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Steric and Electronic Effects of Unidentate Tertiary Phosphine Ligands on Chemical and Absorption Spectral Properties of Their Mixed Cobalt(III) Complexes with Acetylacetonate Ions

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A large number of new unidentate tertiary phosphine–cobalt(III) complexes containing acetylacetonate ions were prepared. The complexes are grouped into four types; (A) *cis*- and *trans*-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$, (B) *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$, (C) *trans*-$[Co(acac)_2(L)(PMe_2Ph)]^{n+}$, and (D) *trans*-(P,P)-$[Co(acac)(CN)_2(PR_nPh_{3-n})_2]$ (acac: acetylacetonate ion, R: CH_3(Me), C_2H_5(Et), *n*-C_3H_7(Pr), *i*-C_3H_7(Pr^i), *n*-C_4H_9(Bu), *i*-C_4H_9(Bu^i), *c*-C_6H_{11} (Cy), Ph: C_6H_5, L: NH_3, CH_3NH_2, C_5H_5N(py), NCS^-). The complexes of type A form cis and trans isomers in a different ratio depending upon the bulkiness and basicity of a phosphine ligand, and the ratios for the complexes with R=Me and Et were examined in some detail. The trans isomers of type A show a strong absorption band in the d-d transition region, which is assumed to involve charge transfer transitions between the cobalt(III) ion and a phosphine ligand, while the cis isomers exhibit the first d-d band split into two components with medium intensity. The complexes of type B show a distinct peak of the first d-d band, the energy shifts of which were discussed in terms of the bulkiness and basicity of phosphine ligands. The complexes of types C and D were prepared to compare the chemical and absorption spectral properties with those of complexes of types A and B.

It is well known that changing substituents on a phosphorus donor atom has a marked influence on physical and chemical properties of metal phosphine complexes.[1] To our knowledge, however, little work has been reported on Co^{III} complexes probably because of the lack of suitable complexes. In a previous paper,[2] we reported that a series of unidentate phosphine ligands, $P(CH_3)_n(C_6H_5)_{3-n}$ (n=1,2,3) forms mixed Co^{III} complexes of the type, $[Co(acac)_2(phosphine)_2]^+$ (acac= acetylacetonate ion). The complexes yielded cis and/or trans isomers depending on the kind of phosphines, and large differences in electronic spectra were observed among the complexes. In order to examine more thoroughly such chemical and spectroscopic properties of Co^{III}–phosphine complexes, we have prepared a large number of Co^{III} complexes containing many kinds of unidentate phosphine ligands. The phosphines used in this study are $PR_nPh_{3-n}(\boldsymbol{P})$ (R= CH_3(Me), C_2H_5(Et), *n*-C_3H_7(Pr), *i*-C_3H_7(Pr^i), *n*-C_4H_9(Bu), *i*-C_4H_9(Bu^i), *c*-C_6H_{11}(Cy), Ph=C_6H_5), and the new (55) and known (10)[2] complexes examined are grouped into the following four types; *cis*- and/or *trans*-$[Co(acac)_2(\boldsymbol{P})_2]^+$(26 complexes), *trans*-$[Co(acac)_2(H_2O)(\boldsymbol{P})]^+$ (18 complexes), *trans*-$[Co(acac)_2(L)(PMe_2Ph)]^{n+}$ (4 complexes with L=NH_3, CH_3NH_2, C_5H_5N(py), or NCS^-), and *trans*(P,P)-$[Co(acac)(CN)_2(\boldsymbol{P})_2]$ (17 complexes).

Experimental

The phosphine ligands were prepared according to the literature methods,[3] and handled under an atmosphere of nitrogen until they formed Co^{III} complexes. Absorption and ^1H NMR spectra were recorded on a Hitachi 323 spectrophotometer, and a Jeol JNM-PMX 60 spectrometer, respectively.

Preparation of Complexes. *1)* cis-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ *and* trans-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$ *(R=Et, Pr, Bu*; n=*1, 2, 3).* These complexes were prepared by two methods a) and b). a) A mixture of $[Co(acac)_3]$[4] (2 mmol), the phosphine ligand (4 mmol), and active charcoal (*ca.* 0.1 g) in ethanol-acetic acid (10:1, 60 cm^3) was stirred at room temperature for 10 h, and then filtered. The filtrate was diluted with water–methanol (2:1, 3 dm^3), and the solution was applied on a small column (ϕ2.7 cm×3 cm) of SP-Sephadex C-25. The Sephadex charged with the product was placed on the top of a column (ϕ2.7 cm×130 cm) of SP-Sephadex C-25. By elution with 0.02 mol/dm^3 NaCl the band separated into two bands. The fraction of the first band, the color of which changing from blue-violet to green during the elution, was collected and concentrated to a small volume under reduced pressure. To the concentrate was added $NaPF_6$ (or $NaClO_4$). The resulting green precipitate was filtered and dissolved in the minimum amount of methanol–water (5:1). The solution was filtered and allowed to stand at room temperature. Green crystals of *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]PF_6$ (or ClO_4) were slowly deposited with evaporation of the solvent, filtered, and air dried. From the second red-brown band were obtained red-brown crystals of *cis*-$[Co(acac)_2(PR_nPh_{3-n})_2]PF_6$ (or ClO_4) by the same procedure as that for the first band. In cases of the PPr_3 and PPr_2Ph complexes, *cis*-$[Co(acac)_2(\boldsymbol{P})_2]^+$ was eluted faster than *trans*-$[Co(acac)_2(H_2O)(\boldsymbol{P})]^+$ was. The combined yield of *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$ and *cis*-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ was 30—60%, and the ratio of the former to the latter increased as the number of phenyl groups of the phosphine ligand increases.

b) $[Co(acac)_2(H_2O)_2]$[5] (2 mmol) and the phosphine ligand (4.1 mmol) were dissolved in a mixture of ethanol (80 cm^3) and acetic acid (1 cm^3), and then PbO_2 (2.1 mmol) was added to the solution. The mixture was stirred for 2 h, and then active charcoal (*ca.* 0.1 g) was added. Stirring was continued for 10 h. The resulting solution was filtered, and the filtrate was diluted with water–methanol (2:1, 2 dm^3). The solution was subjected to column chromatography and the complexes were isolated by the same way as that described in a). The yield was 60—80% and better than that by method a). In particular, the yields of the $PRPh_2$ complexes increased markedly.

2) trans-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$ $(PR_nPh_{3-n}=PPh_3$, PPr^iPh_2, PPr^i_2Ph, PBu^iPh_2, PBu^i_2Ph, PBu^i_3, *and* $PCy_3)$. These complexes were prepared by a method similar to method b). $[Co(acac)_2(H_2O)_2]$ (2mmol) and the phosphine ligand (2mmol) were dissolved in a mixture of ethanol (60cm³) and acetic acid (1cm³). To the solution was added PbO_2 (2.1mmol), and the mixture was stirred for 2h, and then filtered. The filtrate was diluted with water (1dm³), and the solution was applied on a column (ϕ3cm×30cm) of SP-Sephadex C-25. The column was eluted with 0.05mol/dm³ NaCl, and a green fraction was collected. To the fraction was added $NaPF_6$ or $NaClO_4$ until a precipitate appears, and then the solution was allowed to stand at room temperature. Green crystals of *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]PF_6$ or ClO_4 were filtered, washed with a small amount of cold water, and air dried. The yield was 50—80%. The complexes decompose slowly in aqueous solution. No *cis*-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ was formed even though the reaction was carried out in the presence of two molar quantity of the phosphine and active charcoal.

3) trans-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ $(R=Et, Pr, Bu$; $n=0, 1, 2, 3)$ *and* trans-$[Co(acac)_2(PRPh_2)_2]^+$ $(R=Pr^i, Bu^i)$. These complexes can be prepared by two methods a) and b). a) An ethanol solution (30cm³) containing *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]PF_6$ or ClO_4 (0.3mmol) and the phosphine ligand (1mmol) was stirred for 30min. To the resulting solution was added hexane until a red-brown precipitate was no longer formed. The precipitate was filtered and recrystallized from dichloromethane by adding hexane. The yield was *ca.* 80%.

b) $[Co(acac)_2(H_2O)_2]$ (2mmol) and the phosphine ligand (4mmol) were dissolved in a mixture of ethanol (40cm³) and acetic acid (1cm³) with stirring, and then PbO_2 (2.1mmol) was added. After stirring for 2h the mixture was filtered, and excess $NaPF_6$ or $NaClO_4$ was added to the filtrate. The resulting precipitate was filtered and recrystallized from dichloromethane by adding hexane. The yield was *ca.* 80%. The bis(phosphine) complexes of PBu^i_3, PBu^i_2Ph, and PPr^i_2Ph seem to be formed in solution since the solution is intensely colored, but the complexes could not be isolated. The bis(PCy_3) complex seems to be very unstable, since a green ethanol solution of *trans*-$[Co(acac)_2(H_2O)(PCy_3)]^+$ turns intense red-brown on addition of excess PCy_3, but rapidly changes to a pale pink solution indicating the reduction of Co^{III} to Co^{II}.

4) trans-$[Co(acac)_2(L)(PMe_2Ph)]^{n+}$ $(L=NH_3, CH_3NH_2, py, NCS^-)$. A methanol solution (20cm³) containing $[Co(acac)_2(H_2O)(PMe_2Ph)]PF_6$[2] (0.5mmol) and ligand L (5mmol) was stirred for 30min at room temperature, and then water (10cm³) was added. The solution was allowed to stand at room temperature. The crystals which were slowly deposited with evaporation of the solvent were filtered and recrystallized from ethanol by adding an aqueous solution of ligand L. Yields: 40% (NH_3), 50% (CH_3NH_2), 75% (py), and 90% (NCS^-).

5) trans*(P,P)*-$[Co(acac)(CN)_2(PR_nPh_{3-n})_2]$ $(R=Et, Pr, Bu, Bu^i$; $n=1, 2, 3.$ $R=Pr^i$; $n=1)$. These complexes were prepared by a method similar to that for the corresponding $PMePh_2$ complex.[2] A mixture of $K[Co(acac)_2(CN)_2]$ (2mmol) and the phosphine ligand (4mmol) in ethanol (60cm³) was stirred at 30—40°C for 10h for the complexes of R=Et, Pr, and Bu, and at 40—50°C for 24h for the complexes of $R=Bu^i$ and Pr^i. The resulting orange yellow solution was evaporated to dryness under reduced pressure, and the residue was extracted with a small amount of chloroform. The extract was chromatographed by use of an alumina column (ϕ3cm×5cm)

TABLE 1. ANALYTICAL AND SPECTRAL DATA OF $[Co(acac)_2(\boldsymbol{P})_2]^+$

Complex	C(%)	H(%)	Absorption	Solvent	^{1}H NMR acac		Solvent
	Found(Calcd)	Found(Calcd)	$\tilde{\nu}_{max}/10^3cm^{-1}(\log\varepsilon)$		=CH-	$-CH_3$	
cis-$[Co(acac)_2(PEt_3)_2]PF_6$	41.33(41.39)	6.65(6.95)	18.2(2.39), 21.3(2.4)^{sh}	a	5.52	1.80, 2.21	c
cis-$[Co(acac)_2(PPr_3)_2]PF_6$	46.34(46.54)	7.73(7.81)	18.2(2.39), 21.3(2.4)^{sh}	a	5.60	1.81, 2.19	c
cis-$[Co(acac)_2(PBu_3)_2]ClO_4$	53.42(53.65)	9.11(9.00)	18.1(2.41), 21.2(2.4)^{sh}	a	5.56	1.79, 2.18	c
cis-$[Co(acac)_2(PEt_2Ph)_2]PF_6$	49.45(49.06)	6.05(6.04)	18.0(2.41), 20.5(2.5)^{sh}	a	5.57	1.90, 2.16	c
cis-$[Co(acac)_2(PPr_2Ph)_2]PF_6$	51.63(51.65)	6.65(6.63)	18.1(2.41), 20.5(2.5)^{sh}	a	5.57	1.90, 2.16	c
cis-$[Co(acac)_2(PBu_2Ph)_2]PF_6$	53.38(53.90)	7.09(7.14)	18.0(2.43), 20.5(2.5)^{sh}	a	5.61	1.90, 2.17	c
cis-$[Co(acac)_2(PMePh_2)_2]PF_6$	54.14(53.88)	5.03(5.02)	18(2.6)^{sh}, 20.0(2.7)^{sh}	a	5.17	1.74, 1.94	c
cis-$[Co(acac)_2(PEtPh_2)_2]PF_6$	55.22(54.95)	5.28(5.34)	17.2(2.60)	a	5.29	1.71, 1.95	c
cis-$[Co(acac)_2(PPrPh_2)_2]PF_6$	56.02(55.95)	5.76(5.63)	17.2(2.61)	a	5.38	1.72, 1.93	c
cis-$[Co(acac)_2(PBuPh_2)_2]PF_6$	56.89(56.89)	5.93(5.91)	17.2(2.60)	a	5.46	1.76, 1.94	c
trans-$[Co(acac)_2(PEt_3)_2]PF_6$	41.66(41.39)	6.86(6.95)	23.1(4.06)	b	5.47	1.97	c
trans-$[Co(acac)_2(PPr_3)_2]PF_6$	46.55(46.54)	8.06(7.81)	23.0(4.09)	b	5.44	1.98	d
trans-$[Co(acac)_2(PBu_3)_2]PF_6$	50.54(50.62)	8.84(8.50)	23.0(4.10)	b	5.49	1.97	c
trans-$[Co(acac)_2(PEt_2Ph)_2]PF_6$	49.33(49.06)	5.90(6.04)	22.1(4.15)	b	5.15	1.64	c
trans-$[Co(acac)_2(PPr_2Ph)_2]PF_6$	51.84(51.65)	6.60(6.63)	22.0(4.19)	b	5.10	1.64	d
trans-$[Co(acac)_2(PBu_2Ph)_2]ClO_4$	56.24(56.96)	7.45(7.55)	22.0(4.18)	b	5.13	1.66	c
trans-$[Co(acac)_2(PEtPh_2)_2]ClO_4\cdot 1/2H_2O$	57.48(57.46)	5.71(5.71)	20.9(4.17)	b	e	e	
trans-$[Co(acac)_2(PPrPh_2)_2]PF_6$	56.22(55.95)	5.56(5.63)	20.8(4.19)	b	4.70	1.48	d
trans-$[Co(acac)_2(PBuPh_2)_2]ClO_4$	60.23(59.97)	6.71(6.23)	20.8(4.16)	b	4.77	1.50	c
trans-$[Co(acac)_2(PBu^iPh_2)_2]PF_6$	56.61(56.89)	5.89(5.91)	20.5(4.09)^f	b	4.99	1.51	d
trans-$[Co(acac)_2(PPr^iPh_2)_2]PF_6$	55.82(55.95)	5.09(5.63)	19.8(3.97)^f	b	4.99	1.50	d
trans-$[Co(acac)_2(PPh_3)_2]PF_6$	59.81(59.62)	4.68(4.79)	19.0(4.06)^g	b	4.53	1.49	d

a: CH_3OH, b: CH_2Cl_2, c: CD_3Cl, d; CD_2Cl_2. e: No clear peak was observed because of low solubility. f: The spectrum showed a slight change with time. g: The spectrum showed a slight change with time even in the presence of a large excess of PPh_3. For the data of *cis*-$[Co(acac)_2(PMe_3)_2]PF_6$, *cis*-$[Co(acac)_2(PMe_2Ph)_2]PF_6$, *trans*-$[Co(acac)_2(PMe_2Ph)_2]PF_6$, and *trans*-$[Co(acac)_2(PMePh_2)_2]PF_6$, see Ref. 2).

TABLE 2. ANALYTICAL AND SPECTRAL DATA OF *trans*-$[Co(acac)_2(L)(\boldsymbol{P})]^{n+}$

Complex	C(%) Found(Calcd)	H(%) Found(Calcd)	N(%) Found(Calcd)	Absorption $\tilde{\nu}_{max}/10^3cm^{-1}(\log\varepsilon)$	Solvent	¹H NMR acac =CH-	¹H NMR acac -CH₃	Solvent
$[Co(acac)_2(H_2O)(PEt_3)]PF_6\cdot 1/2H_2O$	34.86(35.11)	5.71(5.53)		17.5(2.46)	a	5.75	2.12	c
$[Co(acac)_2(H_2O)(PPr_3)]PF_6$	39.55(39.32)	5.92(6.43)		17.5(2.46)	a	5.75	2.12	c
$[Co(acac)_2(H_2O)(PBu_3)]PF_6$	42.43(42.45)	6.87(6.96)		17.5(2.45)	a	5.78	2.12	c
$[Co(acac)_2(H_2O)(PBu^i_3)]PF_6\cdot H_2O$	41.20(41.26)	7.19(7.08)		17.2(2.38)	a	5.59	1.97	c
$[Co(acac)_2(H_2O)(PCy_3)]ClO_4$	51.16(51.34)	7.53(7.54)		16.3(2.29)^e	b	5.73	2.07	c
$[Co(acac)_2(H_2O)(PEt_2Ph)]PF_6\cdot 1/2H_2O$	40.20(40.35)	5.24(5.42)		17.1(2.47)	a	5.57	1.99	c
$[Co(acac)_2(H_2O)(PPr_2Ph)]PF_6$	43.30(43.01)	5.77(5.74)		17.1(2.48)	a	5.56	2.00	c
$[Co(acac)_2(H_2O)(PBu_2Ph)]PF_6$	44.80(44.87)	6.11(6.12)		17.0(2.47)	a	5.56	1.99	c
$[Co(acac)_2(H_2O)(PBu^i_2Ph)]PF_6$	44.66(44.87)	5.92(6.16)		16.8(2.44)	a	5.59	1.97	c
$[Co(acac)_2(H_2O)(PPr^i_2Ph)]PF_6\cdot H_2O$	41.52(41.78)	5.97(5.90)		16.3(2.34)	a	5.54	2.02	c
$[Co(acac)_2(H_2O)(PEtPh_2)]ClO_4$	48.73(48.95)	5.17(5.31)		16.4(2.46)	a	5.42	1.94	c
$[Co(acac)_2(H_2O)(PPrPh_2)]PF_6$	46.99(46.31)	5.55(5.13)		16.4(2.44)	a	5.43	1.93	c
$[Co(acac)_2(H_2O)(PBuPh_2)]PF_6$	46.87(47.14)	5.44(5.33)		16.4(2.44)	a	5.46	1.94	c
$[Co(acac)_2(H_2O)(PBu^iPh_2)]ClO_4$	50.67(50.62)	5.61(5.72)		16.3(2.40)	a	5.53	1.93	c
$[Co(acac)_2(H_2O)(PPr^iPh_2)]PF_6$	46.52(46.31)	5.17(5.13)		16.2(2.38)	a	5.53	1.95	c
$[Co(acac)_2(H_2O)(PPh_3)]ClO_4$	52.99(52.80)	4.83(4.91)		15.5(2.38)^e	b	5.35	1.93	c
$[Co(acac)_2(NH_3)(PMe_2Ph)]PF_6$	38.82(38.79)	5.15(4.52)	2.47(2.51)	18.6(2.36)	b	5.32	1.95	d
$[Co(acac)_2(CH_3NH_2)(PMe_2Ph)]PF_6$	39.80(39.94)	5.31(5.29)	2.38(2.45)	18.8(2.41)	b	5.31	1.94	d
$[Co(acac)_2(C_5H_5N)(PMe_2Ph)]PF_6$	44.77(44.60)	4.92(4.88)	2.27(2.26)	18.9(2.44)	b	5.12	1.87	d
$[Co(acac)_2(NCS)(PMe_2Ph)]\cdot H_2O$	48.53(48.41)	5.75(5.77)	3.19(2.97)	18.0(2.53)	b	5.25	1.94	d

a: CH_3OH, b: CH_2Cl_2, c: CD_3OD, d: CD_3Cl. e: The spectrum showed a slight change with time. For the data of *trans*-$[Co(acac)_2(H_2O)(PMe_2Ph)]PF_6\cdot 1/2H_2O$ and *trans*-$[Co(acac)_2(H_2O)(PMePh_2)]PF_6$, see Ref. 2).

TABLE 3. ANALYTICAL AND SPECTRAL DATA OF *trans*(P,P)-$[Co(acac)(CN)_2(\boldsymbol{P})_2]$

Complex	C(%) Found(Calcd)	H(%) Found(Calcd)	N(%) Found(Calcd)	Absorption $\tilde{\nu}_{max}/10^3cm^{-1}(\log\varepsilon)$	Solvent	¹H NMR acac =CH-	¹H NMR acac -CH₃	Solvent
$[Co(acac)(CN)_2(PEt_3)_2]$	50.09(50.11)	8.33(8.41)	6.05(6.15)	24.4(3.35)	a	5.27	1.89	b
$[Co(acac)(CN)_2(PPr_3)_2]$	56.54(56.60)	9.27(9.31)	5.25(5.28)	24.4(3.36)	a	5.28	1.88	b
$[Co(acac)(CN)_2(PBu_3)_2]$	60.23(60.57)	9.60(10.00)	4.37(4.56)	24.4(3.38)	a	5.27	1.80	b
$[Co(acac)(CN)_2(PBu^i_3)_2]\cdot 1/2H_2O$	59.55(59.70)	10.12(10.02)	4.74(4.49)	23.8(3.35)	a	5.30	1.91	b
$[Co(acac)(CN)_2(PEt_2Ph)_2]$	60.05(59.78)	6.55(6.88)	5.24(5.16)	23.3(3.53)	a	4.71	1.13	b
$[Co(acac)(CN)_2(PPr_2Ph)_2]$	62.23(62.20)	7.74(7.58)	4.51(4.68)	23.3(3.54)	a	4.69	1.10	b
$[Co(acac)(CN)_2(PBu_2Ph)_2]$	64.34(64.21)	8.15(8.16)	4.30(4.28)	23.3(3.55)	a	4.66	1.10	b
$[Co(acac)(CN)_2(PBu^i_2Ph)_2]\cdot H_2O$	62.69(62.49)	8.11(8.24)	4.43(4.16)	23.0(3.46)	a	4.53	0.97	b
$[Co(acac)(CN)_2(PEtPh_2)_2]$	66.03(65.83)	5.59(5.84)	4.10(4.39)	21.9(3.53)	a	4.67	0.98	b
$[Co(acac)(CN)_2(PPrPh_2)_2]$	65.22(64.91)	6.16(6.33)	3.89(4.09)	21.9(3.57)	a	4.67	0.99	b
$[Co(acac)(CN)_2(PBuPh_2)_2]\cdot 1/2H_2O$	66.37(66.57)	6.46(6.59)	3.91(3.95)	20.8(3.58)	a	4.67	0.98	b
$[Co(acac)(CN)_2(PBu^iPh_2)_2]\cdot 1/2H_2O$	66.45(66.57)	6.54(6.59)	3.78(3.98)	21.8(3.57)	a	4.60	0.93	b
$[Co(acac)(CN)_2(PPr^iPh_2)_2]\cdot 1/2H_2O$	65.82(65.78)	5.75(6.27)	4.05(4.15)	21.2(3.42)	a	4.51	0.77	b

a: CH_3OH, b: $CDCl_3$. For the data of *trans*(P,P)-$[Co(acac)(CN)_2(PMe_3)_2]$, *trans*(P,P)-$[Co(acac)(CN)_2(PMe_2Ph)_2]$, *trans*(P,P)-$[Co(acac)(CN)_2(PMePh_2)_2]$, and *trans*(P,P)-$[Co(acac)(CN)_2(PPh_3)_2]$, see Ref. 2).

and a mixture of hexane and ethanol (1:10). The eluate was concentrated to a small volume, and the concentrate was rechromatographed by use of a column (ϕ3 cm×60 cm) of SP-Sephadex LH-20 and a mixture of hexane and ethanol (5:1). The orange yellow eluate was evaporated to a small volume, and then water was added until a precipitate began to appear. The crystals which were deposited on standing at room temperature were filtered and air-dried. Yields: 45—70% (R=Et, Pr), 20—50% (R=Bu), 10% (R=Pr^i, Bu^i). The yield tends to decrease with the increasing bulkiness of R and the increasing number of phenyl groups of the ligand.

Analytical data of the new complexes are given in Tables 1—3.

Isomer Distribution of $[Co(acac)_2(PR_nPh_{3-n})_2]^+$ *(R=Me, Et; n=0, 1, 2, 3) at Equilibrium.* a) A mixture of *cis-* or *trans*-$[Co(acac)_2(PR_nPh_{3-n})_2]PF_6$ (*ca.* 0.1 mmol), the corresponding phosphine ligand (*ca.* 0.01 mmol), and a small amount of active charcoal in ethanol-dichloromethane (1:1, 20 cm³) was stirred at 20±0.5 °C for 24 h. The mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was stored in a vacuum dessicator overnight for complete elimination of the solvent and moisture. The sample thus obtained was dissolved in CD_2Cl_2, and the ¹H NMR spectrum was recorded. The formation ratio of the cis to trans isomers was determined from the intensity ratio of methine signals of acac in these isomers.

b) $[Co(acac)_2(H_2O)_2]$ (2 mmol) and the phosphine ligand (4.5 mmol) were dissolved in a mixture of ethanol (60 cm³) and acetic acid (1 cm³), and then PbO_2 (2.1 mmol) was added. The mixture was stirred for 2 h, and then active charcoal (*ca.* 0.1 g) was added. The whole was kept at 20±0.5 °C with stirring for 24 h. The resulting mixture was filtered, and the filtrate was chromatographed by the same method as that described in 1) method b) in order to separate the two isomers. The trans isomer completely changed into *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$ during the elution. The abundance of the complex in each fraction was determined by measuring the optical density. The values of formation ratio of the *cis*-bis(phosphine) complex to the *trans*-(aqua)(phosphine) complex thus obtained were almost the same as those determined by the above ^{1}H NMR method.

Results and Discussion

Preparation and Chemical Properties of the Complexes. In a previous paper,[2] we reported that trimethylphosphine and its phenyl analogs, PMe_nPh_{3-n} (n=1, 2, 3) react with $[Co(acac)_3]$ in ethanol in the presence of active charcoal to yield $[Co(acac)_2(PMe_nPh_{3-n})_2]^+$, but the reaction with bulky PPh_3 does not take place under similar conditions. Bulky alkylphosphines such as PBu^i_3, PPr^i_2Ph, and PCy_3 used in this study do not react with $[Co(acac)_3]$ either. Thus reactivity of unidentate phosphine ligands toward $[Co(acac)_3]$ seems to depend on their bulkiness. In this study, however, we have prepared such bulky phosphine complexes of the $[Co(acac)_2(\boldsymbol{P})_2]^+$ type in good yields by oxidizing a mixture of $[Co(acac)_2(H_2O)_2]$ and the phosphine ligand in ethanol with PbO_2. The less bulky phosphine complexes can also be prepared by this method in good yield.

The new preparative method affords only the trans isomer of $[Co(acac)_2(\boldsymbol{P})_2]^+$ when active charcoal is not added to the reaction mixture. In the presence of active charcoal, however, both trans and cis isomers are formed if the complex can exist in the cis isomer. The structure of the complex can be easily assigned from NMR and absorption spectra as reported for the PMe_nPh_{3-n} complexes.[2] The cis isomers, the formation of which was confirmed by column chromatography, are those with PR_nPh_{3-n} (R=Me, Et, Pr, Bu; n=1, 2, 3). For the most bulky PCy_3 ligand, only *trans*-$[Co(acac)_2(H_2O)(PCy_3)]^+$ is isolated, no bis(PCy_3) complex being formed under the given experimental conditions (see Experimental). The Co^{III}–P bond would lengthen and weaken with increasing bulkiness of the phosphine ligand. The bulkiness of phosphine ligands can be estimated in terms of the cone angle(θ°) defined by Tolman.[1] In a series of $[Co(DH)_2(Cl)(\boldsymbol{P})]$ ($\boldsymbol{P}$=PBu_3, PPh_3, PCy_3; DH=dimethylglyoximate ion), the Co^{III}–P bond lengthens in the order of the PBu_3(2.271 Å)[6] <PPh_3(2.327 Å)[7] <PCy_3(2.369 Å)[8] complexes, with the increasing cone angle of the phosphine ligands, PBu_3(132°)<PPh_3(145°)<PCy_3(170°).

Both trans and cis isomers of $[Co(acac)_2(PR_nPh_{3-n})_2]^+$ (R=Me, n=2; R=Et, Pr, Bu, n=1, 2, 3) isomerize to each other in ethanol in the presence of active charcoal, and the isomerization attains equilibrium fairly rapidly. Distributions of the two isomers at 25 °C were examined for the complexes with R=Me and Et. The proportions (%) of the trans isomers are plotted against the cone angles (θ°) of phosphine ligands in Fig. 1. With the increasing cone angle, the proportion of the trans isomer increases, and almost linear relationships are seen among the complexes with PR_nPh_{3-n} (n=2,3) and among those with PR_nPh_{3-n} (n=0, 1). The smallest PMe_3 complex affords only the cis isomer, while the largest PPh_3 complex only the trans one. The $PMePh_2$ and PEt_2Ph ligands have the same cone angle (136°), but form the trans isomer in a remarkably different proportion. The difference might come from the difference in electronic effect of the phosphine ligands. According to the parameter($\sum\chi i/\mathrm{cm}^{-1}$) given by Tolman[1] for the electronic effect of phosphines, PEt_2Ph (7.9) is more basic than $PMePh_2$ (11.2). Thus it is seen that when two kinds of phosphine ligands have a similar steric effect, the complex with the more basic phosphine ligand yields the cis isomer in a larger amount. Cotton *et al.*[9] reported a tendency to isomerize to the trans isomer in $[Mo(CO)_4(PR_3)_2]$ (R=Me, Et, Bu) with an increasing bulkiness of PR_3. Ounapu *et al.*[10] observed also a similar trend in $[W(CO)_4(PRPh_2)_2]$ (R=Me, Et, Pr^i, Bu^t, Ph); the value of the trans/cis ratio increases with an increase in bulkiness of R.

All of *trans*-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ rapidly hydrolyze when dissolved in ethanol (not anhydrous) to afford *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$. The hydrolysis is depressed by addition of the free phosphine ligand, and hence the complex in solution will exist in the following equilibrium;

$$\textit{trans}\text{-}[Co(acac)_2(PR_nPh_{3-n})_2]^+ \underset{PR_nPh_{3-n}}{\overset{H_2O}{\rightleftarrows}} \textit{trans}\text{-}[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$$

The rapid hydrolysis can be attributed to a strong trans effect of PR_nPh_{3-n}. Similar solvolyses were reported for *trans*-$[Co(acac)_2(NO_2)_2]^-$ in water[11] and *trans*-$[Co(acac)_2(CN)(py)]$ in dimethyl sulfoxide(DMSO),[12] which rapidly yield *trans*-$[Co(acac)_2(NO_2)(H_2O)]$ and *trans*-$[Co(acac)_2(CN)(DMSO)]$, respectively. The resulting *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$ complexes are stable to further hydrolysis, although those with bulky PCy_3, PPr^i_2Ph and PPh_3 decompose slowly to

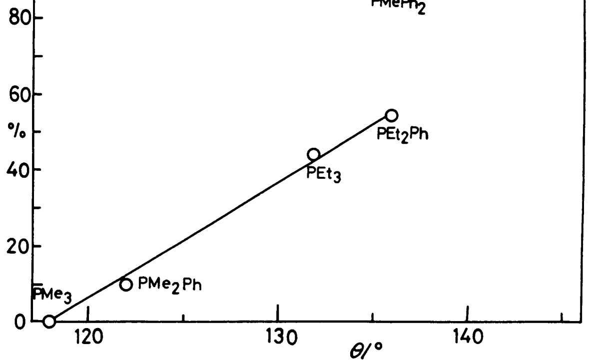

Fig. 1. Proportion(%) of *trans*-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ at equilibrium in C_2H_5OH–CH_2Cl_2 (1:1) at 25 °C *vs.* Tolman's cone angle (θ°) of the phosphine ligand.

give Co^{II} species. The aqua ligand in *trans*-[Co(acac)$_2$(H$_2$O)(PR$_n$Ph$_{3-n}$)]$^+$ is readily replaced by various bases (L) to afford *trans*-[Co(acac)$_2$(L)(PR$_n$Ph$_{3-n}$)]$^{n+}$. We have isolated complexes of this type for PMe$_2$Ph and L=NH$_3$, CH$_3$NH$_2$, py, or NCS$^-$. All of these complexes immediately lose L to give original *trans*-[Co(acac)$_2$(H$_2$O)(PMe$_2$Ph)]$^+$ when dissolved in methanol or ethanol (not anhydrous). This is in marked contrast to the inertness of *trans*-[Co(acac)$_2$(NO$_2$)(NH$_3$ or py)] in solvolysis.13) The trans effects of cyanide and phosphine ligands should be much greater than that of NO$_2^-$.14) When PMePh$_2$ for L is added to a methanol solution of *trans*-[Co(acac)$_2$(H$_2$O)(PMe$_2$Ph)]$^+$, a disproportionation reaction takes place to yield *trans*-[Co(acac)$_2$(PMe$_2$Ph)$_2$]$^+$ and *trans*-[Co(acac)$_2$(PMePh$_2$)$_2$]$^+$ in addition to *trans*-[Co(acac)$_2$(PMe$_2$Ph)(PMePh$_2$)]$^+$. The reaction of CN$^-$ with [Co(acac)$_2$(H$_2$O)(PMe$_2$Ph)]$^+$ affords *cis*-[Co(acac)$_2$(CN)(PMe$_2$Ph)], no trans isomer being formed. Since CN$^-$ has strong ability of trans influence as a phosphine and is much smaller in size, the complex would be greatly stabilized in the cis isomer.

The [Co(acac)(CN)$_2$(PR$_n$Ph$_{3-n}$)$_2$]-type complexes have been prepared from *cis*-[Co(acac)$_2$(CN)$_2$]$^-$ and PR$_n$Ph$_{3-n}$ by a method similar to that for the corresponding PMe$_n$Ph$_{3-n}$ complexes.2) All the complexes yield only the trans (P,P) isomer of three possible geometrical isomers. The assignment of the trans (P,P) isomer can be made easily from NMR spectra as reported for the PMe$_n$Ph$_{3-n}$ complexes.2) The stereoselective formation of the trans (P,P) isomer over various kinds of phosphines might result from stronger trans influence of CN$^-$ than that of a phosphine ligand. Furthermore, the steric effect of bulky phosphine ligands would facilitate formation of the trans (P,P) isomer. The yield of the complex decreases with increasing bulkiness of phosphines, and extremely bulky phosphines such as PPr$^i_2$Ph and PCy$_3$ do not react with *cis*-[Co(acac)$_2$(CN)$_2$]$^-$. All the complexes obtained are stable in methanol or ethanol, and show no solvolysis in contrast to trans-[Co(acac)$_2$(PR$_n$Ph$_{3-n}$)$_2$]$^+$ stated previously. The reason for this remains unknown. Since the *trans*-[Co(CN)$_4$(PMe$_n$Ph$_{3-n}$)$_2$]$^-$ (n=0, 1, 2) complexes are also inert to solvolysis,2) strong and soft cyanide ions in such trans (P,P) complexes might play an important role in strengthening the Co^{III}–P bond.

^{1}H NMR Spectra. In Tables 1—3 are listed data of the methine and methyl signals of acac in ^{1}H NMR spectra of the complexes. General features in chemical shift of these signals are similar to those reported for the complexes of PMe$_n$Ph$_{3-n}$.2) For *trans*-[Co(acac)$_2$(PR$_n$Ph$_{3-n}$)$_2$]$^+$ the methine signal of acac shows a remarkable high field shift as the number of phenyl groups on the phosphorus atom increases. The methyl signal also shows the same high field shift, but the extent of shift is not so large as that of the methine signal. As suggested in our previous papers,2,15) the high field shift of these protons can be attributed to a shielding effect by the ring current of phenyl groups of the phosphine ligand located over the acac ring. No such remarkable high field shifts are observed for *cis*-[Co(acac)$_2$(PR$_n$Ph$_{3-n}$)$_2$]$^+$ (n=1, 2). In a previous paper, we examined the crowded structure of *cis*-[Co(acac)$_2$(PMe$_2$Ph)$_2$]$^+$ with molecular models, and suggested a structure where the methyl proton (s) of PMe$_2$Ph is placed over the acac ring. This structure is supported by the fact that the chemical shift of the methine proton is very similar to that in *cis*-[Co(acac)$_2$(PMe$_3$)$_2$]$^+$. A similar structure can be assigned to other PR$_2$Ph complexes of this type (R=Et, Pr, Bu), since all methine proton signals of these complexes and *cis*-[Co(acac)$_2$(PR$_3$)$_2$]$^+$ (R=Et, Pr, Bu) are observed at nearly the same position. The methine signals of *cis*-[Co(acac)$_2$(PRPh$_2$)$_2$]$^+$ shift to a high field compared with those of the PR$_3$ and PR$_2$Ph complexes, but the magnitudes of shift are much smaller than those observed in the corresponding trans isomers. Thus the PRPh$_2$ complexes would also have a structure similar to that of the PR$_2$Ph complexes; the R group is located over the acac ring.

In contrast to *trans*-[Co(acac)$_2$(PR$_n$Ph$_{3-n}$)$_2$]$^+$ (n=0, 1, 2), *trans*-[Co(acac)$_2$(H$_2$O)(PR$_n$Ph$_{3-n}$)]$^+$ (n=0, 1, 2) show a very small high field shift in the methine signals, although both types of complex are similar and have the phosphine ligand at the apical site to the plane formed by two acac ligands. In these aqua complexes, the two acac chelate rings might not be planar, but bent toward the small aqua ligand to release the crowding with the bulky phosphine ligand as have been observed for *trans*-[Co(DH)$_2$(Cl)($\boldsymbol{P}$)] ($\boldsymbol{P}$=PBu$_3$6), PPh$_3$7), PCy$_3$8)). Accordingly, the methine proton would not be effectively shielded by the phenyl group to give a very small high field shift. The same explanation can be offered for the small high field shift of the methine signals in *trans*-[Co(acac)$_2$(L)(PMe$_2$Ph)]$^{n+}$ (L=NH$_3$, CH$_3$NH$_2$,py, NCS$^-$). Both methine and methyl signals of *trans*(P,P)-[Co(acac)(CN)$_2$(PR$_n$Ph$_{3-n}$)$_2$] (n=0, 1, 2) are observed at a remarkably high field compared with those of the corresponding PR$_3$ complexes. The magnitudes of shift, in particular those in the PR$_2$Ph complexes are even larger than those observed in *trans*-[Co(acac)$_2$(PR$_n$Ph$_{3-n}$)$_2$]$^+$ (n=0, 1, 2). As stated previously, these dicyano complexes are quite stable to solvolysis, and hence the Co^{III}–P bonds would be stronger and shorter than those in *trans*-[Co(acac)$_2$(PR$_n$Ph$_{3-n}$)$_2$]$^+$ which rapidly undergo solvolysis. The large high field shift might be caused by such strong coordination of the PR$_n$Ph$_{3-n}$ (n=0, 1, 2) ligands at the apical position.

Absorption Spectra. In Fig. 2 are shown absorption spectra of PPr$_n$Ph$_{3-n}$ complexes of the types, *trans*- and *cis*-[Co(acac)$_2$($\boldsymbol{P}$)$_2$]$^+$, *trans*-[Co(acac)$_2$(H$_2$O)($\boldsymbol{P}$)]$^+$, and *trans*(P,P)-[Co(acac)(CN)$_2$($\boldsymbol{P}$)$_2$]. The spectral patterns remain almost unchanged by changing the kind of alkyl groups. Tables 1—3 list the data of absorption bands observed in the low energy region.

All of *trans*-[Co(acac)$_2$(PR$_n$Ph$_{3-n}$)$_2$]$^+$ show a very

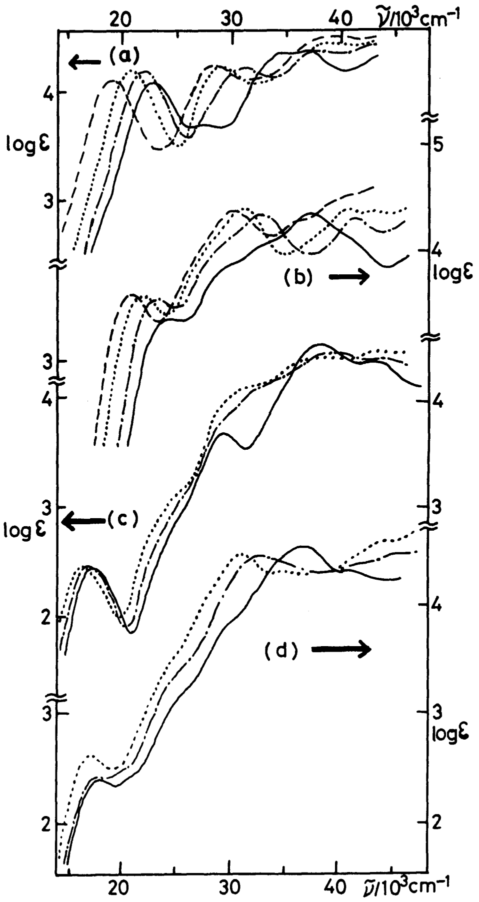

Fig. 2. Absorption spectra of a) *trans*-$[Co(acac)_2(\boldsymbol{P})_2]^+$ b) *trans*(P,P)-$[Co(acac)(CN)_2(\boldsymbol{P})_2]$, c) *trans*-$[Co(acac)_2(H_2O)(\boldsymbol{P})]^+$, d) *cis*-$[Co(acac)_2(\boldsymbol{P})_2]^+$ where denote PPr_3 (——), PPr_2Ph (–·–·–), $PPrPh_2$ (······), and PPh_3 (----).

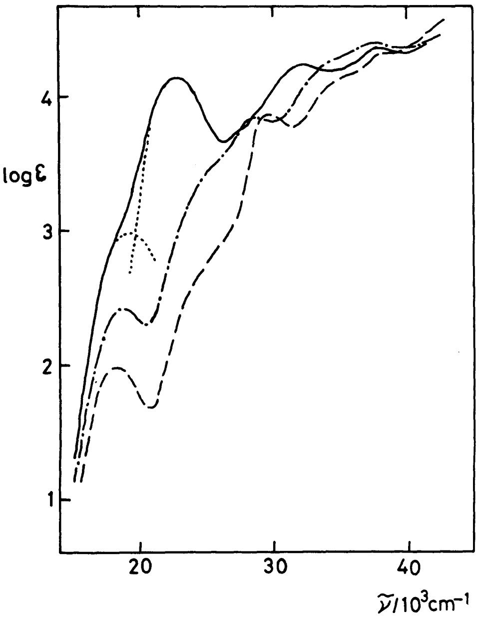

Fig. 3. Absorption spectra of *trans*-$[Co(acac)_2(PMe_2Ph)_2]^+$ (——), *trans*-$[Co(acac)_2(CH_3NH_2)(PMe_2Ph)]^+$ (–·–·–), and *trans*-$[Co(acac)_2(CH_3NH_2)_2]^+$ (-----).

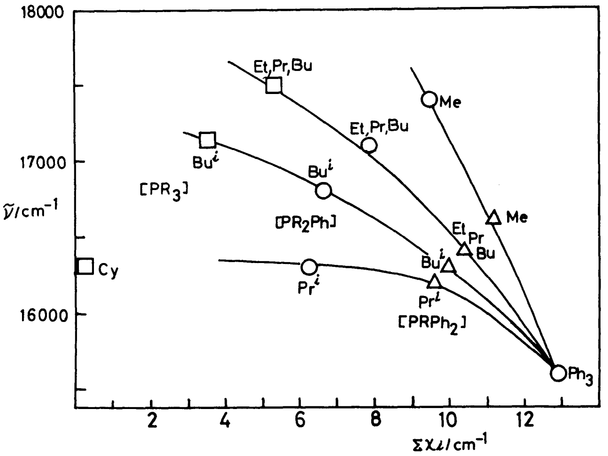

Fig. 4. Plots of the first absorption band(cm^{-1}) of *trans*-$[Co(acac)_2(H_2O)(\boldsymbol{P})]^+$ *vs*. Tolman's substituent additivity value, $\sum\chi i(cm^{-1})$ of the phosphine ligand.

strong band in the 19000—23000 cm^{-1} region. Because of the strong intensity, these bands may be assigned to a charge transfer transition. However, no such low energy, strong bands are observed in the phosphine complexes of other types studied here. The bands shift largely to the low energy side as the number of phenyl groups in PR_nPh_{3-n} increases. The first absorption band of the complexes is almost hidden by this strong band, but the shoulders in the lowest energy region observed in the PR_3 and PR_2Ph complexes can be assigned to a part of the first absorption band. The spectra of a series of *trans*-$[Co(acac)_2(CH_3NH_2)_n(PMe_2Ph)_{2-n}]^+$ (n=0, 1, 2) given in Fig. 3 show more clearly that *trans*-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ has the first absorption band on the low energy side of the strong band. Neither *cis*-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ nor *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$ exhibit such a strong band in the low energy region. The complexes show a band of medium intensity in this region, which can be assigned to the first absorption band from a comparison with the spectra shown in Fig. 3 and those of *cis*-$[Co(acac)_2(CN)_n(PMe_3)_{2-n}]^{(1-n)+}$ (n=0, 1, 2).[2] The *trans*-(P,P)-$[Co(acac)(CN)_2(PR_nPh_{3-n})_2]$ complexes give a fairly strong band in the 21000—24000 cm^{-1} region. These bands may be assigned to the first absorption band, since the $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH_2CH_2CH_2PPh_2$ complexes of the *cis*-$[Co(acac)(CN)_2(diphosphine)]$ type also show a similar band in this region with a little smaller intensity of $\log\varepsilon=3.03$ and 3.12, respectively. It has been reported that the first absorption band of *trans*(P,P)-phosphine complexes is always stronger than that of the corresponding cis(P,P) isomers.[2] The same relation is seen between the first absorption bands of *trans*- and *cis*-$[Co(acac)_2(PR_nPh_{3-n})_2]^+$ shown in Fig. 2a and 2d. In the higher energy region, all of the complexes show complicated spectra, and no clear assignment can be made at present.

In Fig. 4 are plotted the absorption maxima of the first bands of *trans*-$[Co(acac)_2(H_2O)(PR_nPh_{3-n})]^+$ *vs*. Tolman's parameters, $\sum\chi i$ (electronic effect) for the

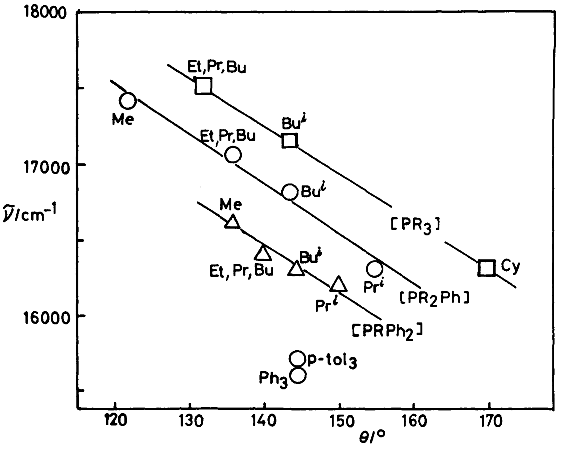

Fig. 5. Plots of the first absorption band(cm^{-1}) of *trans*-[Co(acac)$_2$(H$_2$O)(***P***)]$^+$ *vs*. Tolman's cone angle (θ°) of the phosphine ligand.

phosphine ligands. In general, the absorption maxima shift to high energy with decreasing the value of $\sum \chi i$ (increasing basicity). However, the extent of shift depends clearly on the kind of R on PR$_n$Ph$_{3-n}$; the more bulky the R group becomes, the smaller the extent of shift arises. The PCy$_3$ ligand is much more basic than PPr$^i_2$Ph, but the former is more bulky (Tolman's cone angle: 170°) than the latter (155°), and consequently the complexes of these two phosphines show the first absorption band at nearly the same position. Of the phosphines, four PBu^i_nPh$_{3-n}$ (n=0, 1, 2, 3) have a similar cone angle (*ca*. 145°). Hence the line connecting the points of these phosphines in Fig. 4 would show the electronic effect of phosphines with a constant cone angle (*ca*. 145°) on the first absorption bands of *trans*-[Co(acac)$_2$(H$_2$O)(PR$_n$Ph$_{3-n}$)]$^+$. The complexes with a less bulky phosphine and those with a more bulky one than PB^i_nPh$_{3-n}$ give the first absorption band at higher and lower energy, respectively, than values on the line, when the phosphine has the same $\sum \chi i$ value as that of PBu^i_nPh$_{3-n}$.

Figure 5 shows a plot of the first absorption maxima *vs*. Tolman's cone angles(θ°) (steric effect) for phosphine ligands in the same *trans*-[Co(acac)$_2$(H$_2$O)-(PR$_n$Ph$_{3-n}$)]$^+$ complexes. Good linear relations are seen between the absorption maxima and each group of phosphines, PR$_3$, PR$_2$Ph, and PRPh$_2$, *i.e.*, for each group of phosphines, the absorption maxima shift linearly to lower energy with an increase in cone angle of the phosphine ligand. As stated previously, four PBu^i_nPh$_{3-n}$ have a similar cone angle. The energy difference in absorption maxima of these phosphine complexes should come from the difference in basicity of the phosphines. Thus Figs. 4 and 5 clearly demonstrate that the ligand field strength of phosphines to the Co$^{\text{III}}$ ion is dependent not only on the basicity but also on the bulkiness strongly. Similar dependence is seen for the lowest energy bands of the *trans*(P,P)-[Co(acac)(CN)$_2$(PR$_n$Ph$_{3-n}$)$_2$] complexes.

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References

1) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).

2) K. Kashiwabara, K. Katoh, T. Ohishi, J. Fujita, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **55**, 149 (1982).

3) L. Maier, "Organic Phosphorus Compounds," ed by L. Maier and G. M. Kosolapott, Wiley, New York (1972), Vol. 1, p. 1.

4) *Inorg. Synth.*, **5**, 188 (1957).

5) *Inorg. Synth.*, **11**, 83 (1968).

6) N. Bresciani-Pahor, M. Calligaris, and L. Randaccio, *Inorg. Chim. Acta*, **39**, 173 (1980).

7) S. Brückner and L. Randaccio, *J. Chem. Soc., Dalton*, **1974**, 1017.

8) N. Bresciani-Pahor, M. Calligaris, L. Randaccio, and L. G. Marzilli, *Inorg. Chim. Acta*, **32**, 181 (1979).

9) F. A. Cotton, D. J. Darensbourg, S. Klein, and B. W. S. Kolthammer, *Inorg. Chem.*, **21**, 2661 (1982).

10) L. M. Ounapu, J. A. Mosbo, J. M. Risley, and B. N. Storhoff, *J. Organomet. Chem.*, **194**, 337 (1980).

11) B. P. Cotosoradis and R. D. Archer, *Inorg. Chem.*, **6**, 800 (1967); **4**, 1584 (1965).

12) L. J. Boucher, C. G. Coe, and D. R. Herrington, *Inorg. Chim. Acta*, **11**, 123 (1974).

13) L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

14) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York (1967).

15) K. Kashiwabara, I. Kinoshita, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **54**, 725 (1981).