Syntheses and Crystal Structures of Bis(dimethyldithiocarbamato)-(4,6-diphenyl-4,6-diphosphanonane-1,9-diammonium)cobalt(III) and Chloro(4,9-diphenyl-4,9-diphosphadodecane-1,12-diamine)nickel(II) Complexes

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The reaction of tetramethylthiuram disulfide with a methanol solution containing $CoCl_2 \cdot 6H_2O$ and 4,6-diphenyl-4,6-diphosphanonane-1,9-diamine (313NPPN) gave complexes of $[Co(dtc)_2\{rac(P)$- or $meso(P)$-313HNPPNH$\}]^{3+}$ (313HNPPNH=diprotonated form of 313NPPN, dtc=dimethyldithiocarbamate ion). The crystal structure of the perchlorate salt of the $meso(P)$ isomer was determined by X-ray analysis. Crystal data: monoclinic, $P2_1/c$, $a = 10.789(2)$, $b = 30.325(9)$, $c = 12.888(2)$ Å, $\beta = 102.06(1)°$, $V = 4123(1)$ Å^3, $D_x = 1.55$ g cm^{-3}, $Z = 4$, and $R = 0.077$ for 3347 reflections. The 313HNPPNH ligand in the complex coordinates to the Co(III) center through two phosphorus atoms as a didentate four-membered chelate ligand. The crystal structure of $[Co(dtc)_2\{NH_2(CH_2)_3P(CH_2OH)(C_6H_5)\}]B(C_6H_5)_4$, which formed as a by-product in the preparation of the above Co(III)–313HNPPNH complexes, was also determined. Crystal data: triclinic, $P\bar{1}$, $a = 13.817(2)$, $b = 15.277(3)$, $c = 10.737(2)$ Å, $\alpha = 109.90(1)$, $\beta = 94.14(2)$, $\gamma = 101.00(1)°$, $V = 2068.8(7)$ Å^3, $D_x = 1.31$ g cm^{-3}, $Z = 2$, and $R = 0.053$ for 4303 reflections. $[NiCl\{rac(P)$-343NPPN$\}]PF_6$ (343NPPN=4,9-diphenyl–4,9-diphosphadodecane-1,12-diamine) was prepared by the reaction of 343NPPN with $NiCl_2 \cdot 6H_2O$, and the crystal structure was determined. Crystal data: monoclinic, $P2_1/n$, $a = 8.367(2)$, $b = 24.058(2)$, $c = 13.988(2)$ Å, $\beta = 106.17(1)°$, $V = 2704(1)$ Å^3, $D_x = 1.54$ g cm^{-3}, $Z = 4$, and $R = 0.053$ for 3043 reflections. The geometry of the complex is a distorted square pyramid with a chloride ion at the apical position, and the 343NPPN ligand functions as a tetradentate chelate ligand.

The chemistry of polydentate tertiary phosphine ligands has been an area of active research interest, because chiral phosphorus atoms in those ligands are very stable for inversion (racemization) and such ligands undergo various novel and stereoselective reactions with their metal complexes.[1,2] With the view to revealing the characteristics of chiral phosphorus groups, we have also had an interest in linear tetradentate diphosphine ligands having hybrid donor atom sets such as PNNP,[3] NPPN,[4—6] and SPPS,[7] and have found that these hybrid ligands generate different coordination behaviors from those of the corresponding tetradentate tetramine analogues in their cobalt(III) complexes, and the coordination modes greatly depend on the absolute configuration of the chiral phosphorus atoms. As an extension of our previous work[6] on $NH_2(CH_2)_3P(C_6H_5)(CH_2)_nP(C_6H_5)(CH_2)_3NH_2$ ($n = 2$: 323NPPN, $n = 3$: 333NPPN), we report here the preparation and structural characterization of metal complexes of new hybrid ligands 313NPPN and 343NPPN ($n = 1$ and 4 in the above formula) to examine the complexation ability and coordination modes of these ligands. One of the features of the ligands is to involve four- and seven-membered chelate rings, respectively, in complexation to one metal through two central phosphorus atoms. There are only a few metal complexes of ligands bearing such $n1n$- or $n4n$-type ($n = 2$ or 3) skeltons, e.g., $[Rh_2(norbornadiene)_2\{(Et_2P(CH_2)_2PPh)_2CH_2\}](BF_4)_2$ (an excellent hydroformylation catalyst),[8] $[Ni_2Cl_4\{(Et_2P(CH_2)_2PPh)_2CH_2\}]$,[9] and $[Cu\{NH_2(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2\}](ClO_4)_2$[10] although the former two complexes are dimers. For hybrid donor linear C_2-tetradentates, to our knowledge, 313NPPN and 343NPPN are the first examples of a ligand forming four- and seven-membered chelate rings, respectively, in complexation. This paper is concerned with the preparation and structural characterization of $[Co(dtc)_2\{rac(P)$- or $meso(P)$-313HNPPNH$\}]^{3+}$ (313HNPPNH=diprotonated form of 313NPPN, dtc=dimethyldithiocarbamate ion) and $[NiCl\{rac(P)$-343NPPN$\}]PF_6$.

Experimental

The phosphine ligands 313NPPN and 343NPPN were prepared and handled under an atmosphere of nitrogen using Schlenk techniques until their cobalt(III) and Ni(II) complexes formed. All of

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the solvents used for the preparation were made oxygen-free by bubbling with nitrogen immediately before use. Absorption and ^1H and ^{13}C NMR spectra were recorded on a Hitachi U-3400 spectrophotometer and an R-90H spectrometer, respectively.

Preparation of 313NPPN and 343NPPN. To a liquid ammonia solution (100 cm^3) of sodium metal pieces (0.46 g, 20 mmol) was added (3-aminopropyl)phenylphosphine[6] (3.0 g, 18 mmol) dropwise with stirring at −78 °C and the soluthion was then stirred for a further 3 h. To the solution was added dichloromethane (0.85 g, 10 mmol) or 1,4-dichlorobutane (1.27 g, 10 mmol) dropwise from a syringe. The solution was stirred for another 3 h, changing in color from orange to colorless. Liquid ammonia was evaporated with stirring at room temperature. To the residue were added water (50 cm^3) and diethyl ether (200 cm^3) with stirring. The ethereal layer was separated from the aqueous layer and dried over Na_2SO_4 (5 g) overnight. The solvent was evaporated under vacuum, leaving a colorless oily product. Yield: 2.1 g and 3.1 g for crude oily 313NPPN and 343NPPN, respectively, which were used for preparing metal complexes without further purification.

Preparation of Cobalt(III) Complexes. To a methanol solution (40 cm^3) containing $CoCl_2 \cdot 6H_2O$ (0.68 g, 2.85 mmol) and crude 313NPPN (1.0 g, 2.9 mmol) was added a dichloromethane solution (10 cm^3) of tetramethylthiuram disulfide (0.35 g, 1.45 mmol) dropwise with stirring. The solution was stirred at room temperature overnight to yield a red-brown solution, and then evaporated to dryness. The residue was washed with diethyl ether to remove green [Co(dtc)$_3$] and then dissolved in water (3 dm^3). The aqueous solution was applied to a column (ϕ 3 cm×120 cm) of SP-Sephadex C-25 (Na^+-form). The adsorbed products were eluted with an aqueous 0.1 mol dm^{-3} NaCl solution, affording a minor brown band first and two slowly developing major red bands. To the eluate of the brown band was added an aqueous solution of $NaB(C_6H_5)_4$, yielding a brown precipitate (complex **1**). The precipitate was recrystallized from acetone and water. Yield: ca. 0.1 g (ca. 5%). Anal. Found: C, 58.91; H, 5.96; N, 5.16%. Calcd for $C_{40}H_{48}N_3BOPS_4Co$=[Co(dtc)$_2${$NH_2(CH_2)_3P(CH_2OH)(C_6H_5)$}]$B(C_6H_5)_4$: C, 58.89; H, 5.93; N, 5.15%. The crystal was subjected to X-ray analysis. The complex is soluble in methanol, acetone, chloroform, or dichloromethane, but not soluble in water or diethyl ether.

After the elution of the first brown band (complex **1**), two slowly developing major red bands were eluted with an aqueous 0.5 mol dm^{-3} NaCl solution. To each eluate of the two red bands was added an aqueous solution of $NaB(C_6H_5)_4$, yielding red-brown precipitates (complexes **2** and **3** in the elution order). The precipitates were recrystallized from methanol and water. Each yield for complexes **2** and **3**: ca. 0.3 g (ca. 10%). Anal. Found for complex **2**: C, 63.34; H, 5.72; N, 3.81%. Calcd for $C_{73}H_{82}N_4B_2NaP_2S_4Cl_2Co$=[Co(dtc)$_2$(313HNPPNH)]{$B(C_6H_5)_4$}$_2$· Cl·NaCl: C, 63.53; H, 5.99; N, 4.06%. Found for complex **3**: C, 65.64; H, 6.07; N, 3.90%. Calcd for $C_{73}H_{84}N_4B_2OP_2S_4ClCo$=[Co(dtc)$_2$(313HNPPNH)]{$B(C_6H_5)_4$}$_2$·Cl·$H_2O$: C, 65.45; H, 6.32; N, 4.18%. The complexes are soluble in methanol or acetone, but not soluble in water, dichloromethane, chloroform, or diethyl ether.

Preparation of [NiCl(343NPPN)]PF_6. To a methanol solution (30 cm^3) of $NiCl_2 \cdot 6H_2O$ (0.90 g, 3.8 mmol) was added a methanol solution (30 cm^3) of 343NPPN (1.5 g, 3.9 mmol) dropwise and the solution was stirred for a further 30 min. The resulting deep red solution was evaporated under reduced pressure to ca. 20 cm^3 and then applied to a column (ϕ 4.5 cm×40 cm) of Toyopearl HW-40. The adsorbed products were developed with methanol, affording two major red bands. The eluate of the first red band was mixed with a methanol solution of excess NH_4PF_6. The solvent was slowly evaporated at room temperature in air, yielding red crystals. The crystals were found to be [NiCl{*rac*(*P*)-343NPPN}]PF_6 by X-ray analysis (vide post). Yield: 0.35 g (15%). Anal. Found: C, 42.67; H, 5.78; N, 4.32%. Calcd for $C_{22}H_{34}N_2F_6P_3ClNi$: C, 42.11; H, 5.46; N, 4.46%. The complex is soluble in methanol, acetonitrile, acetone, nitromethane or *N*,*N*-dimethylformamide, but not soluble in water or diethyl ether.

The complex of the second red band could not be isolated even with various counter anions because of the oily propensity, and it may be the complex containing *meso*(*P*)-343NPPN.

Crystal Structure Determinations. [Co(dtc)$_2$(313HNPPNH)]-{$B(C_6H_5)_4$}$_2$·Cl·H_2O (complex **3**) was converted into the perchlorate as follows. Complex **3** was stirred with QAE-Sephadex A-25 (ClO_4^- form) in methanol and water (3 : 1) at room temperature overnight and filtered. The filtrate was adjusted to pH ca. 4 with $HClO_4$ and then allowed to stand at room temperature to afford red crystals, one of which was used for X-ray analysis. The crystal data and refinement information are listed in Table 1 together with those for [NiCl(343NPPN)]PF_6 and complex **1**.

The X-ray intensities were measured using graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71073 Å) on Rigaku AFC-5R (for the perchlorate of complex **3** and [NiCl(343NPPN)]PF_6) and AFC-5 (for complex **1**) four-circle diffractometers at 23 °C. Absorption corrections were not applied, since the linear absorption coefficient for each compound was relatively low (μ(Mo $K\alpha$)≤1.1 mm^{-1}). The structures were solved by the usual heavy-atom method. All non-hydrogen atoms were refined anisotropically. H atoms, which were introduced at the positions located by difference Fourier syntheses or calculated theoretically, were included in the structure factor calculations. The calculations were carried out on a Fujitsu S-4/IX workstation using the Xtal 3.2[11] program package. The atomic parameters are listed in Tables 2, 3, and 4. Tables of the coordinates of hydrogen atoms, the anisotropic thermal parameters of non-hydrogen atoms, the bond lengths and angles, and the observed and calculated structure factors are kept as Document No. 69037 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

In our previous paper,[6] we reported on the preparation of a large number of new cobalt(III)–323NPPN and –333NPPN complexes mixed with 2,4-pentanedionate (acac) or oxalate (ox) ligand. In order to extend the study with a variety of chelate rings, we have tried to prepare metal complexes of new ligands, 313NPPN and 343NPPN. Although we have failed to prepare mixed-ligand cobalt(III) complexes containing 313NPPN or 343NPPN and acac or ox ligands, the [Co(dtc)$_2${*rac*(*P*)- or *meso*(*P*)-313HNPPNH}]$^{3+}$ complexes were readily isolated from the reaction mixture of $CoCl_2 \cdot 6H_2O$, 313NPPN, and tetramethylthiuram disulfide, in which 313HNPPNH is a diprotonated form of 313NPPN and acts as a didentate ligand through two phosphorus atoms. For 343NPPN, several attempts failed to isolate and characterize cobalt(III)–343NPPN complexes; the reaction solutions afforded a mixture of too many products which could not be separated by column chromatography. On the other hand, [NiCl{*rac*(*P*)-343NPPN}]PF_6 was isolated and structurally determined by X-ray analysis, in which 343NPPN functions as a tetradentate ligand. Although the reaction of

Table 1. Crystal Data and Refinement Information of the Complexes

Compound	[Co(dtc)$_2${*meso*(*P*)-313HNPPNH}](ClO$_4$)$_3$·H$_2$O	[NiCl{*rac*(*P*)-343NPPN}]PF$_6$	[Co(dtc)$_2${NH$_2$(CH$_2$)$_3$-PPh(CH$_2$OH)}]BPh$_4$
Chemical formula	$C_{25}H_{44}Cl_3CoN_4O_{13}P_2S_4$	$C_{22}H_{34}ClF_6N_2NiP_3$	$C_{40}H_{48}BCoN_3OPS_4$
Formula weight	964.12	627.58	815.82
Color	Red	Red	Red
Crystal size/mm^3	0.6 × 0.3 × 0.1	0.5 × 0.3 × 0.2	0.5 × 0.3 × 0.3
Temperature/°C	23	23	23
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Lattice group			
a/Å	10.789(2)	8.367(2)	13.817(2)
b/Å	30.325(9)	24.058(2)	15.277(3)
c/Å	12.888(2)	13.988(2)	10.737(2)
α/deg	90	90	109.90(1)
β/deg	102.06(1)	106.17(1)	94.14(2)
γ/deg	90	90	101.00(1)
V/Å^3	4123(1)	2704(1)	2068.8(7)
Z	4	4	2
D_x/Mg m^{-3}	1.55	1.54	1.31
μ(Mo $K\alpha$)/mm^{-1}	0.94	1.05	0.68
Reflns. measured	10427	8546	12370
R_{int}	0.021	0.017	0.011
Reflns. used for calculation[a)]	3347	3043	4303
No. of parameters refined	637	452	648
R[b)]	0.077	0.053	0.053
R_w[c)]	0.080	0.053	0.056
S[d)]	2.12(3)	1.41(2)	1.64(2)
$\Delta\rho$/e Å^{-3}	−1.22—1.32	−0.39—0.55	−0.45—0.63

a) $|F_o| > 3\sigma(|F_o|)$. b) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. c) $R_w=(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ ($w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$).
d) $S=(\Sigma w(|F_o|-|F_c|)^2)^{1/2}/(n_{data}-n_{par})$.

313NPPN with $NiCl_2·6H_2O$ in methanol gave a solution with a color change from pale green to red, the red complex could not be obtained because of instability during the cource of the isolation. The characterization and structural features of the isolated Co(III) and Ni(II) complexes containing 313NPPN and 343NPPN, respectively, are given below.

Cobalt(III) Complexes. Oxidation of a solution containing 313NPPN and $CoCl_2·6H_2O$ by tetramethylthiuram disulfide gave complexes of [Co(dtc)$_2${*rac*(*P*)- or *meso*(*P*)-313HNPPNH}]$^{3+}$ (complexes **2** and **3** in the Experimental section) as major products. The column chromatography of the reaction solution gave no indication of the formation of [Co(dtc)(313NPPN)]$^{2+}$ where 313NPPN functioned as a tetradentate ligand. The perchlorate of complex **3** was obtained by acidifying with $HClO_4$ and the crystal was subjected to X-ray analysis.

A perspective view of the complex cation in the perchlorate of complex **3** is shown in Fig. 1. The selected bond lengths and angles are listed in Table 5. The Co atom is coordinated by four sulfur and two phosphorus atoms in a slightly distorted octahedron. The 313HNPPNH ligand, which is a diprotonated form of 313NPPN, acts as a didentate diphosphine ligand forming a four-membered chelate ring. The P–Co–P angle (74.8(1)°) is nearly equal to those (av 74.3(2)°) in [Co(dtc)(dmpm)$_2$](BF$_4$)$_2$[12] (dmpm=bis(dimethylphosphino)methane) where dmpm is a four-membered chelate ring. The large deviation from 90° may enforce the 313NPPN ligand to act as, not a tetradentate, but a didentate ligand. The geometries around P(1), P(2), and C(4) are also fairly distorted from a tetrahedron. The Co–P bond lengths (2.193(4) and 2.215(4) Å) are almost equal to that (2.205(1) Å) in [Co(S$_2$COC$_2$H$_5$)$_2$(dmpe)]$^+$ (dmpe=1,2-bis(dimethylphosphino)ethane)[13] in which dmpe is a five-membered chelate ligand. Most of the Co–P bond lengths in Co(III)–phosphine complexes are in the range 2.22—2.30 Å.[14] The Co–P bonds in complex **3** are slightly shorter than these values, probably because of the steric advantage of the two small dtc ligands.

The geometries of the dtc moieties in complex **3** are usual. The S–Co–S angles (av 74.2°) are almost equal to that (75.97(9)°) in [Co(dtc)(dmpm)$_2$](BF$_4$)$_2$,[12] and those (av 76.4°) in [Co(dtc)$_3$].[15] The Co–S(2) and Co–S(4) bond lengths in complex **3** (av 2.289 Å) are similar to those (av 2.286 Å) in [Co(dtc)(dmpm)$_2$](BF$_4$),[12] these bonds being *trans* to phosphorus, and slightly longer than those in [Co(dtc)$_3$] (av 2.264 Å) and [Co(dtc)(en)$_2$]$^{2+}$ (av 2.263 Å).[16] The elongation in the phosphine complexes is due to the strong *trans* influence of the phosphino group.

The two asymmetric phosphorus atoms in complex **3** take the opposite configuration, i.e. a *meso*(*P*) configuration. The ^{1}H NMR spectrum of complex **3** chloride obtained from the eluate in the column chromatographic separation exhibits four singlet peaks (δ = 2.57, 2.97, 3.31, and 3.40 in CD$_3$OD) for N–CH$_3$ of dtc, which is consistent with the geometry of

Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (U_{eq}[a)]) of [Co(dtc)$_2${*meso*(*P*)-313HNPPNH}](ClO$_4$)$_3$·H$_2$O

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Co	0.1718(1)	0.57665(5)	0.6852(1)	0.0355(6)
Cl(1)	0.1174(4)	0.7824(2)	0.8049(4)	0.075(2)
Cl(2)	−0.3210(5)	0.6289(2)	0.9572(4)	0.087(2)
Cl(3)	−0.3723(7)	0.7105(3)	0.3173(6)	0.155(4)
S(1)	0.0766(3)	0.5123(1)	0.7118(3)	0.046(1)
S(2)	0.3378(3)	0.5284(1)	0.7344(3)	0.049(1)
S(3)	0.2984(3)	0.6284(1)	0.6318(3)	0.047(1)
S(4)	0.1505(3)	0.5633(1)	0.5081(3)	0.053(1)
P(1)	−0.0016(3)	0.6161(1)	0.6693(3)	0.038(1)
P(2)	0.1787(3)	0.6050(1)	0.8447(3)	0.037(1)
O(1)	0.164(1)	0.7918(4)	0.9124(9)	0.108(6)
O(2)	0.146(3)	0.7435(6)	0.774(1)	0.27(2)
O(3)	0.004(2)	0.792(1)	0.775(1)	0.31(2)
O(4)	0.178(2)	0.8054(7)	0.745(1)	0.24(1)
O(5)	−0.366(1)	0.6486(4)	1.0432(9)	0.100(6)
O(6)	−0.411(1)	0.6288(9)	0.866(1)	0.25(1)
O(7)	−0.212(1)	0.6480(6)	0.946(1)	0.19(1)
O(8)	−0.293(3)	0.5873(6)	0.975(2)	0.27(2)
O(9)	−0.408(1)	0.7339(4)	0.398(1)	0.136(7)
O(10)	−0.472(1)	0.6934(5)	0.245(1)	0.136(7)
O(11)	−0.285(3)	0.671(1)	0.362(3)	0.40(3)
O(12)	−0.302(2)	0.7398(6)	0.275(1)	0.22(1)
O(13)	0.552(1)	0.7096(7)	0.678(1)	0.22(1)
N(1)	−0.212(2)	0.7710(7)	0.568(2)	0.095(9)
N(2)	0.330(2)	0.7433(6)	1.090(1)	0.071(7)
N(3)	0.247(1)	0.4469(4)	0.752(1)	0.064(5)
N(4)	0.321(1)	0.6122(4)	0.4310(9)	0.062(5)
C(1)	−0.114(2)	0.7404(5)	0.549(1)	0.065(7)
C(2)	−0.124(1)	0.6967(5)	0.604(1)	0.049(6)
C(3)	−0.013(1)	0.6667(5)	0.593(1)	0.052(6)
C(4)	0.024(1)	0.6315(5)	0.809(1)	0.048(6)
C(5)	0.292(1)	0.6489(5)	0.890(1)	0.050(6)
C(6)	0.267(1)	0.6752(5)	0.985(1)	0.056(6)
C(7)	0.368(2)	0.7108(6)	1.014(1)	0.062(7)
C(8)	−0.157(1)	0.5896(4)	0.633(1)	0.036(4)
C(9)	−0.250(1)	0.5984(5)	0.690(1)	0.063(6)
C(10)	−0.368(1)	0.5775(6)	0.662(1)	0.069(7)
C(11)	−0.394(1)	0.5494(5)	0.578(1)	0.059(6)
C(12)	−0.301(1)	0.5410(5)	0.522(1)	0.067(7)
C(13)	−0.182(1)	0.5613(5)	0.549(1)	0.055(6)
C(14)	0.188(1)	0.5694(4)	0.958(1)	0.046(5)
C(15)	0.299(2)	0.5478(6)	0.999(1)	0.066(7)
C(16)	0.307(3)	0.5183(7)	1.084(2)	0.11(1)
C(17)	0.201(4)	0.5109(8)	1.126(2)	0.13(2)
C(18)	0.092(3)	0.5340(7)	1.087(2)	0.13(1)
C(19)	0.086(2)	0.5626(5)	1.004(1)	0.078(8)
C(20)	0.225(1)	0.4887(4)	0.737(1)	0.044(5)
C(21)	0.147(2)	0.4136(8)	0.747(3)	0.09(1)
C(22)	0.379(2)	0.4295(7)	0.774(3)	0.10(1)
C(23)	0.264(1)	0.6027(4)	0.510(1)	0.049(5)
C(24)	0.421(3)	0.6450(9)	0.441(3)	0.09(1)
C(25)	0.283(3)	0.588(1)	0.328(2)	0.10(1)

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (U_{eq}[a)]) of [NiCl{*rac*(*P*)-343-NPPN}]PF$_6$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Ni	0.6598(1)	0.59642(3)	0.59783(6)	0.0281(3)
Cl	0.3701(2)	0.54896(7)	0.5807(1)	0.0351(6)
P(1)	0.7902(2)	0.61258(7)	0.7523(1)	0.0315(6)
P(2)	0.5374(2)	0.67647(7)	0.5811(1)	0.0313(6)
P(3)	0.9027(3)	0.62917(9)	0.2718(2)	0.0489(8)
F(1)	1.0317(6)	0.6791(2)	0.2902(4)	0.070(2)
F(2)	0.9591(7)	0.6143(2)	0.3871(3)	0.097(3)
F(3)	0.7657(7)	0.6688(2)	0.2909(5)	0.099(3)
F(4)	0.8442(6)	0.6446(2)	0.1573(3)	0.082(2)
F(5)	1.0405(6)	0.5886(2)	0.2542(4)	0.091(3)
F(6)	0.7756(6)	0.5788(2)	0.2540(4)	0.087(2)
N(1)	0.7932(7)	0.5266(2)	0.6142(4)	0.031(2)
N(2)	0.6267(8)	0.5897(3)	0.4490(4)	0.036(2)
C(1)	0.975(1)	0.5350(3)	0.6241(5)	0.041(3)
C(2)	1.069(1)	0.5530(3)	0.7289(5)	0.044(3)
C(3)	1.0138(9)	0.6098(3)	0.7620(6)	0.043(3)
C(4)	0.773(1)	0.6792(3)	0.8126(6)	0.040(3)
C(5)	0.616(1)	0.6855(4)	0.8452(6)	0.046(3)
C(6)	0.4575(9)	0.6660(3)	0.7699(5)	0.038(3)
C(7)	0.4153(9)	0.6950(3)	0.6679(5)	0.040(3)
C(8)	0.377(1)	0.6836(3)	0.4627(5)	0.039(3)
C(9)	0.439(1)	0.6693(3)	0.3724(5)	0.045(3)
C(10)	0.475(1)	0.6066(3)	0.3692(5)	0.042(3)
C(11)	0.7593(8)	0.5624(3)	0.8433(5)	0.032(2)
C(12)	0.853(1)	0.5674(3)	0.9435(5)	0.049(3)
C(13)	0.823(1)	0.5304(4)	1.0144(6)	0.062(4)
C(14)	0.706(1)	0.4899(4)	0.9867(6)	0.057(4)
C(15)	0.613(1)	0.4846(4)	0.8875(6)	0.050(3)
C(16)	0.6386(9)	0.5209(3)	0.8164(6)	0.040(3)
C(17)	0.6790(8)	0.7334(3)	0.5765(5)	0.034(2)
C(18)	0.635(1)	0.7894(3)	0.5856(6)	0.045(3)
C(19)	0.745(1)	0.8318(4)	0.5804(6)	0.057(4)
C(20)	0.899(1)	0.8198(4)	0.5670(7)	0.063(4)
C(21)	0.943(1)	0.7648(4)	0.5555(7)	0.063(4)
C(22)	0.832(1)	0.7217(3)	0.5597(6)	0.050(3)

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

the *meso*(*P*) isomer. On the other hand, complex **2** shows an absorption spectrum quite similar to that of complex **3** and seems to be the *rac*(*P*) isomer. The ^{1}H NMR spectrum of complex **2** exhibits two singlet peaks (δ = 3.11 and 3.22) for N–CH$_3$ of dtc, indicating that complex **2** is one of two diastereomers possible for the *rac*(*P*) isomer, i.e. Λ and Δ isomers for an *SS*(*P*) or *RR*(*P*) configuration. We could not specify which diastereomer formed. Another diastereomer did not form under the reaction conditions described in the Experimental section.

A perspective view of the complex cation in complex **1** which was formed as a by-product in the preparation of complex **3** is shown in Fig. 2. The phosphine ligand in the complex is unexpected NH$_2$(CH$_2$)$_3$P(C$_6$H$_5$)(CH$_2$OH), which may be formed as a by-product in the preparation of the 313NPPN ligand by the reaction of CH$_2$Cl$_2$ with NaP(C$_6$H$_5$)-(CH$_2$)$_3$NH$_2$. The formation of complex **1** was reproducible in several attempts of preparing the Co(III)–313NPPN complex, the yield always being low (ca. 5%). Since the coordinating phosphorus atom is asymmetric, two diastereomers are possible (Δ and Λ isomers for an *R*(*P*) or *S*(*P*) configuration). Complex **1** is a $\Delta S(P)/\Lambda R(P)$ isomer as shown in

Table 4. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (U_{eq}[a)]) of $[Co(dtc)_2\{NH_2(CH_2)_3PPh(CH_2OH)\}]BPh_4$

Atom	x/a	y/b	z/c	U_{eq}
Co	0.21072(6)	0.11710(5)	0.25203(8)	0.0438(3)
S(1)	0.2081(1)	0.0494(1)	0.4101(2)	0.0588(8)
S(2)	0.0605(1)	0.0033(1)	0.1859(2)	0.0599(8)
S(3)	0.1815(1)	0.1904(1)	0.1062(2)	0.0511(7)
S(4)	0.1314(1)	0.2281(1)	0.3650(2)	0.0516(7)
P	0.3576(1)	0.2159(1)	0.3293(2)	0.0475(7)
O	0.5072(9)	0.2221(7)	0.495(1)	0.225(8)
N(1)	0.2770(5)	0.0191(4)	0.1338(7)	0.057(3)
N(2)	0.0418(5)	−0.0901(4)	0.3579(7)	0.073(3)
N(3)	0.1011(4)	0.3397(4)	0.2259(6)	0.059(3)
C(1)	0.3477(6)	0.0396(6)	0.0439(8)	0.065(4)
C(2)	0.4456(5)	0.1060(5)	0.1199(8)	0.065(4)
C(3)	0.4376(5)	0.2082(5)	0.2001(7)	0.054(3)
C(4)	0.3651(4)	0.3430(4)	0.4070(6)	0.052(3)
C(5)	0.3547(5)	0.3977(5)	0.3284(8)	0.064(3)
C(6)	0.3502(6)	0.4936(5)	0.388(1)	0.083(4)
C(7)	0.3583(7)	0.5331(6)	0.525(1)	0.100(5)
C(8)	0.3704(7)	0.4812(7)	0.602(1)	0.101(5)
C(9)	0.3716(6)	0.3848(6)	0.5451(8)	0.082(4)
C(10)	0.4083(6)	0.1851(7)	0.438(1)	0.048(3)
C(11)	0.0950(5)	−0.0226(4)	0.3222(7)	0.057(3)
C(12)	0.078(1)	−0.1066(9)	0.478(1)	0.095(6)
C(13)	−0.0519(8)	−0.1511(8)	0.276(1)	0.104(6)
C(14)	0.1320(4)	0.2639(4)	0.2312(6)	0.048(3)
C(15)	0.1139(9)	0.3705(9)	0.111(1)	0.085(5)
C(16)	0.0545(9)	0.3942(7)	0.334(1)	0.090(6)
C(17)	0.6992(4)	0.4170(4)	−0.0069(7)	0.051(3)
C(18)	0.7569(6)	0.4827(5)	0.1097(8)	0.065(3)
C(19)	0.7500(7)	0.5787(5)	0.1629(9)	0.082(4)
C(20)	0.6807(8)	0.6088(6)	0.098(1)	0.094(5)
C(21)	0.6215(7)	0.5468(6)	−0.019(1)	0.085(5)
C(22)	0.6310(6)	0.4522(5)	−0.0702(8)	0.065(4)
C(23)	0.8011(4)	0.3275(4)	−0.1765(6)	0.043(3)
C(24)	0.7792(6)	0.3101(5)	−0.3124(7)	0.059(3)
C(25)	0.8529(7)	0.3341(5)	−0.3874(8)	0.071(4)
C(26)	0.9492(7)	0.3746(5)	−0.328(1)	0.073(4)
C(27)	0.9736(6)	0.3950(5)	−0.1936(9)	0.064(4)
C(28)	0.9014(5)	0.3726(4)	−0.1207(7)	0.051(3)
C(29)	0.7606(4)	0.2678(4)	0.0316(6)	0.043(2)
C(30)	0.8392(5)	0.2211(4)	0.0189(7)	0.050(3)
C(31)	0.8675(6)	0.1802(4)	0.1097(7)	0.061(3)
C(32)	0.8172(6)	0.1859(5)	0.2174(8)	0.073(4)
C(33)	0.7380(6)	0.2305(5)	0.2340(7)	0.068(3)
C(34)	0.7126(5)	0.2721(5)	0.1425(6)	0.056(3)
C(35)	0.6193(4)	0.2273(4)	−0.1607(6)	0.048(3)
C(36)	0.5219(5)	0.2316(5)	−0.1332(7)	0.059(3)
C(37)	0.4403(6)	0.1558(6)	−0.1990(9)	0.075(4)
C(38)	0.4530(7)	0.0716(6)	−0.2945(9)	0.082(4)
C(39)	0.5476(7)	0.0649(6)	−0.3216(9)	0.076(4)
C(40)	0.6280(6)	0.1411(5)	−0.2577(7)	0.059(3)
B	0.7189(5)	0.3098(5)	−0.0792(7)	0.044(3)

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Fig. 2. The ^{1}H NMR spectrum of complex **1** exhibits three peaks for N–CH_3 of dtc (δ = 2.60, 2.89, and 3.31 (double intensity) in CD_3OD), indicating it contains one diastereomer. In the column chromatographic separation, a minor brown band was eluted just behind that of complex **1**. The yield of the brown complex was less than one-third that of complex **1**. Although we could not isolate the pure complex because of the low yield, the eluate of the minor brown band gives an absorption spectrum similar to that of complex **1** and the ^{1}H NMR spectrum exhibits four singlet peaks for N–CH_3 of dtc (δ = 3.13, 3.21, 3.26, and 3.31 in $CDCl_3$). It may be another diastereomer ($\Lambda S(P)/\Delta R(P)$) of complex **1**.

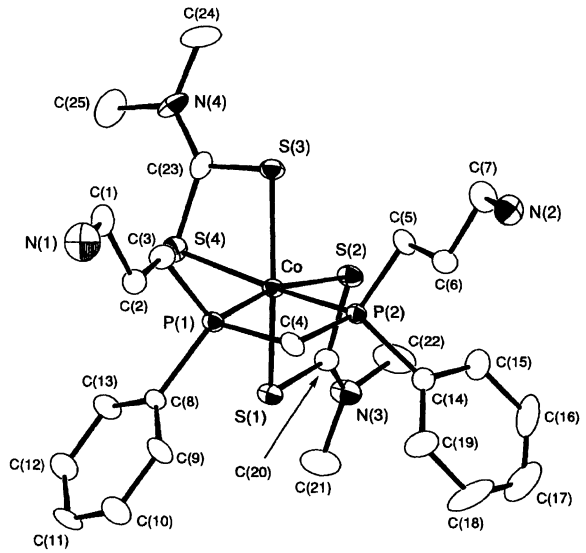

Fig. 1. Perspective drawing of the complex cation in $[Co(dtc)_2\{meso(P)\text{-}313HNPPNH\}](ClO_4)_3\cdot H_2O$.

The phosphine ligand in complex **1** is a didentate ligand having P and N donor atoms and forms a six-membered chelate ring with a chair conformation. The P–Co–N(1) angle (89.1(2)°) is nearly equal to the P–Co–N angles (89.4(1)° and 89.2(1)°) in *trans*(*Cl*,*Cl*)*cis*(*P*,*P*)-$[CoCl_2(NH_2(CH_2)_3PMe_2)_2]PF_6$[17] and to the N–Co–N chelate angles (av 91.0°) in $(-)_{589}$-$[Co(tn)_3]Cl_3\cdot H_2O$ (tn=1, 3-diaminopropane),[18] which are typical values for a six-membered chelate ring in Co(III) complexes.[19] The Co–P bond length (2.195(2) Å) is similar to those in complex **3** and is one of the shortest ones among many structurally determined cobalt(III)–phosphine complexes in our previous works (2.194—2.353 Å).[14] The Co–S(2) bond (2.325(2) Å) *trans* to phosphorus is remarkably longer than the others (av 2.261(2) Å) in complex **1**, due to the *trans* influence of the phosphino group, the difference between them (Δ = 0.064 Å) being fairly larger than the corresponding differences in the analogous $[CoS_4P_2]^+$-type complexes such as *cis*-$[Co(dtc)_2\{P(OCH_2)_3CC_2H_5\}_2]BF_4$ (Δ = 0.016 Å)[20] and $[Co(dtc)_2(dmpf)]BF_4$ (Δ = 0.026 Å; dmpf=1,1′-bis(dimethylphosphino)ferrocene).[21]

Ni(II) Complexes. From the reaction of $NiCl_2\cdot 6H_2O$ with 343NPPN was isolated $[NiCl\{rac(P)\text{-}343NPPN\}]PF_6$ (vide infra for the molecular structure). The corresponding *meso*(*P*)-343NPPN complex could not be isolated because of the oily prospensity even with various counter anions. The *rac*(*P*)-343NPPN complex is slightly unstable in solution, and decomposes gradually during rechro-

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

[Co(dtc)$_2$\{*meso*(*P*)-313HNPPNH\}](ClO$_4$)$_3$·H$_2$O

Co–S(1)	2.265(4)	Co–S(2)	2.297(4)	Co–S(3)	2.279(4)
Co–S(4)	2.282(4)	Co–P(1)	2.193(4)	Co–P(2)	2.215(4)

S(1)–Co–S(2)	72.2(1)	S(1)–Co–S(3)	163.4(1)
S(1)–Co–S(4)	92.6(1)	S(1)–Co–P(1)	94.6(1)
S(1)–Co–P(2)	97.0(1)	S(2)–Co–S(3)	92.3(1)
S(2)–Co–S(4)	94.2(1)	S(2)–Co–P(1)	166.8(2)
S(2)–Co–P(2)	96.8(1)	S(3)–Co–S(4)	76.2(1)
S(3)–Co–P(1)	98.6(1)	S(3)–Co–P(2)	96.1(1)
S(4)–Co–P(1)	95.6(1)	S(4)–Co–P(2)	166.9(1)
P(1)–Co–P(2)	74.8(1)		

[NiCl\{*rac*(*P*)-343NPPN\}]PF$_6$

Ni–P(1)	2.167(2)	Ni–P(2)	2.163(2)	Ni–N(1)	1.995(5)
Ni–N(2)	2.029(5)	Ni–Cl	2.629(2)		

Cl–Ni–P(1)	111.35(7)	Cl–Ni–P(2)	88.86(7)
Cl–Ni–N(1)	96.7(2)	Cl–Ni–N(2)	90.7(2)
P(1)–Ni–P(2)	92.28(7)	P(1)–Ni–N(1)	85.8(2)
P(1)–Ni–N(2)	157.6(2)	P(2)–Ni–N(1)	174.4(2)
P(2)–Ni–N(2)	92.0(2)	N(1)–Ni–N(2)	87.9(2)

[Co(dtc)$_2$\{NH$_2$(CH$_2$)$_3$PPh(CH$_2$OH)\}]BPh$_4$

Co–S(1)	2.268(2)	Co–S(2)	2.325(2)	Co–S(3)	2.268(2)
Co–S(4)	2.247(2)	Co–P	2.195(2)	Co–N(1)	2.022(6)

S(1)–Co–S(2)	72.24(7)	S(1)–Co–S(3)	167.78(8)
S(1)–Co–S(4)	93.11(8)	S(1)–Co–P	97.43(7)
S(1)–Co–N(1)	92.1(2)	S(2)–Co–S(3)	96.51(7)
S(2)–Co–S(4)	89.70(7)	S(2)–Co–P	173.42(9)
S(2)–Co–N(1)	89.3(2)	S(3)–Co–S(4)	76.84(7)
S(3)–Co–P	90.04(7)	S(3)–Co–N(1)	97.7(2)
S(4)–Co–P	92.47(6)	S(4)–Co–N(1)	174.3(2)
P–Co–N(1)	89.1(2)		

matography on Toyopearl HW-40. The reaction of Ni(ClO$_4$)$_2$·6H$_2$O with 343NPPN in methanol yielded the orange diamagnetic compound [Ni(343NPPN)](ClO$_4$)$_2$ (yield ca. 20%). (Anal. Found: C, 40.81; H, 5.26; N, 4.26%. Calcd for $C_{22}H_{34}N_2O_8P_2Cl_2Ni$: C, 40.90; H, 5.30; N, 4.34%). The geometry would be a square planar with the P_2N_2 donor atom set. The separation of two diastereomers due to *rac*(*P*) and *meso*(*P*) configurations was unsuccessful in similar procedures of column chromatography. The complex isolated by fractional crystallizations seemed to be [Ni\{*meso*(*P*)-343NPPN\}](ClO$_4$)$_2$ by an X-ray analysis, but the accuracy was poor (R=0.13). The ^{13}C NMR spectrum of the complex suggests that it consisted of one species, i.e. for the phenyl carbons: *o*-C, 134.4(t); *m*-C, 131.2(t); *p*-C, 134.1(s) ppm, for the methylene carbons: 42.5(s), 25.9(t), 23.9(t), 23.4(s), 23.1(s) ppm. The corresponding [Ni\{*rac*(*P*)-343NPPN\}]$^{2+}$ isomer could not be isolated as a pure compound.

A perspective view of [NiCl\{*rac*(*P*)-343NPPN\}]$^+$ is shown in Fig. 3. The selected bond lengths and angles are listed in Table 5. The Ni(II) ion forms a square pyramid, distorted to a trigonal bipyramid, with N_2P_2 donor atoms in the basal plane and a chloride ion at the apical position with a long Ni–Cl bond length. The chiralities of the coordinating phosphorus atoms are (*RR*/*SS*), i.e. a

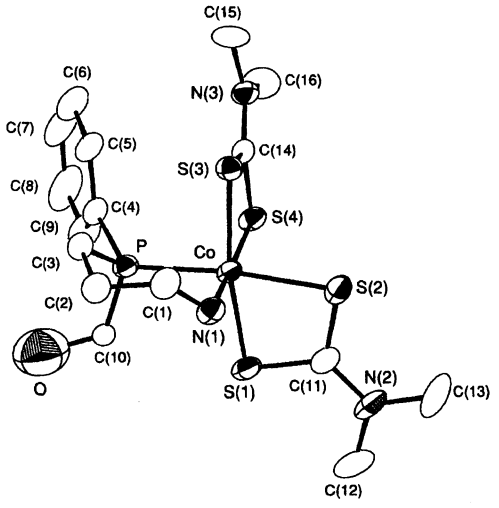

Fig. 2. Perspective drawing of the complex cation in [Co(dtc)$_2$\{NH$_2$(CH$_2$)$_3$PPh(CH$_2$OH)\}]BPh$_4$.

racemic(*P*) configuration. The seven-membered chelate ring forms a skew conformation and two six-membered ones are in a chair conformation (Fig. 3(b)). The bond lengths of Ni–P, Ni–N, and Ni–Cl in the complex are almost equal to those for [NiCl\{*meso*(*P*)-333NPPN\}]PF$_6$ (Ni–P: 2.178(4),

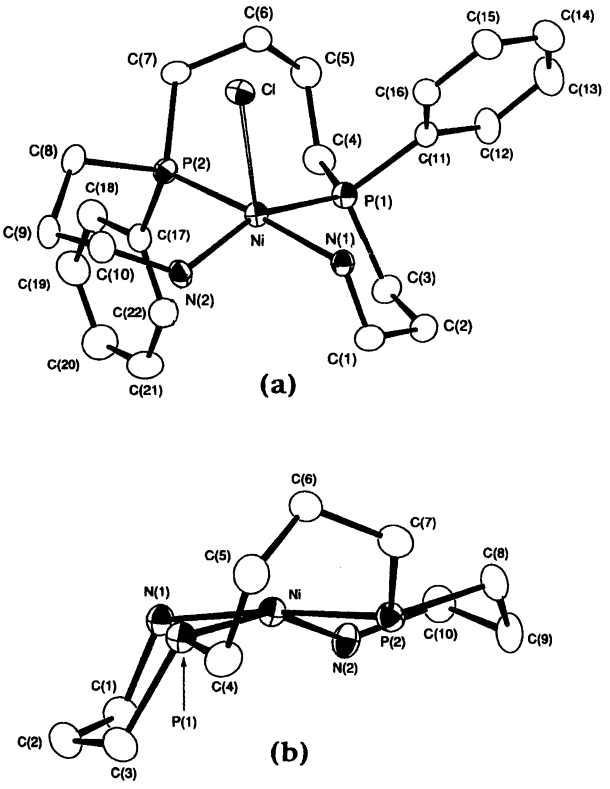

Fig. 3. (a) Perspective drawing of the complex cation in [NiCl{*rac*(*P*)-343NPPN}]PF_6. (b) Conformations of the six- and seven-membered 343NPPN chelate rings in [NiCl{*rac*(*P*)-343NPPN}]PF_6. Cl and phenyl rings are omitted for clarity.

2.168(4) Å; Ni–N: 2.006(10), 2.036(11) Å; Ni–Cl: 2.699(7) Å).[22] The ^{13}C NMR spectrum of [NiCl{*rac*(*P*)-343NPPN}]-PF_6 in CD_3NO_2 exhibits the signals of one kind of phenyl ring (*o*-C: 134.7(t), *m*-C: 130.7(t), *p*-C: 133.4(s) ppm) and five different methylene carbons (41.6(s), 30.0(t), 26.2(t), 24.3(s), and 23.9(s)), suggesting a rapid exchange of the apical chloride ion on the NMR time scale. This may be caused by the long Ni–Cl bond length. The distance between the Ni(II) atom and the best plane formed by the P_2N_2 donor atoms is 0.245(2) Å, which is appreciably longer than that (0.105(5) Å) for [NiCl{*meso*(*P*)-333NPPN}]$^+$. The P(1)–Ni–N(2) angle is 157.6(2)° and appreciably smaller than 180°, while the P(2)–Ni–N(1) angle is 174.4(2)°. Thus, the deviation from a square pyramid to a trigonal bipyramid is larger in [NiCl{*rac*(*P*)-343NPPN}]$^+$ than in [NiCl{*meso*(*P*)-333NPPN}]$^+$.

Concluding Remarks. In contrast to the case of 323NPPN and 333NPPN,[6] 313NPPN and 343NPPN did not coordinate to a cobalt(III) ion as a tetradentate ligand; 313NPPN functioned only as a didentate diphosphine chelate forming a four-membered ring in [Co(dtc)$_2$(313HNPPNH)]$^{3+}$. Probably the steric requirement of 313NPPN and 343NPPN to coordinate as a tetradentate ligand does not fit with a Co(III) ion of a typical hard acid. On the other hand, [NiCl(343NPPN)]$^+$ was obtained in which 343NPPN acts as a tetradentate ligand. The difference in complexation between the Co(III) and Ni(II) complexes may be due to the fact that Ni(II) is larger in size and more flexible in its coordination geometry than Co(III). Thus, the coordination mode of the ligands forming an unusual chelate ring in complexation greatly depends on the nature of the metal ion, and also the absolute configuration of the chiral phosphorus atoms.

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