Crystal Structures of Cobalt(III)–Methyldiphenylphosphine Complexes.
Co(III)–P Bond Lengths and Their Cleavages

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The crystal structures of *trans*-[Co(acac)$_2$(PMePh$_2$)$_2$]PF$_6$ (acac=2,4-pentanedionate ion) (**1**), *trans*-[Co(acac)$_2$(H$_2$O)(PMePh$_2$)]ClO$_4$ (**2**), and *trans(P,P)*-[Co(acac)(CN)$_2$(PMePh$_2$)$_2$] (**3**) were determined by the X-ray diffraction method. Complex **1** crystallizes in the monoclinic, space group $P2/n$, with two molecules in a unit cell of dimensions a=17.151(2), b=10.347(2), c=10.996(2) Å, β=107.84(1)°, V=1857.6(6) Å^3. Complex **2** crystallizes in the monoclinic, space group $P2_1/c$, with four molecules in a unit cell of dimensions a=10.161(3), b=17.291(5), c=14.938(3) Å, β=91.76(2)°, V=2623(1) Å^3. Complex **3** crystallizes in the monoclinic, space group $C2/c$, with four molecules in a unit cell of dimensions a=21.628(1), b=8.974(1), c=16.203(1) Å, β=106.396(2)°, V=3012.9(1) Å^3. The Co–P bond length for complex **1**, 2.329(1) Å, is significantly longer than those for complexes **2** (2.213(1) Å) and **3** (2.2698(4) Å). These lengths are discussed with the hydrolytic properties.

In previous papers,[1,2] we reported the syntheses and properties of a large number of cobalt(III)–phosphine complexes, *trans*- and *cis*-[Co(acac)$_2$(PR$_3$)$_2$]$^+$ (acac = 2,4-pentanedionate ion), *trans*-[Co(acac)$_2$(H$_2$O)(PR$_3$)]$^+$, and *trans(P,P)*-[Co(acac)(CN)$_2$(PR$_3$)$_2$]. Among those complexes, *trans*-[Co(acac)$_2$(PR$_3$)$_2$]$^+$ complexes were all easily hydrolyzed in hydrated solvents, whereas the other complexes were quite stable against hydrolysis under similar conditions. With a view to understanding such interesting properties, we have tried to determine the crystal structures of three representative cobalt(III)–methyldiphenylphosphine(PMePh$_2$) complexes: *trans*-[Co(acac)$_2$(PMePh$_2$)$_2$]PF$_6$ (**1**), *trans*-[Co(acac)$_2$(H$_2$O)(PMePh$_2$)]ClO$_4$ (**2**), and *trans(P,P)*-[Co(acac)(CN)$_2$(PMePh$_2$)$_2$] (**3**).

Experimental

Complexes. The preparations for complexes **1**, **2**, and **3** were reported in our previous paper.[1] *trans*-[Co(acac)$_2$(H$_2$O)(PMePh$_2$)]ClO$_4$ was derived from the hexafluorophosphate[1] using NaClO$_4$. The single crystals suitable for X-ray analysis were obtained from dichloromethane-diethyl ether for complexes **1** and **3**, and from methanol for complex **2**.

X-Ray Structure Determinations of *trans*-[Co(acac)$_2$(PMePh$_2$)$_2$]PF$_6$ (1), *trans*-[Co(acac)$_2$(H$_2$O)(PMePh$_2$)]ClO$_4$ (2), and *trans(P,P)*-[Co(acac)(CN)$_2$(PMePh$_2$)$_2$] (3). Crystal data and experimental details for complexes **1**, **2**, and **3** are summarized in Table 1. Diffraction data for **1** and **2** were obtained with a Rigaku AFC-5R and those for **3** with an Enraf–Nonius CAD-4 four-circle automated diffractometer. The reflection intensities for **1** and **2** were monitored by three standard reflections at every 150 measurements and those for 3 at every 2 hours. The decays of intensities for all crystals were within 2%. Reflection data were all corrected for Lorentz and polarization effects. Absorption corrections for crystals **1** and **2** were applied by Gauss numerical integration method[3] and that for crystal **3** by DIFABS.[4]

The structures were solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Each refinement was continued until all shifts were smaller than one-third of esd of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from Ref. 5. Hydrogen atoms were located from difference Fourier maps, and their positions were isotropically refined. The final R and R_w values were 0.033 and 0.039 for **1**, 0.061 (w=1.0) for **2**, and 0.040 and 0.048 for **3**, respectively. The weighting scheme $w^{-1}=\{\sigma^2(F_o)+(0.015\times F_o)^2\}$ was employed for

Table 1. Crystallographic Data and Experimental Details for Complexes **1**, **2**, and **3**

Complex	**1**	**2**	**3**
Formula	$CoP_3O_4F_6C_{36}H_{40}$	$CoClPO_9C_{23}H_{29}$	$CoP_2O_2N_2C_{33}H_{33}$
Fw	802.56	574.84	354.26
Color	Purple	Blue green	Orange
Crystal size/mm^3	0.55×0.30×0.25	0.50×0.40×0.35	0.40×0.35×0.30
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/n$	$P2_1/c$	$C2/c$
a/Å	17.151(2)	10.161(3)	21.628(1)
b/Å	10.347(2)	17.291(5)	8.974(1)
c/Å	10.996(2)	14.938(3)	16.203(1)
β/deg	107.84(1)	91.76(2)	106.396(2)
V/Å^3	1857.6(6)	2623(1)	3012.9(1)
Z	2	4	4
Scan mode	θ–2θ	θ–2θ	θ–2θ
2θmax/deg	55	60	60
D_x/Mg m^{-3}	1.43	1.46	1.56
λ(Mo $K\alpha$)/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	0.652	0.860	0.703
T/K	293	293	293
Refls. measured	4499	4029	3373
Refls. used ($\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$)	3050	3178	3056
R/%	0.033	0.061	0.040
R_w/%	0.039	0.061 (w=1.0)	0.048

Table 2. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors (Å^2) of *trans*-$[Co(acac)_2(PMePh_2)_2]PF_6$ (**1**)

Atom	x	y	z	B_{eq}
Co	5000	5000	0	2.3
P(1)	4893.2(3)	4772.2(5)	2050.0(5)	2.4
P(2)	7500	1638(1)	−2500	4.0
F(1)	7298(1)	546(2)	−3564(2)	6.4
F(2)	6569(1)	1643(1)	−2513(2)	6.2
F(3)	7707(1)	2731(2)	−1436(2)	6.3
O(1)	5732(1)	6401(1)	565(1)	2.7
O(2)	4046(1)	6035(1)	−519(1)	2.8
C(1)	6191(2)	8453(2)	1385(3)	4.3
C(2)	5505(1)	7543(2)	756(2)	2.9
C(3)	4698(1)	7969(2)	418(2)	3.3
C(4)	4029(1)	7242(2)	−254(2)	2.9
C(5)	3199(2)	7858(2)	−764(3)	4.2
C(6)	4967(1)	3096(2)	2562(2)	2.7
C(7)	4294(1)	2297(2)	2007(2)	3.4
C(8)	4304(2)	1008(2)	2341(2)	4.4
C(9)	4978(2)	500(3)	3217(3)	5.0
C(10)	5647(2)	1264(3)	3789(3)	5.3
C(11)	5641(1)	2569(2)	3460(2)	3.9
C(12)	5679(1)	5649(2)	3247(2)	2.7
C(13)	5484(1)	6558(2)	4043(2)	3.7
C(14)	6099(2)	7254(3)	4901(3)	4.9
C(15)	6907(2)	7041(3)	4988(3)	5.1
C(16)	7113(1)	6150(3)	4209(2)	4.3
C(17)	6503(1)	5466(2)	3333(2)	3.4
C(18)	3911(1)	5294(2)	2183(2)	3.6

crystals **1** and **3**. The calculations for **1** were performed on FACOM M780/10 computer at Keio University by using the program UNICS III,[6)] those for **2** on HITAC M680H computer at Institute for Molecular Science by using the same program system, and those for **3** on Micro VAX 3100 with the program system SDP-MolEN.[7)]

Table 3. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors (Å^2) of *trans*-$[Co(acac)_2(H_2O)(PMePh_2)]ClO_4$ (**2**)

Atom	x	y	z	B_{eq}
Co	303.6(5)	1195.1(4)	1044.0(4)	2.3
Cl	4011(1)	−418(1)	2605(1)	3.9
P	−365(1)	2411(1)	941(1)	2.4
O(1)	914(3)	1246(2)	−129(2)	2.9
O(2)	1871(3)	1558(2)	1608(2)	2.9
O(3)	−268(3)	1089(2)	2226(2)	3.1
O(4)	−1252(3)	805(2)	496(2)	2.8
O(5)	954(4)	72(2)	1157(3)	3.7
O(6)	4578(8)	−1158(5)	2717(6)	8.5
O(7)	4646(8)	97(6)	3235(5)	9.0
O(8)	2642(6)	−513(6)	2641(7)	10.2
O(9)	4239(12)	−86(7)	1753(5)	10.6
C(1)	−671(6)	2782(4)	2047(3)	3.7
C(2)	872(4)	3045(3)	480(3)	2.8
C(3)	1798(5)	3406(3)	1049(4)	3.6
C(4)	2731(5)	3893(4)	686(5)	4.7
C(5)	2758(6)	4021(4)	−219(5)	4.7
C(6)	1852(6)	3668(4)	−783(5)	4.7
C(7)	906(5)	3173(3)	−439(4)	3.6
C(8)	−1842(4)	2564(3)	256(3)	3.2
C(9)	−2045(6)	2193(4)	−560(4)	3.8
C(10)	−3172(7)	2337(5)	−1072(4)	5.0
C(11)	−4096(6)	2867(6)	−777(5)	6.2
C(12)	−3892(7)	3244(7)	23(6)	6.7
C(13)	−2774(6)	3093(5)	536(4)	4.8
C(14)	2373(6)	1410(4)	−1304(4)	4.3
C(15)	2107(5)	1414(3)	−325(3)	3.0
C(16)	3103(4)	1599(3)	290(4)	3.4
C(17)	2952(4)	1676(3)	1205(3)	3.1
C(18)	4081(5)	1921(4)	1814(4)	4.2
C(19)	−1611(7)	735(4)	3423(4)	4.7
C(20)	−1418(5)	848(3)	2433(3)	3.1
C(21)	−2448(5)	708(4)	1830(4)	3.8
C(22)	−2336(4)	680(3)	915(3)	3.0
C(23)	−3505(5)	485(4)	331(4)	4.2

Table 4. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors (Å^2) of *trans*(*P*,*P*)-[Co(acac)(CN)$_2$(PMePh$_2$)$_2$] (**3**)

Atom	*x*	*y*	*z*	B_{eq}
Co	0	1653.6(3)	2500	1.8
P	−865.2(2)	1593.5(5)	1317.4(3)	2.1
O(1)	−422.4(5)	3129(1)	3017.5(7)	2.6
N(1)	−603.2(7)	−717(2)	3345(1)	3.3
C(1)	−373.1(7)	173(2)	3016(1)	2.2
C(2)	−384.4(9)	4535(2)	2931(1)	3.4
C(3)	0	5251(3)	2500	4.5
C(4)	−809(1)	5423(3)	3340(2)	6.2
C(11)	−715.4(9)	2698(2)	459(1)	3.3
C(21)	−1604.1(8)	2347(2)	1483(1)	2.6
C(22)	−1802.9(9)	1914(3)	2194(1)	4.0
C(23)	−2383(1)	2422(3)	2292(2)	5.1
C(24)	−2761(1)	3379(3)	1712(2)	4.8
C(25)	−2559(1)	3864(3)	1029(2)	4.5
C(26)	−1986.6(9)	3343(2)	903(1)	3.5
C(31)	−1096.8(8)	−223(2)	832(1)	2.4
C(32)	−1460(1)	−1192(3)	1159(1)	4.5
C(33)	−1638(1)	−2570(3)	779(2)	6.2
C(34)	−1461(1)	−2963(3)	49(2)	5.1
C(35)	−1101(1)	−2021(3)	−275(1)	4.0
C(36)	−912.8(8)	−653(2)	110(1)	3.2

The final atomic parameters for non-hydrogen atoms for **1**, **2**, and **3** are given in Tables 2, 3, and 4, respectively.[8)]

Results and Discussion

Perspective drawings of complexes **1**, **2**, and **3** are shown in Figs. 1, 2, and 3, respectively. The Co atom of complex **1** lies on the center of symmetry, and the Co and C(3) atoms of complex **3** on the twofold axis. The selected bond lengths and angles for their complexes are listed in Table 5. All the geometries of the complexes agree well with those previously spectroscopically determined.[1)]

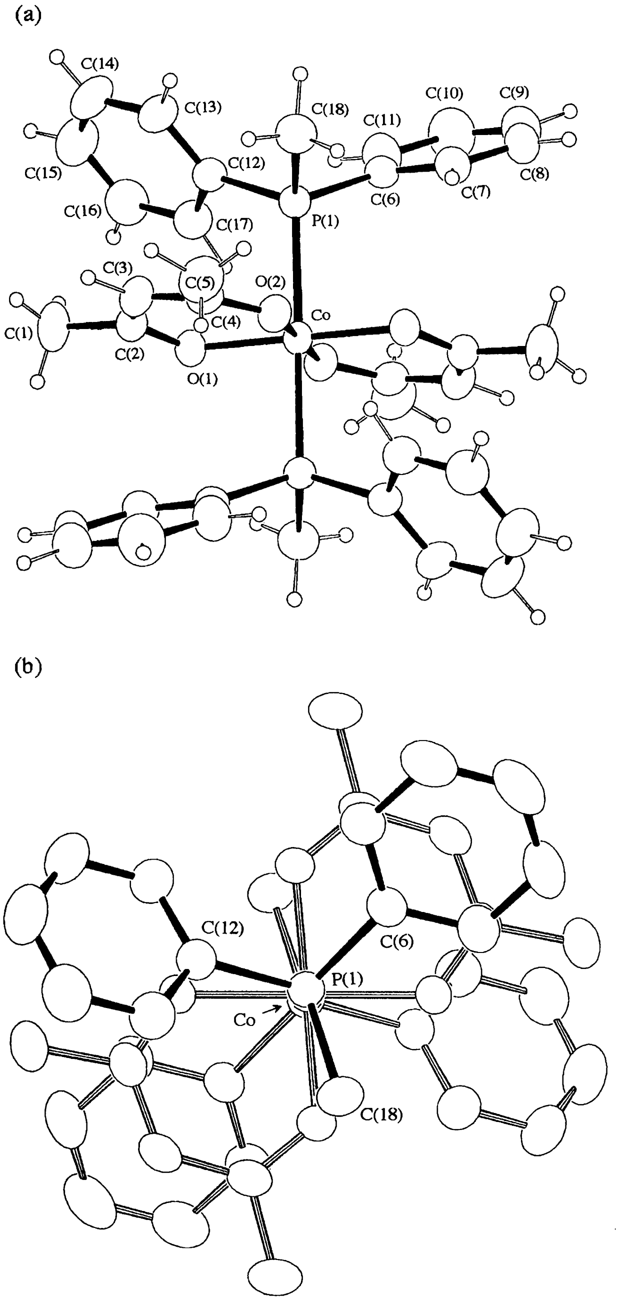

Fig. 1. Perspective views of *trans*-[Co(acac)$_2$(PMePh$_2$)$_2$]$^+$.

The most striking structural feature is the large difference (0.116 Å) between the Co–P bond lengths for complexes **1** (2.329(1) Å) and **2** (2.213(1) Å). A similar difference has also been detected between [Co(mmtp)$_2$][Co(CN)$_6$]·2.25H$_2$O[9)] (Co–P: av 2.331 Å) (mmtp = 1,1,1-tris(dimethylphosphinomethyl)ethane) and [CoX$_3$(mmtp)] (Co–P: av 2.203 Å for X=Cl$^-$, av 2.228 Å for X=CN$^-$).[10)] In the former bis-mmtp complex and complex **1**, phosphino groups are in the position trans to one another, whereas those in the latter mmtp complexes (X=Cl$^-$ and CN$^-$) and complex **2** coordinate in the positions trans to Cl$^-$, CN$^-$, and H$_2$O, respectively. Such longer Co–P bonds in complex **1**, therefore, may be attributable to the strong trans influence of mutually trans-positioned PMePh$_2$. We tried unsuccessfully to crystallize *cis*-[Co(acac)$_2$(PMePh$_2$)$_2$]PF$_6$, the poor yield prevented success. The structure of [Co(acac)$_2$(dppe)]BF$_4$ (dppe=1,2-bis(diphenylphosphino)ethane) has been determined, although the accuracy was poor.[11)] The Co–P bond lengths in the dppe complex are 2.20(1)—2.25(1) Å (av 2.23 Å), which are shorter than that in complex **1** (2.329(1) Å). In the crystals of *trans*- and *cis*-[Co(acac)$_2$(PMe$_3$)$_2$]PF$_6$ isomers similar differences have been observed between the Co–P bond lengths in the former (2.308(1) Å) and latter isomers (2.238(4) Å).[12)] These facts indicate that the large difference between the Co–P bond lengths in complexes **1** and **2** is mainly due to the strong trans influence of PMePh$_2$.

As described in the Introduction, complex **1** is rapidly hydrolyzed, whereas complex **2** is quite inert to hydrolysis. Such a hydrolysis may be correlated with the Co–P bond length; the hydrolysis of the complex with

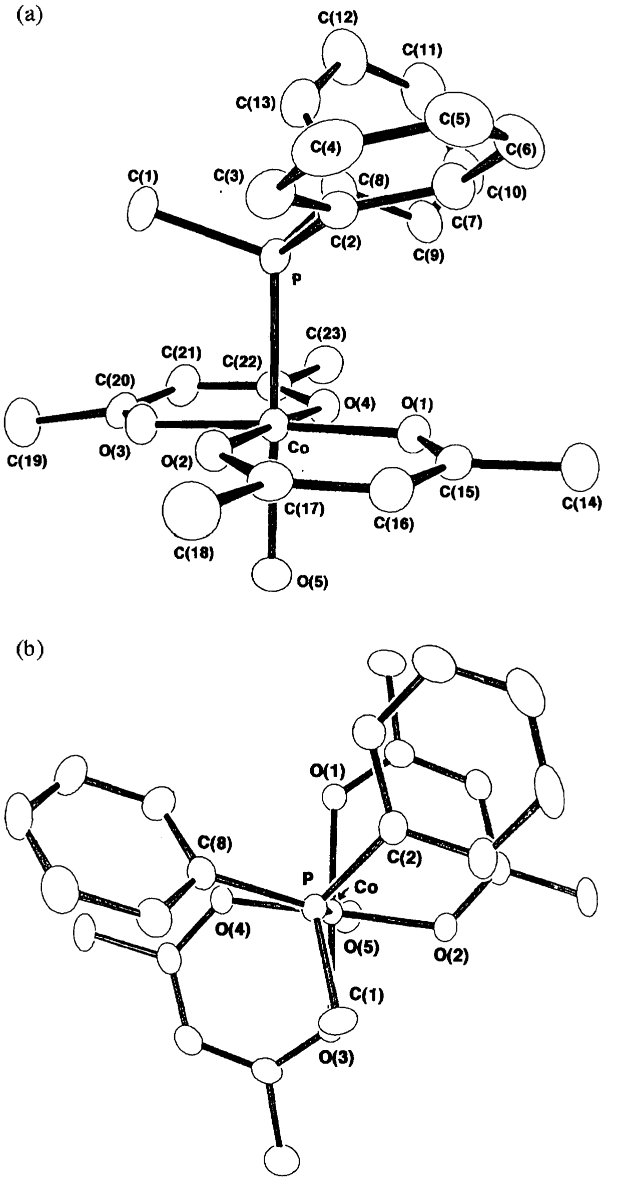

Fig. 2. Perspective views of *trans*-[Co(acac)$_2$(H$_2$O)(PMePh$_2$)]$^+$.

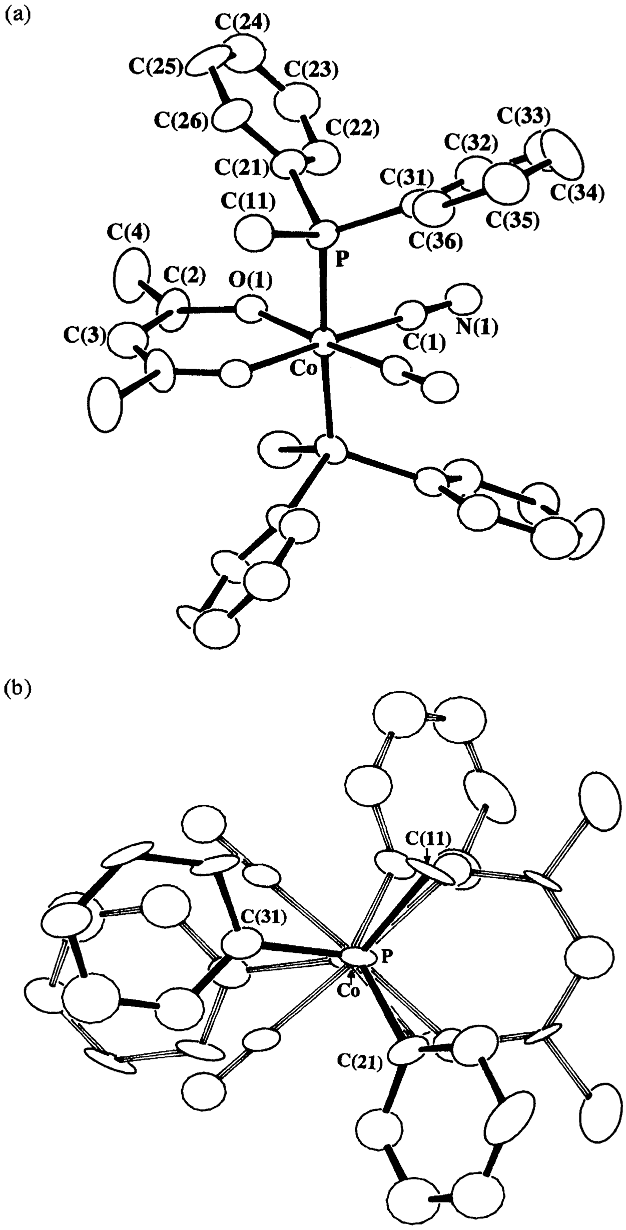

Fig. 3. Perspective views of *trans*(*P*,*P*)-[Co(acac)(CN)$_2$(PMePh$_2$)$_2$].

long Co–P bonds is promoted. This is also supported from the observation that *trans*-[Co(acac)$_2$(PMe$_3$)$_2$]PF$_6$ (Co–P: 2.308(1) Å) exhibits rapid hydrolysis, whereas the cis isomer (Co-P: 2.238(1) Å) is quite inert. On the other hand, complex **3** is not hydrolyzed under similar condition in spite of the presence of two PMePh$_2$ ligands mutually trans-positioned. The Co–P bond length in complex **3**, 2.2698(4) Å, is just intermediate between those in complexes **1** (2.329(1) Å) and **2** (2.213(1) Å). The short Co–P bond in complex **3**, therefore, may be correlated with the inertness to hydrolysis. The difference in the Co–P bond lengths between complexes **1** and **3** would be caused by the differences in the steric and electronic effects between acac (complex **1**) and CN$^-$ (complex **3**) ligands. CN$^-$ is smaller in size and a better π-acceptor ligand than acac. These factors act effectively to explain the shorter Co–P bond length in the cyanide complex.

In complex **3**, the large trans influence due to CN$^-$ also appeared. Although the Co–O bond lengths in complexes **1** (1.891(1), 1.894(1) Å) and **2** (1.879(4)—1.886(4) Å) are almost equal to those in [Co(acac)$_3$] (1.883(4)—1.892(4) Å),[14] that in complex **3** (1.930(1) Å) is significantly longer than them. A similar long Co–O bond caused by the trans influence of CN$^-$ has also been detected in *cis*-[Co(acac)(CN)$_2$(dppe)] (1.937(3) Å).[15] On the other hand, the Co–CN bond in complex **3** (1.870(2) Å) is slightly shorter than that in [Co(NH$_3$)$_6$][Co(CN)$_6$] (av 1.894(4) Å).[16] Similar short Co–CN bonds also appeared in *cis*-[Co(acac)(CN)$_2$(dppe)] (1.884(4) Å) and *trans*(*C*,*N*)-[Co(acac)-

Table 5. Selected Bond Lengths (l/Å) and Angles (ϕ/°)

Complex **1**: *trans*-$[Co(acac)_2(PMePh_2)_2]PF_6$[a)]

Co–P(1)	2.329(1)	Co–O(1)	1.894(1)	Co–O(2)	1.891(1)
P(1)–C(6)	1.816(2)	P(1)–C(12)	1.812(2)	P(1)–C(18)	1.817(2)
O(1)–C(2)	1.281(2)	O(2)–C(4)	1.285(2)		

P(1)–Co–O(1)	90.04(4)	P(1)–Co–O(2)	91.84(5)
P(1)–Co–P(1′)	180	O(1)–Co–O(2)	95.21(6)
Co–P(1)–C(6)	112.22(7)	Co–P(1)–C(12)	113.00(6)
Co–P(1)–C(18)	113.43(6)	C(6)–P(1)–C(12)	106.7(1)
C(6)–P(1)–C(18)	103.7(1)	C(12)–P(1)–C(18)	107.1(1)
Co–O(1)–C(2)	123.7(1)	Co–O(2)–C(4)	124.0(1)

Complex **2**: *trans*-$[Co(acac)_2(H_2O)(PMePh_2)]ClO_4$

Co–P	2.213(1)	Co–O(1)	1.879(4)	Co–O(2)	1.886(4)
Co–O(3)	1.884(4)	Co–O(4)	1.882(3)	Co–O(5)	2.056(4)
P–C(1)	1.808(6)	P–C(2)	1.819(5)	P–C(8)	1.810(6)
O(1)–C(15)	1.289(6)	O(2)–C(17)	1.285(6)	O(3)–C(20)	1.287(6)
O(4)–C(22)	1.302(6)				

P–Co–O(1)	90.0(1)	P–Co–O(2)	88.2(1)
P–Co–O(3)	93.1(1)	P–Co–O(4)	93.4(1)
P–Co–O(5)	178.9(1)	O(1)–Co–O(2)	95.9(2)
O(1)–Co–O(4)	84.7(2)	O(1)–Co–O(5)	90.4(2)
O(2)–Co–O(3)	83.9(2)	O(2)–Co–O(5)	90.7(2)
O(3)–Co–O(4)	95.4(2)	O(3)–Co–O(5)	86.5(2)
O(4)–Co–O(5)	87.7(2)	Co–P–C(1)	109.5(2)
Co–P–C(2)	112.7(2)	Co–P–C(8)	115.2(2)
C(1)–P–C(2)	105.8(3)	C(1)–P–C(8)	107.6(3)
C(2)–P–C(8)	105.6(2)	Co–O(1)–C(15)	124.2(3)
Co–O(2)–C(17)	124.5(3)	Co–O(3)–C(20)	124.4(3)
Co–O(4)–C(22)	124.2(3)		

Complex **3**: *trans*(*P*,*P*)-$[Co(acac)_2(CN)_2(PMePh_2)_2]$[b)]

Co–P	2.2698(4)	Co–O(1)	1.930(1)	Co–C(1)	1.870(2)
P–C(11)	1.810(2)	P–C(21)	1.823(2)	P–C(31)	1.818(2)
O(1)–C(2)	1.275(2)	N(1)–C(1)	1.148(2)		

P–Co–O(1′)	91.61(3)	P–Co–O(1)	90.26(3)
P–Co–C(1)	90.22(4)	P–Co–C(1′)	87.85(4)
P–Co–P′	177.28(2)	O(1)–Co–O(1′)	93.34(5)
O(1)–Co–C(1)	88.64(6)	O(1)–Co–C(1′)	177.30(6)
C(1)–Co–C(1′)	89.45(8)	Co–P–C(11)	110.61(8)
Co–P–C(21)	114.52(8)	Co–P–C(31)	116.57(8)
C(11)–P–C(21)	105.33(9)	C(11)–P–C(31)	104.23(9)
C(21)–P–C(31)	104.49(8)	Co–O(1)–C(2)	125.33(7)

a) Symmetry transformation used to generate equivalent atoms: (′) $1-x$, $1-y$, $-z$.
b) Symmetry transformation used to generate equivalent atoms: (′) $-x$, y, $\frac{1}{2}-z$.

$(CN)_2(NH_2CH_2CH_2PPh_2)]$ (1.874(3), 1.881(2) Å)[15)] in which the CN^- ligand occupies the position trans to O or N donor atoms.

In the crystal structures of complexes **1** and **2**, the stacking structure between one of the phenyl rings of $PMePh_2$ and the acac chelate ring was observed (Fig. 1(b), Fig. 2(b)). Since the ^1H NMR spectra of the methine protons of acac ligands in complexes **1** (δ=4.47) and **2** (δ=5.27) have showed a significant upfield shift in comparison with that in $[Co(acac)_2(en)]^+$ (en=1,2-ethanediamine) (δ=5.64), the stacking effect seems to act also in solution. The significantly large difference between the upfield shifts in complexes **1** and **2** may be caused by the difference in the number of phenyl groups: complex **1** has two, whereas complex **2** has one $PMePh_2$ ligand. Examples of similar upfield shift have often been observed in our previous works on Co(III)-phosphine complexes.[1,2,17—23)] In complex **3**, no such stacking has appeared in either the molecular or the crystal structures. (Fig. 3(b)) The ^1H NMR spectrum of the methine proton of acac in solution, however, showed upfield shift (δ=4.71) by a ring current effect, which may be caused by the rapid rotation of $PMePh_2$ around the Co–P bond axis in solution.

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