Crystal Structures of *trans*-$[CoCl_2\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_2]ClO_4$, *trans*(*Cl,Cl*)*cis*(*P,P*)-$[CoCl_2\{NH_2CH_2CH_2P(CH_3)_2\}_2]PF_6 \cdot 0.5CH_3OH$, and *trans*-$[CoCl_2(NH_2CH_2CH_2NH_2)_2]NO_3$

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The crystal structures of *trans*-$[CoCl_2(dmpe)_2]ClO_4$ (dmpe=1,2-bis(dimethylphosphino)ethane) (**1**), *trans*(*Cl,Cl*)*cis*(*P,P*)-$[CoCl_2(edmp)_2]PF_6 \cdot 0.5CH_3OH$ (edmp=(2-aminoethyl)dimethylphosphine) (**2**) and *trans*-$[CoCl_2(en)_2]NO_3$ (en=1,2-ethanediamine) (**3**) were determined by the single-crystal X-ray diffraction method. Crystal data and final R values are: for **1**, orthorhombic, *Ccca*, $a=15.192(3)$, $b=16.221(4)$, $c=18.129(3)$ Å, $V=4468(1)$ Å^3, $D_x=1.58$, $D_m=1.60$ g cm^{-3}, and $Z=8$, and $R=0.041$ for 2360 reflections; for **2**, orthorhombic, $C222_1$, $a=15.295(4)$, $b=18.583(5)$, $c=14.680(4)$ Å, $V=4172(2)$ Å^3, $D_x=1.59$, $D_m=1.63$ g cm^{-3}, and $Z=8$, and $R=0.099$ for 4626 reflections; for **3**, monoclinic, $P2_1/n$, $a=6.348(1)$, $b=9.304(1)$, $c=9.853(1)$ Å, $\beta=101.79(1)°$, $V=569.6(1)$ Å^3, $D_x=1.82$, $D_m=1.85$ g cm^{-3}, and $Z=2$, and $R=0.043$ for 1024 reflections. The Co–P bond distances (av 2.196(3) Å) in **2** is shorter by 0.063 Å than that (av 2.259(1) Å) in **1**, while the Co–N bond distance (av 2.039(7) Å) in **2** is longer by 0.079 Å than that (av 1.960(3) Å) in **3**, indicating the trans influence of the phosphino group. The metal-ligand bond distances were compared with those of the corresponding *trans*-dichloro complexes of Fe(II), Fe(III), Cr(III), and Rh(III).

In a course of our investigations on cobalt(III)-phosphine complexes, we have prepared *trans*-$[CoCl_2(dmpe)_2]^+$ (dmpe=1,2-bis(dimethylphosphino)-ethane[1] and *trans*(*Cl,Cl*)-$[CoCl_2(edmp)_2]^+$ (edmp=(2-aminoethyl)dimethylphosphine).[2] These phosphine complexes are fairly stable towards hydrolysis in aqueous solutions, the properties being quite different from that of *trans*-$[CoCl_2(en)_2]^+$ (en=1,2-ethanediamine). With the intention of comparing structural parameters among these complexes, the crystal structures of above dmpe- and edmp-dichloro complexes have been determined, and that of *trans*-$[CoCl_2(en)_2]NO_3$[3] has been also redetermined in this paper. The Co–P, Co–N, and Co–Cl bond distances in these complexes were compared with those in *trans*-$[MCl_2(dmpe)_2]^{n+}$ (M=Fe(II), Fe(III), and Cr(III)) and related phosphine complexes of Rh(III) and Co(III) to examine the metal-ligand bonding properties. For Co(III)-phosphine complexes of the so-called Werner type, only a few structural data have been reported so far,[4] except our studies[5] and dimethylglyoximato-Co(III) complexes (cobaloximes) by Marzilli et al.[6]

Experimental

Preparation of the Complexes. *trans*-$[CoCl_2(dmpe)_2]ClO_4$[1] and *trans*-$[CoCl_2(en)_2]NO_3$[3] were prepared by the literature methods. *trans*-$[CoCl_2(edmp)_2]PF_6 \cdot 0.5CH_3OH$ was obtained by adding $NaPF_6$ to a methanol solution of the chloride[2] and recrystallized from methanol and diethyl ether. Crystals of these complexes were grown from methanol solutions. For the edmp complex the crystal for X-ray data collection was coated with an adhesive to prevent efflorescence.

Crystal Structure Determination. Crystal data, experimental conditions and refinement information for X-ray analyses of *trans*-$[CoCl_2(dmpe)_2]ClO_4$ (**1**), *trans*-$[CoCl_2(edmp)_2]PF_6 \cdot 0.5CH_3OH$ (**2**) and *trans*-$[CoCl_2(en)_2]NO_3$ (**3**) are listed in Table 1. The X-ray intensities were measured using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) on automatic Rigaku four-circle diffractometers AFC-5R (for **1** and **2**) and AFC-5 (for **3**) at Institute for Molecular Science. The θ–2θ scan technique was employed. Absorption correction was made by the Gauss numerical integration method.[7] The structures were solved by the heavy atom method. The cobalt atoms of **1** and **3** were located, respectively, on the two-fold axis and the inversion center. The counter anions of **1** and **3** were also located on the special positions, the site symmetries being 222 and $\bar{1}$, respectively. Non-hydrogen atoms were located in Fourier syntheses and were refined anisotropically. All the H atoms were included in the structure factor calculations except for those in the disordered chelate edmp rings, and those in methanol of crystallization of **2**. Complex neutral-atom scattering factors were used.[8] The calculations for **1** and **3** were carried out with the computation program system UNICS-III[9] on a HITAC M680H computer at Institute for Molecular Science, and those for **2** with the CRYSTAN-GM software[10] on a SUN-SPARC 2 workstation at Keio University. For **2** there are two possible positions of the C(7) atom, indicating the disorder of the edmp chelate ring. The complex cation exists in a general position and two independent PF_6^- ions and one methanol molecule lie on the crystallographic twofold axes. The B_{eq} values of the F atoms are in the range from 14 to 34 Å^2, suggesting the orientational disorder of the PF_6^- ions. Relatively large R value 0.099 may be partly due to the disorder. The atomic parameters are listed in Table 2, the selected bond distances and angles in Table 3.[11]

Table 1. Crystal Data and Refinement Informations for *trans(Cl,Cl)*-$[CoCl_2(L)_2]X$

	1: L=dmpe X=ClO_4	**2**: L=edmp X=$PF_6 \cdot 0.5CH_3OH$	**3**: L=en X=NO_3
Chemical formula	$C_{12}H_{32}O_4P_4Cl_3Co$	$C_{8.5}H_{26}N_2O_{0.5}F_6P_3Cl_2Co$	$C_4H_{16}N_5O_3Cl_2Co$
Formular weight	529.6	501.1	312.0
Color and shape	Green prism	Green prism	Green prism
Space group and Z	*Ccca*, 8	$C222_1$, 8	$P2_1/n$, 2
Cell dimensions			
a/Å	15.192(3)	15.295(4)	6.348(1)
b/Å	16.221(4)	18.583(5)	9.304(1)
c/Å	18.129(3)	14.680(4)	9.853(1)
β/°	—	—	101.79(1)
V/Å^3	4468(1)	4172(2)	569.6(1)
D_m/g cm^{-}3	1.60	1.63	1.85
D_x/g cm^{-}3	1.58	1.59	1.82
μ(Mo $K\alpha$)/mm^{-1}	1.43	1.35	1.97
Size/mm^3	0.70×0.60×0.50	0.50×0.50×0.40	0.45×0.30×0.30
$2\theta_{max}$/°	60	60	60
Measured reflections	3597	6567	1889
Observed reflections ($F>3\sigma(F)$)	2360	4626	1024
R value	0.041	0.099	0.043

Results and Discussion

Perspective drawings[12] of the complex ions in **1**, **2**, and **3** are shown in Figs. 1, 2, and 3, respectively. The geometrical structures of the complex ions are consistent with those assigned previously on the basis of the ligand field absorption spectra.[2,13] In Table 4 are given the bond distances around the metal ions in various *trans(Cl,Cl)*-$[MCl_2(L)_2]^{n+}$-type complexes.

The Co(III)–P bond distances (av 2.259(1) Å) in *trans*-$[CoCl_2(dmpe)_2]ClO_4$ (**1**) are longer by 0.023 Å than the Fe(II)–P bond distances (av 2.236(1) Å) in *trans*-$[FeCl_2(dmpe)_2]$[14] which is the same low-spin d^6-type complex, despite the shorter ionic radius of the low-spin Co^{3+} ion (0.69 Å) than that of the low-spin Fe^{2+} ion (0.75 Å).[15] The Fe(II)–P bonds might involve effective π-back donation. On the other hand, the Cr(III)–P bond (av 2.445(5) Å) in *trans*-$[CrCl_2(dmpe)_2]$-$B(C_6H_5)_4 \cdot CH_2Cl_2$[16] is longer by 0.186 Å than the Co(III)–P bond, and the difference between these distances is much larger than that (Δ=0.07 Å) in ionic radius between the Cr^{3+} (0.76 Å)[15] and Co^{3+} ions. The Fe(III)–P bond (av 2.304 Å) in *trans*-$[FeCl_2(dmpe)_2][FeCl_4]$[17] (low-spin d^5) is also longer by 0.045 Å than the Co(III)–P bond, the ionic radii of low-spin Fe^{3+} and Co^{3+} ions being 0.69 Å.[15] The differences in these bond distances may be understood in terms of the HSAB rule, since dmpe is a soft Lewis base to have stronger affinity towards soft Lewis acids and the order of the softness of metal ions would be Fe(II)>Co(III)>Fe(III)>Cr(III).[18] For $[MCl_3(mmtp)]$ (M=Cr(III), Co(III); mmtp=1,1,1-tris(dimethylphosphinomethyl)ethane), it has been reported that the Cr(III)–P bond distance (av 2.456(2) Å)[19] is longer by 0.253 Å than the Co(III)–P bond distance.[20] The differences between the Cr(III)–N and

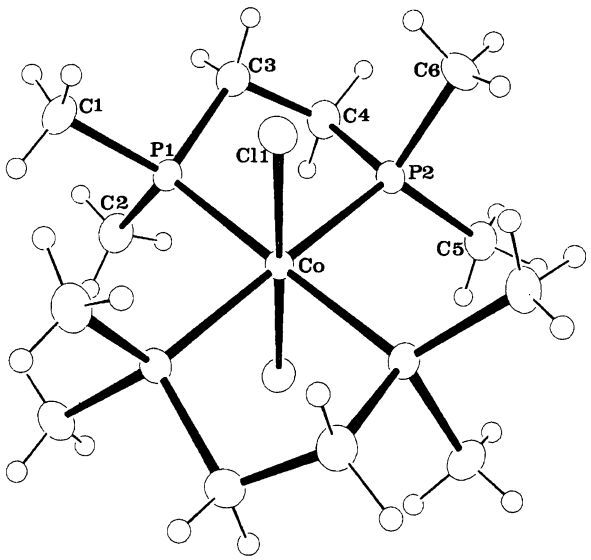

Fig. 1. A perspective view of *trans*-$[CoCl_2(dmpe)_2]^+$.

the Co(III)–N bond distances in amine complexes are, in general, about 0.1 Å; $[Co(en)_3]^{3+}$ (av 1.964(2) Å)[21] and $[Cr(en)_3]^{3+}$ (av 2.078(4) Å).[22] Such long Cr(III)–P bond distances in the above dmpe and mmtp complexes seem to indicate that affinity of phosphine ligands is weak towards Cr(III) which is a typical hard Lewis acid.

Table 4 compares the Co(III)–P bond distances in *trans(Cl,Cl)cis(P,P)*-$[CoCl_2(edmp)_2]^+$ (**2**) and the corresponding *R*-ebpp ((*R*)-(2-aminoethyl)butylphenylphosphine)[2] and edpp ((2-aminoethyl)diphenylphosphine)[2] complexes. The average distances become short in the order of the complexes of edmp (2.196(3) Å) <*R*-ebpp (2.232(3) Å) <edpp (2.255(3) Å). The bulkiness of the phosphino group of these ligands mea-

Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors for *trans(Cl, Cl)*-$[CoCl_2(L)_2]X$ (L=dmpe (X=ClO_4): **1**, L=edmp (X=$PF_6 \cdot 0.5CH_3OH$): **2**, and L=en (X=NO_3): **3**)

Atom	x	y	z	B_{eq}/Å^2	Occupancy
$[CoCl_2(dmpe)_2]ClO_4$ (**1**)					
Co	2500	0	5200.3(2)	2.0	
Cl(1)	1364.9(4)	900.2(4)	5193.2(4)	2.9	
Cl(2)	5000	−2500	7500	4.9	
Cl(3)	5000	2500	7500	3.3	
P(1)	3180.1(4)	793.7(4)	4351.7(4)	2.4	
P(2)	3213.2(4)	768.8(4)	6052.4(4)	2.5	
O(1)	5319(18)	−1732(12)	7550(21)	20	
O(2)	4464(3)	1992(3)	7959(2)	7.0	
C(1)	2542(2)	1227(2)	3597(2)	3.5	
C(2)	4135(2)	374(2)	3880(2)	3.6	
C(3)	3647(2)	1682(2)	4841(2)	3.5	
C(4)	4050(2)	1374(2)	5562(2)	3.5	
C(5)	3793(2)	258(2)	6797(2)	3.4	
C(6)	2586(2)	1559(2)	6531(2)	3.7	
$[CoCl_2(edmp)_2]PF_6 \cdot 0.5CH_3OH$ (**2**)					
Co	−1796.6(7)	1330.0(6)	−1349.6(8)	2.8	
Cl(1)	−1347(2)	1500(2)	−2789(2)	4.6	
Cl(2)	−2191(2)	1107(1)	91(2)	4.3	
P(1)	−3180(2)	1282(1)	−1730(2)	3.7	
P(2)	−1742(2)	2496(1)	−1096(2)	4.4	
N(1)	−1752(5)	252(4)	−1592(6)	4.0	
N(2)	−515(5)	1304(5)	−960(6)	4.3	
C(1)	−3492(8)	1634(8)	−2837(8)	6.3	
C(2)	−4017(7)	1665(6)	−958(8)	5.9	
C(3)	−3352(7)	309(6)	−1789(9)	5.9	
C(4)	−2467(7)	−14(6)	−2140(8)	5.4	
C(5)	−1997(9)	3127(6)	−2002(9)	6.8	
C(6)	−2340(10)	2860(7)	−150(10)	8.4	
C(7A)	−530(10)	2580(10)	−1000(10)	4.5	0.7
C(7B)	−640(30)	2700(20)	−380(40)	9.0	0.3
C(8)	−195(7)	1972(7)	−481(9)	5.7	
P(3)	0	−1262(3)	−2500	5.5	
P(4)	−5870(4)	0	0	5.8	
F(1)	0	−2059(8)	−2500	19	
F(2)	0	−431(7)	−2500	14	
F(3)	−807(9)	−1260(10)	−3090(10)	23	
F(4)	−649(9)	−1233(8)	−1720(10)	19	
F(5)	−4880(10)	0	0	27	
F(6)	−6740(10)	0	0	34	
F(7)	−5860(10)	759(6)	−280(10)	20	
F(8)	−5670(20)	−150(20)	−900(10)	31	
O(1)	−8870(10)	0	0	15	
C(9)	−9770(10)	0	0	12	
$[CoCl_2(en)_2]NO_3$ (**3**)					
Co	0	0	5000	1.3	
Cl	−2845(1)	1500(1)	4478(1)	2.2	
N(1)	1657(5)	1282(3)	4040(4)	1.9	
N(2)	896(5)	976(3)	6791(3)	2.0	
C(1)	1024(7)	1046(5)	2523(4)	2.5	
C(2)	578(7)	−537(5)	2290(4)	2.6	
N(3)	0	5000	5000	3.1	
O(1)	667(33)	4391(13)	6018(11)	7.6	0.5
O(2)	255(14)	4357(9)	3831(9)	4.1	0.5
O(3)	−1439(12)	5906(8)	4843(12)	5.2	0.5

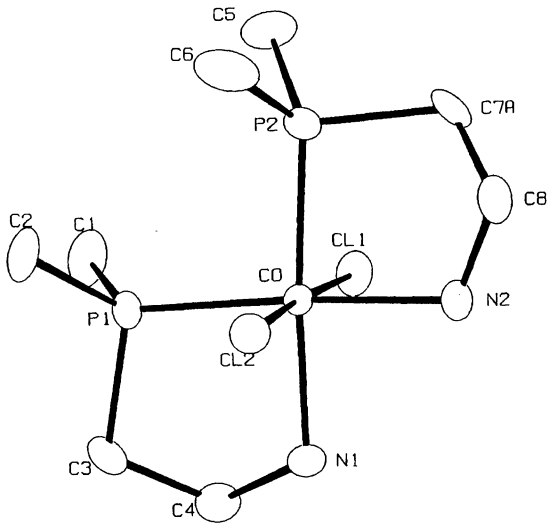

Fig. 2. A perspective view of *trans(Cl, Cl)cis(P, P)*-$[CoCl_2(edmp)_2]^+$ (C7B is omitted for clarity).

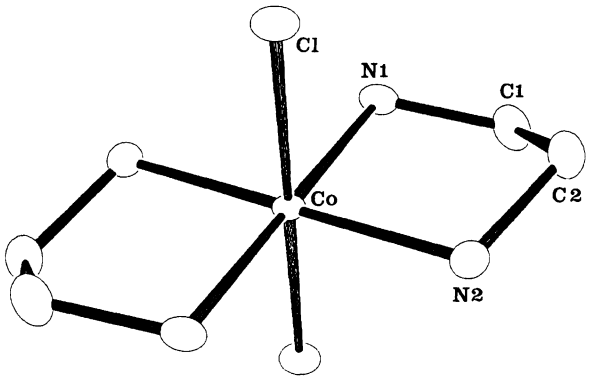

Fig. 3. A perspective view of *trans*-$[CoCl_2(en)_2]^+$.

sured by the cone angle[23] increases in the order of edmp < *R*-ebpp < edpp, while the basicity decreases in the order of edmp > *R*-ebpp > edpp.[23] Thus edmp is the most favorable one among these three ligands in complex formation with metal ions of the high oxidation number such as Co(III) from both steric and electronic conditions. The steric and electronic effects of the ligands can be seen on the ligand field spectra of the complexes. The peak positions of the first d–d band (Ia component) are shifted to higher energy in the order of the edpp (15900 cm^{-1}) < *R*-ebpp (16300 cm^{-1}) < edmp (16600 cm^{-1}) complexes.[2] The P–Co–P bond angles increasing in the order of the edmp (96.9(1)°) < *R*-ebpp (99.4(1)°) < edpp (103.1(1)°) complexes would be attributable to the bulkiness of the phosphino group.

The average Co–N bond distance (2.039(7) Å) in **2** is longer by 0.079 Å than that (1.960(3) Å) in *trans*-$[CoCl_2(en)_2]^+$ (**3**), while the average Co–P bond distance (2.196(3) Å) in **2** is shorter by 0.063 Å than that (2.259(1) Å) in *trans*-$[CoCl_2(dmpe)_2]^+$ (**1**). The lengthening of the Co–N bond and the shortening of the Co–P bond in **2** (or the lengthening of the Co–P bond in **1**) are attributable to the strong trans influence of the dimethylphosphino group. The same lengthening or shortening of the Rh–N and Rh–P bonds is seen for the corresponding *trans*-dichloro Rh(III) complexes of dmpe,[24] edmp,[24] and en[25] (Table 4). The Rh–N and

Table 3. Selected Bond Distances (l/Å) and Bond Angles (ϕ/°) for *trans(Cl,Cl)*-$[CoCl_2(L)_2]X$ (**1**—**3**)

$[CoCl_2(dmpe)_2]ClO_4$ (**1**)			
Co–Cl(1)	2.260(1)	Co–P(1)	2.256(1)
Co–P(2)	2.262(1)	P(1)–C(1)	1.817(4)
P(1)–C(2)	1.817(4)	P(1)–C(3)	1.835(3)
P(2)–C(4)	1.836(4)	P(2)–C(5)	1.813(4)
P(2)–C(6)	1.818(4)	C(3)–C(4)	1.527(5)
Cl(1)–Co–P(1)	88.68(3)	Cl(1)–Co–P(2)	90.75(3)
P(1)–Co–P(2)	86.08(3)	Co–P(1)–C(1)	119.3(1)
Co–P(1)–C(2)	118.3(1)	Co–P(1)–C(3)	107.2(1)
C(1)–P(1)–C(2)	102.5(2)	C(1)–P(1)–C(3)	105.4(2)
C(2)–P(1)–C(3)	102.3(2)	Co–P(2)–C(4)	107.2(1)
Co–P(2)–C(5)	119.3(1)	Co–P(2)–C(6)	117.7(1)
C(4)–P(2)–C(5)	105.6(2)	C(4)–P(2)–C(6)	102.5(2)
C(5)–P(2)–C(6)	102.8(2)		
$[CoCl_2(edmp)_2]PF_6 \cdot 0.5CH_3OH$ (**2**)			
Co–Cl(1)	2.244(3)	Co–Cl(2)	2.238(3)
Co–P(1)	2.190(2)	Co–P(2)	2.201(3)
Co–N(1)	2.035(7)	Co–N(2)	2.042(7)
P(1)–C(1)	1.82(1)	P(1)–C(2)	1.85(1)
P(1)–C(3)	1.83(1)	P(2)–C(5)	1.82(1)
P(2)–C(6)	1.80(2)	P(2)–C(7A)	1.86(2)
P(2)–C(7B)	2.02(5)	N(1)–C(4)	1.45(1)
N(2)–C(8)	1.51(2)	C(3)–C(4)	1.57(2)
C(7A)–C(8)	1.50(5)	C(7B)–C(8)	1.46(2)
Cl(1)–Co–Cl(2)	176.7(1)	Cl(1)–Co–P(1)	93.5(1)
Cl(1)–Co–P(2)	90.6(1)	Cl(1)–Co–N(1)	87.9(2)
Cl(1)–Co–N(2)	88.5(2)	Cl(2)–Co–P(1)	88.5(1)
Cl(2)–Co–P(2)	91.8(1)	Cl(2)–Co–N(1)	89.6(2)
Cl(2)–Co–N(2)	89.4(2)	P(1)–Co–P(2)	96.9(1)
P(1)–Co–N(1)	87.0(2)	P(1)–Co–N(2)	176.0(2)
P(2)–Co–N(1)	175.9(2)	P(2)–Co–N(2)	86.5(3)
N(1)–Co–N(2)	89.6(3)	Co–P(1)–C(1)	117.9(4)
Co–P(1)–C(2)	119.7(4)	Co–P(1)–C(3)	101.0(4)
C(1)–P(1)–C(2)	103.2(5)	C(1)–P(1)–C(3)	106.0(6)
C(2)–P(1)–C(3)	107.9(6)	Co–P(2)–C(5)	120.2(4)
Co–P(2)–C(6)	118.8(4)	Co–P(2)–C(7A)	97.7(5)
Co–P(2)–C(7B)	107(1)	C(5)–P(2)–C(6)	102.3(6)
C(5)–P(2)–C(7A)	102.4(7)	C(5)–P(2)–C(7B)	117(2)
C(6)–P(2)–C(7A)	114.7(8)	C(6)–P(2)–C(7B)	87(2)
Co–N(1)–C(4)	114.0(6)	Co–N(2)–C(8)	115.0(6)
P(1)–C(3)–C(4)	105.4(7)	N(1)–C(4)–C(3)	109.8(9)
P(2)–C(7A)–C(8)	109(1)	P(2)–C(7B)–C(8)	100(3)
N(2)–C(8)–C(7A)	106(1)	N(2)–C(8)–C(7B)	129(2)
$[CoCl_2(en)_2]NO_3$ (**3**)			
Co–Cl	2.257(1)	Co–N(1)	1.957(3)
Co–N(2)	1.963(3)	N(1)–C(1)	1.482(6)
N(2)–C(2)	1.491(6)	C(1)–C(2)	1.508(6)
Cl–Co–N(1)	89.8(1)	Cl–Co–N(2)	89.4(1)
N(1)–Co–N(2)	86.2(1)	Co–N(1)–C(1)	109.6(3)
Co–N(2)–C(2)	109.7(3)	N(1)–C(1)–C(2)	107.6(4)
N(2)–C(2)–C(1)	108.1(5)		

Table 4. Bond Distances (l/Å) around the Metal in *trans(Cl,Cl)*-$[MCl_2(L)_2]^{n+}$

Complex	M–P	M–N	M–Cl	Ref.
$[CoCl_2(dmpe)_2]ClO_4$	2.256(1)		2.260(1)	a)
	2.262(1)			
$[FeCl_2(dmpe)_2]$	2.241(1)		2.352(1)	14)
	2.230(1)			
$[FeCl_2(dmpe)_2][FeCl_4]$	2.304		2.240	17)
	(average)		(average)	
$[CrCl_2(dmpe)_2]B(C_6H_5)_4 \cdot CH_2Cl_2$	2.443(5)		2.293(4)	16)
	2.447(5)			
$[CoCl_2(edmp)_2]PF_6 \cdot 0.5CH_3OH$[b)]	2.190(3)	2.035(7)	2.238(3)	a)
	2.201(3)	2.042(7)	2.244(3)	
$[CoCl_2(R\text{-ebpp})_2]ClO_4$[b)]	2.235(3)	2.048(7)	2.248(2)	2)
	2.229(3)	2.037(8)	2.227(3)	
$[CoCl_2(edpp)_2]_2[CoCl_4]$[b)]	2.255(3)	2.028(8)	2.239(3)	2)
	2.254(3)	2.020(7)	2.240(3)	
$[CoCl_2(en)_2]NO_3$		1.957(3)	2.257(1)	a)
		1.963(3)		
$[RhCl_2(dmpe)_2]CF_3SO_3$	2.335(1)		2.359(2)	24)
	2.341(2)		2.357(2)	
	2.335(1)			
	2.337(2)			
$[RhCl_2(edmp)_2]PF_6$[b)]	2.258(1)	2.162(4)	2.332(1)	24)
	2.249(2)	2.168(3)	2.348(1)	
$[RhCl_2(en)_2]NO_3$		2.063(2)	2.3325(3)	25)

a) This work. b) *cis(P,P)* geometry. *R*-ebpp=(*R*)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$, edpp=$NH_2CH_2CH_2P(C_6H_5)_2$.

Rh–P bond distances in $[RhCl_2(edmp)_2]^+$ are longer by 0.102 Å and shorter by 0.083 Å, respectively, compared with those in the en and dmpe complexes. These values are larger by 0.02 Å than the corresponding values for the Co(III) complex. The dimethylphosphino group might exert trans influence more strongly on Rh^{3+} than Co^{3+}, since the dimethylphosphino group is a soft Lewis base to have stronger affinity towards a more soft Lewis acid, Rh^{3+} than Co^{3+}.

The average Co–Cl bond distance (2.242(3) Å) in **2** is similar to those in **1**, **3**, and other Co(III)-phosphine complexes given in Table 4. The green *trans*-$[CoCl_2(en)_2]^+$ complex is known to aquate fairly rapidly to give a dark red solution. However, all of the *trans*-dichloro Co(III) complexes of phosphines given in Table 4 are stable in water, the color of solutions being not changed for a week at room temperature. Since the Co–Cl bond distances in these *trans*-dichloro complexes are similar, the less reactive phosphine complexes to aquation would be attributable to the presence of hydrophobic alkyl or aryl groups on the phosphorus donor atom. These hydrophobic groups would prevent access of solvent water molecules.

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