C(3)	104.3(3)
C(2)–P(1)–C(3)	103.9(3)	Co–P(2)–C(5)	112.4(2)
Co–P(2)–C(6)	116.9(2)	Co–P(2)–C(7)	115.7(2)
C(5)–P(2)–C(6)	103.4(3)	C(5)–P(2)–C(7)	106.3(2)
C(6)–P(2)–C(7)	100.7(3)	Co–P(3)–C(8)	112.9(2)
Co–P(3)–C(9)	115.6(2)	Co–P(3)–C(10)	116.6(2)
C(8)–P(3)–C(9)	106.2(2)	C(8)–P(3)–C(10)	103.6(3)
C(9)–P(3)–C(10)	100.4(3)	P(1)–C(3)–C(4)	115.5(3)
C(3)–C(4)–C(5)	111.2(4)	C(3)–C(4)–C(8)	111.2(8)
C(3)–C(4)–C(11)	107.4(4)	C(5)–C(4)–C(8)	111.2(4)
C(5)–C(4)–C(11)	107.7(4)	C(8)–C(4)–C(11)	108.0(4)
P(2)–C(5)–C(4)	116.8(3)	P(3)–C(8)–C(4)	116.8(3)
Co–C(12)–N(1)	178.2(5)	Co–C(13)–N(2)	177.9(5)
Co–C(14)–N(3)	179.1(4)		

we reported that the Co–C bond distance trans to P in *cis*-$[Co(CN)_2(acac)(dppe)]$(acac $= CH_3C(O)CHC(O)CH_3^-$, dppe $= (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) is 1.924(5) Å, while those trans to O or N in this and *trans*(*C*,*N*)-$[Co(CN)_2(acac)(edpp)]\cdot H_2O$ (edpp $= NH_2CH_2CH_2P(C_6H_5)_2$) complexes are in the range 1.874(3)—1.884(4) Å. The Co–C bond distances (1.927(2) and 1.930(2) Å) in *trans*-$[Co(CN)_2(tn)_2]^+$ (tn$=NH_2CH_2CH_2CH_2NH_2$)$^{18)}$ are longer than those in the above *cis*-$[Co(CN)_2(en)_2]^+$ due to the mutual trans influence of CN^-. In complex **2**, however, neither the $-P(CH_3)_2$ nor the CN^- ligands seems to exert appreciable trans influence to each other.

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