Preparation and Characterization of Cobalt(III)–Phosphine Complexes of the Type [Co(CN)$_2$(acetylacetonate)(L)] (L: Tertiary 2-Aminoethylphosphines, and 1,2- and 1,3-Diphosphines)

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Synopsis. Four new cobalt(III)–phosphine complexes of the type [Co(CN)$_2$(acetylacetonate)(L)] (L= $NH_2CH_2CH_2P(C_6H_5)_2$, $NH_2CH_2CH_2P(CH_3)_2$, $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, and $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$) were prepared. The geometrical structures of the 2-aminoethylphosphine, and 1,2- and 1,3-diphosphine complexes were assigned to have *trans(C,N)* and *cis* configurations, respectively on the basis of the ^{1}H and ^{13}C NMR spectra.

In previous papers,[1,2] we reported usefulness of ^{1}H and ^{13}C NMR spectra for assigning geometrical structures of mixed cobalt(III)–phosphine complexes. In order to extent such studies, we have prepared mixed cobalt(III)–phosphine complexes of the type [Co(CN)$_2$(acac)(L)], where acac denotes an acetylacetonate ion, and L is $NH_2CH_2CH_2P(C_6H_5)_2$(edpp), $NH_2CH_2CH_2P(CH_3)_2$(edmp), $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$(dpee), $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$(dppe), or $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$(dppp), and assigned their geometrical structures by means of ^{1}H and ^{13}C NMR techniques.

Experimental

The edpp[2] and edmp[3] ligands were prepared by the methods reported and handled under nitrogen atmosphere until they formed the cobalt(III) complexes. The dpee, dppe, and dppp ligands were purchased from Strem Chemicals Inc. Absorption, and ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi 323 spectrophotometer, and JEOL JNM-PMX 60 and JNM-FX 100 spectrometers, respectively.

[Co(CN)$_2$(acac)(edpp)]·H$_2$O. A solution of K[Co(CN)$_2$(acac)$_2$][4] (638 mg, 1.8 mmol) and edpp (282 mg, 1.2 mmol) in oxygen-free methanol (100 cm^3) was stirred for 4 h at 50 °C. Water (400 cm^3) and diethyl ether (100 cm^3) were added to the solution to extract the unreacted edpp. The aqueous solution was passed through columns of SP-Sephadex C-25 and DEAE Sephadex A-25 ion exchangers successively to remove charged species. The effluent was evaporated to dryness under reduced pressure, and the residue was extracted with a small amount of methanol. The extract was chromatographed with an alumina column (ϕ1 cm×30 cm) and an eluent of benzene–ethanol (10:1), giving three orange bands. The complexes in the first and last bands were too small in the amount and not isolated. The eluate of the main second band was concentrated under reduced pressure to yield orange crystals of the complex. Yield: *ca.* 10%. Found: C, 54.69; H, 5.31; N, 8.98%. Calcd for $C_{21}H_{25}N_3CoO_3P$: C, 55.15; H, 5.51; N, 9.19%. The complex is hardly soluble in water, but soluble in common organic solvents.

[Co(CN)$_2$(acac)(edmp)]·1/2 H$_2$O. A solution of K[Co(CN)$_2$(acac)$_2$] (656 mg 1.9 mmol) and edmp (198 mg, 0.86 mmol) in oxygen-free methanol (80 cm^3) was stirred for 10 h at room temperature. The unreacted edmp and charged species in the resulting solution were removed by the procedures described above. The methanol extract containing only noncharged species was chromatographed with a column (ϕ2 cm×40 cm) of LH-20 Sephadex and an eluent of benzene–ethanol (10:1), yielding only one yellow-orange band. The complex was very soluble in water and common organic solvents, so that it was obtained as powder by evaporating the eluate to dryness. Yield: *ca.* 10%. Found: C, 40.89; H, 6.62; N, 12.54%. Calcd for $C_{11}H_{20}N_3CoO_{2.5}P$: C, 40.75; H, 6.22; N, 12.96%.

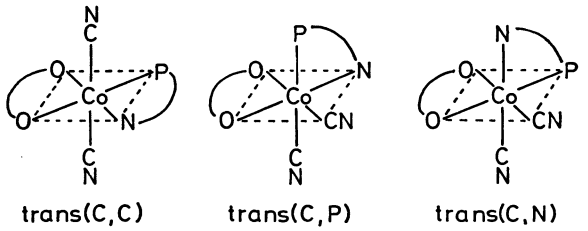

Fig. 1. Geometrical isomers of [Co(CN)$_2$(acac)(edpp or edmp)].

In the preparation of these edpp and edmp complexes, use of an equimolar amount of the aminoalkylphosphine ligand decreases the yield of the desired complex, affording dicyanobis(aminoalkylphosphine) complexes. No such reactions take place between [Co(CN)$_2$(acac)$_2$]$^-$ and diphosphine ligands as described below.

[Co(CN)$_2$(acac)(dpee)]·CHCl$_3$. This complex was prepared by a method similar to that for [Co(CN)$_2$(acac)(dppe)],[1] using K[Co(CN)$_2$(acac)$_2$] (348 mg, 1 mmol) and dpee (396 mg, 1 mmol), and recrystallized from chloroform. Yield: *ca.* 40%. Found: C, 56.31; H, 3.63; N, 3.58%. Calcd for $C_{34}H_{30}N_2CoCl_3O_2P_2$: C, 56.26; H, 4.16; N, 3.68%. The complex is insoluble in water but soluble in common organic solvents.

[Co(CN)$_2$(acac)(dppp)]·C$_6$H$_6$. A mixture of K[Co(CN)$_2$(acac)$_2$] (303 mg, 0.87 mmol), dppp (359 mg, 0.87 mmol), and a small amount of active charcoal in oxygen-free methanol (100 cm^3) was stirred for 10 h at 50 °C, and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was extracted with hot benzene (50 cm^3). On standing at room temperature the extract gave orange crystals of the complex. Yield: *ca.* 10%. Found: C, 68.10; H, 5.34; N, 3.98%. Calcd for $C_{40}H_{39}N_2CoO_2P_2$: C, 68.57; H, 5.61; N, 4.00%. The complex is insoluble in water but soluble in common organic solvents.

[Co(CN)$_2$(acac)(dppe)] was prepared by the method reported.[1]

Results and Discussion

The [Co(CN)$_2$(acac)(edpp or edmp)] complex can have three geometrical isomers (Fig. 1). In this study, each of the edpp and edmp complexes formed only one isomer. The isomers were resolved partially by the chromatographic method of Norden[5] using an alumina–(+)-lactose column. In the ^{13}C NMR spectra, the edpp and edmp complexes show signals due to two kinds of the phenyl and methyl (on P) groups, respectively, the two substituents on the phosphorus atom being diastereomeric. Thus both isomers are chiral and have either the *trans(C,P)* or the *trans(C,N)* structure. Of these two structures, the edpp complex

Table 1. ^{1}H and ^{13}C NMR spectral data for $[Co(CN)_2(acac)(L)]$, chemical shifts (δ/ppm) and ^{13}C–^{31}P coupling constants (J/Hz) in parentheses[a]

	^{1}H NMR		^{13}C NMR					
	acac		acac			L		
L	CH_3	CH	CH_3	CH	CO	P-CH_2- or P-CH=	N-CH_3	P-CH_3
edpp[b]	1.50	5.41	26.5	99.9	186.5	30.3(d, 28.1)	40.2	
	2.04		27.6(d, 5.0)		190.1(d, 2.4)			
edmp	1.97	5.67	27.4	99.9	191.0	33.3(d, 26.9)	41.9	8.4(d, 33.0)
	2.15		27.8(d, 6.1)		191.5(b)			13.7(d, 39.1)
dpee	0.82	4.90	26.2	99.5	187.5	146.1(61.6)[c]		
	1.99		27.7(d, 6.1)		190.0(d, 2.6)	148.0(69.6)[c]		
dppe	1.11	4.96	26.7	99.5	187.5	23.3(36.6)[c]		
	1.93		27.7(d, 6.1)		190.0(d, 2.4)	27.5(46.6)[c]		
dppp	1.47	5.16	26.9	99.6	186.2	26.5(80.5)[c]		
	1.57		27.2(d, 6.1)		189.5(d, 2.4)	27.3(120.9)[c]		

a) Solvent: $CDCl_3$ except for the edmp complex (CD_3OD), internal reference: TMS, d: doublet, b: broad. b) For the phenyl part,[2] P-C_1: 126.5(d, 48.8), 127.9(d, 57.3), *o*-C: 131.1(d, 8.6), 131.7(d, 8.6), *m*-C: 128.3(d, 10.8), 128.8(d, 11.0), *p*-C: 132.5(d, 3.7), 133.1(d, 3.7). c) J represents $|J_{AX}+J_{BX}|$ of an ABX system.

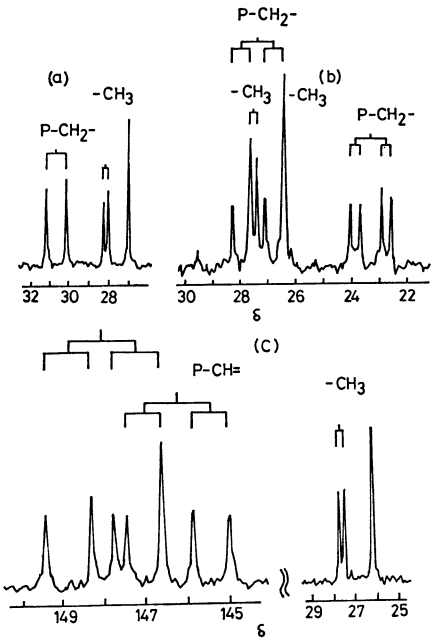

Fig. 2. ^{13}C NMR spectra of $[Co(CN)_2(acac)(L)]$. L: edpp(a), dppe(b), and dpee(c).

can be assigned to the *trans(C,N)* isomer from the ^{1}H NMR spectrum (Table 1). The methine proton of acac in this complex is observed at a fairly lower field than those of the corresponding diphosphine complexes and one methine proton of $[Co(acac)_2(edpp)]^+$ (4.93 ppm).[2] One phenyl group of edpp in $[Co(acac)_2(edpp)]^+$ is disposed over one acac ring and its methine proton is shielded by this phenyl group to resonate at a high field. Thus $[Co(CN)_2(acac)(edpp)]$ has no phenyl group over the acac ring, and is assigned to the *trans(C,N)* isomer. This assignment is supported by the ^{13}C NMR spectrum. Each one of the two carbonyl and two methyl carbons of acac in this complex shows a doublet signal due to the three-bond and four-bond ^{13}C–^{31}P couplings, respectively (Fig. 2(a)). Such couplings have been observed only when C and P atoms are situated in *trans* positions to each other through central Co(III).[2] The edmp complex shows similar patterns in the carbonyl and methyl regions of acac. Thus it is concluded that both edpp and edmp complexes have the *trans(C,N)* structure in which the phosphino group takes the position *trans* to one of the oxygen donor atoms of acac.

The structures of the diphosphine complexes can be assigned in a similar manner to *cis* configuration from the ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR spectra of the complexes show two kinds of signal due to the methyl group and doublet signals due to one carbonyl and one methyl carbons. Furthermore, the methylene and methine carbons bonded to the P atom become a quartet, the two P atoms of the diphosphine ligand being non-equivalent. All these features support conclusively *cis* configuration for the diphosphine complexes.

The data for the first absorption bands of the complexes are as follows (cm^{-1} (log ε)); edpp: 23250(2.65), edmp: 24170(2.80), dpee: 23420(3.07), dppe: 23360 (3.12), dppp:23250(3.03). Thus the spectrochemical series of the ligands is edpp, dppp<dppe<dpee< edmp.

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