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Synthesis and Characterization of Square-Pyramidal Nickel(II) and Cobalt(II) Complexes with a Linear Tetradentate Diphosphine Diamine Ligand. Crystal Structures of $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$ and $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$

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Two five-coordinate complexes, $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$ and $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$, have been isolated, in which 3,3,3- N_2P_2 is the linear tetradentate diphosphine diamine $\text{CH}_2[\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2]_2$. The Ni(II) complex is low spin with $\mu_{\text{eff}} = 0.58 \mu_{\text{B}}$. Spectral and conductivity measurements in DMF showed the complex to be square pyramidal and a 1:1 electrolyte. The presence of a singlet in the $^{31}\text{P}\{\text{H}\}$ NMR spectrum suggested a single isomer, the meso or the *dl* pair. X-ray structural determinations on both the Ni(II) and the Co(II) complexes confirm the meso isomer. Both complexes crystallize in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. Unit cell dimensions are nearly identical: $a = 14.095$ (11) Å, $b = 19.232$ (13) Å, and $c = 9.681$ (8) Å for Ni and $a = 14.088$ (7) Å, $b = 19.279$ (12) Å, and $c = 9.347$ (4) Å for Co. Least-squares refinement of the nickel complex using 1978 reflections with $I > 2\sigma$ gave $R_F = 0.056$ and $R_{wF} = 0.093$; least-squares refinement (H atom positions included) of the cobalt complex using 2525 reflections with $I > 1\sigma$ gave $R_F = 0.031$ and $R_{wF} = 0.047$. Both complexes are square pyramidal with the chlorine atom occupying the axial site. In-plane bond distances are as follows: Ni-N, 2.006 (10), 2.036 (11); Co-N, 2.036 (5), 2.060 (5); Ni-P, 2.178 (4), 2.168 (4); Co-P, 2.194 (4), 2.183 (3) Å. All chelate rings are in the chair conformation. The Ni-Cl and Co-Cl bond lengths are 2.699 (7) and 2.430 (3) Å, respectively. The axial elongation in the Ni(II) case can be correlated with greater electron density in the d_{z^2} orbital for the d^8 ion compared to that for the d^7 case. Hydrogen bonding of some of the amine protons with the Cl atom, inferred from infrared spectra, was confirmed by X-ray analysis in the Co(II) complex.

Introduction

Polyphosphine ligands with mixed donor atoms have been used to investigate the stereochemistry and the magnetic-crossover point of first-row transition-metal complexes. In addition to the composite set of donor atoms, ligand geometry can influence the spin state and stereochemistry of the resulting complex.^{2,3} For example, Sacconi² found that cobalt(II) could be either high spin and trigonal bipyramidal or low spin and square pyramidal, depending on whether the polyphosphine ligand was the tripodal *N,N*-bis[2-(diphenylphosphino)ethyl]-*N,N'*-diethylethylenediamine (($\text{Ph}_2\text{PCH}_2\text{CH}_2$)₂ $\text{N}-\text{CH}_2\text{CH}_2\text{NET}_2$, PPNN) or the linear tetradentate *N,N'*-bis[2-(diphenylphosphino)ethyl]-*N,N'*-dimethylethylenediamine (PNNP). The fifth donor atom could be either bromide or chloride. The nickel(II) complexes resulting from both these ligands are low-spin, square-pyramidal complexes. Molecular models indicated that the open-chain tetradentate ligand PNNP should favor formation of the square-pyramidal complex, since the ligand cannot fit around the metal ion in a trigonal-bipyramidal arrangement without creating considerable strain. Further, it was suggested that a trigonal-bipyramidal complex would be favored if the four donor atoms in PNNP were connected through trimethylene bridges.²

In our attempts to prepare nickel(II) and cobalt(II) complexes of macrocycles derived from the linear tetradentate ligand $\text{CH}_2[\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2]_2$ (3,3,3- N_2P_2), two five-coordinate complexes, $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4$ and $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$, were isolated. Since our N_2P_2 ligand has trimethylene linkages between the donor atoms, it was of interest to study the stereochemistry of these complexes and to compare their structures with the earlier predictions.² We now wish to report the results of our syntheses, characterizations, and X-ray diffraction analyses of $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8 \text{H}_2\text{O}$ and $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$.⁴

Experimental Section

Reagents. Phenylphosphine was obtained from either Strem Chemical Co. or Pressure Chemical Co., and it was used as received. The amine salt 3-chloropropylamine hydrochloride was purchased from Aldrich Chemical Co. and used as received. All other organic reagents, solvents, and metal salts were reagent-grade commercial materials. The organic compounds were distilled under nitrogen for purification. Organic solvents were dried with either lithium aluminum hydride or sodium metal, distilled under nitrogen, and then degassed with a stream of high-purity nitrogen before use.

All reactions in the synthesis of the ligands and metal complexes were carried out under a nitrogen atmosphere with Schlenk-type airless glassware. Standard techniques were employed for the manipulation of air-sensitive compounds.⁵ All transfers were completed by using syringes that were flushed with nitrogen before use or by using stainless-steel transfer tubes, rubber septums, and positive nitrogen pressure. Minute traces of water and oxygen were removed from commercially available prepurified nitrogen by passage of the gas through two 40 × 3 in. columns packed with Drierite and hot (180 °C) BASF active copper catalyst, respectively.

(A) Synthesis of the Phosphorus Compounds. 1. Ph(H)- $\text{PCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. A solution containing 15.2 g (0.14 mol) of phenylphosphine dissolved in 30 mL of THF was added dropwise with stirring at 0 °C to 3.4 g (0.15 mol) of sodium metal in 30 mL of THF. During the addition, the solution turned orange and H_2 gas was evolved. After the addition was complete, the mixture was warmed to 25 °C and stirred for 6 h. Next ~0.14 mol of 3-chloropropylamine, which had been dissolved in diethyl ether, was added dropwise at 0 °C until the orange solution turned colorless. The sodium chloride that precipitated during the reaction was removed by filtration, and the bidentate ligand ((3-aminopropyl)phenylphosphine) was recovered by vacuum distillation at 86 °C (<1 torr). The yield based on phenylphosphine was 55%. The ligand was characterized by infrared and ^1H NMR spectra.

The 3-chloropropylamine was prepared in situ by neutralizing 3-chloropropylamine hydrochloride in H_2O with NaOH at ~0 °C. The liberated 3-chloropropylamine was then extracted with diethyl ether, and the solution was dried over MCB 3A molecular sieves and

(1) (a) Department of Chemistry, Wright State University. (b) Department of Geology, Wright State University. (c) Department of Chemistry, The Ohio State University.
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subsequently purged with nitrogen gas for 30 min before being used.

2. $\text{CH}_2[\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2]_2, 3,3,3\text{-N}_2\text{P}_2$. A solution containing 8.9 g (53 mmol) of (3-aminopropyl)phenylphosphine dissolved in 30 mL of THF was added dropwise with stirring at 0 °C to 1.3 g (56 mmol) of sodium metal in 30 mL of THF. After the addition was complete, the orange solution was warmed to 25 °C and stirred for 6 h. Next, 2.98 g (26 mmol) of 1,3-dichloropropane that had been dissolved in 30 mL of THF was added dropwise with stirring at 0 °C until the orange solution was colorless. At that point the solution was warmed to 25 °C and stirred for 3 h. The THF was removed by distillation and replaced with diethyl ether, which precipitated the sodium chloride. The NaCl was removed by filtration, and the solvent was removed under vacuum to give a colorless oil (yield 77%). The resultant ligand was characterized by infrared and ^1H NMR spectra.

(B) Synthesis of Five-Coordinate Metal Complexes. 1. $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.658 g, 2.76 mmol) dissolved in 40 mL of methanol was added dropwise with stirring at 20 °C to 1.0 g (2.77 mmol) of 3,3,3- N_2P_2 dissolved in 30 mL of methanol. The solution was refluxed for 16 h, during which it turned dark red-brown. The hexafluorophosphate salt was isolated after adding a methanolic solution of NaPF_6 (0.93 g, 5.5 mmol) and allowing the solvent to evaporate slowly. The resulting red-brown crystals were recrystallized from a methanol/ethanol mixture. Crystals suitable for X-ray structural determination were obtained. Anal. Calcd for $\text{NiC}_{21}\text{H}_{32}\text{N}_2\text{P}_3\text{ClF}_6$: C, 41.10; H, 5.25; N, 4.56. Found: C, 41.38; H, 5.31; N, 4.43.

2. $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$. This complex was prepared by the above procedure with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, NaBF_4 , and 3,3,3- N_2P_2 . Only a few crystals were isolated from the reaction mixture, after it had been concentrated and cooled in a refrigerator for 3 weeks.

(C) Physical Measurements. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN. The samples were dried in vacuo at 100 °C for at least 5 h before analysis.

A Perkin-Elmer Model 457 infrared spectrophotometer was used to record the infrared spectra. Polystyrene was used as a standard to calibrate each Nujol mull spectrum. Visible and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Solution spectra were run in matched 5.0-, 1.0-, and 0.1-cm quartz cells, and solid-state spectra were recorded with use of the diffuse-transmittance technique.⁶ Conductivities were calculated from resistance measurements on $\sim 10^{-3}$ M solutions with a Yellow Springs Instruments Model 31 conductivity bridge. Magnetic susceptibilities of the complexes were measured with a Faraday apparatus. The diamagnetic corrections for the ligands were calculated with Pascal's constants.⁷ Values reported are averages of measurements made at field strengths of 7.0 and 5.0 kG.

Proton magnetic resonance spectra were collected on a Varian A60A or an EM-360 NMR spectrometer with Me_4Si as an internal standard. Fourier-mode, proton-noise-decoupled phosphorus-31 NMR spectra were collected at ~ 30 °C on a Bruker HX-90 spectrometer operating at 36.43 MHz. Coaxial 10-mm NMR tubes with concentric 5-mm inserts (containing the deuterium lock and trimethyl phosphate as a secondary standard) were used for the ^{31}P spectra; the chemical shifts are reported relative to external 85% H_3PO_4 and are reproducible to ± 0.05 ppm. Positive chemical shifts are downfield from the resonance position of 85% H_3PO_4 .

(D) Crystal Structure Determinations. Dark red-brown crystals of $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$ and $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$ were obtained from methanol. The unit cell dimensions and the symmetry were determined from precession photographs taken with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405$ Å). Diffraction patterns of both crystals are very similar. Both have Laue symmetry *mmm*, and systematic absences of reflections (*h*00) with *h* odd, (0*k*0) with *k* odd, and (00*l*) with *l* odd indicated space group $P2_12_12_1$ as a possibility. More exact unit cell dimensions were determined with a manually operated counter diffractometer ($\text{Cu K}\alpha$ and $\text{Cu K}\beta$ radiation) and an automatic Picker FACS-1 diffractometer with Zr-filtered $\text{Mo K}\alpha$ radiation ($\lambda = 0.70169$ Å). In both cases, the least-squares refinements of the unit cell dimensions were based on 20–30 reflections. A summary of the crystallographic data for the nickel and cobalt complexes is provided in Table I for comparison purposes. The crystals were stable during

Table I. Summary of Crystallographic Data for $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$ and $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$

	$[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$	$[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$
<i>a</i> , Å	14.095 (11)	14.088 (7)
<i>b</i> , Å	19.232 (13)	19.279 (12)
<i>c</i> , Å	9.681 (8)	9.347 (4)
cryst syst	orthorhombic	orthorhombic
<i>V</i> , Å ³	2605	2535
<i>Z</i>	4	4
<i>d</i> (calcd), g cm ⁻³	1.56	1.50
<i>d</i> (obsd), g cm ⁻³ ^a	1.53	1.46
space group	$P2_12_12_1$	$P2_12_12_1$
cryst dimens, mm	0.15 × 0.10 × 0.22	0.20 × 0.25 × 0.40
abs coeff (μ), cm ⁻¹	10.76 ^b	10.28
scan type	θ - 2θ	θ - 2θ
scan width	1.40 + 0.72 tan θ	1.60 + 0.71 tan θ
scan rate, deg min ⁻¹	1.0	2.0
scan range, deg	0 ≤ 2θ ≤ 42°	0 ≤ 2θ ≤ 42°
total no. of reflectns	5908	5280
no. of indep reflectns	2651	2560
no. of reflectns used in refinement	1978 ^c	2525 ^d
<i>R</i>	0.056	0.031
<i>R</i> _w	0.093	0.047

^a Determined by flotation in CHBr_3 and CCl_4 . ^b Due to the irregular shape of the crystal, no absorption correction was attempted. ^c $|F_o| > 2\sigma$. ^d $|F_o| > 1\sigma$.

X-ray exposure since the intensities of the standard reflections were constant during the data collection (2 standard reflections were collected after each 50 data reflections). After correction for background, intensities were converted to structure factors and put on an absolute scale with use of standard computer programs.⁸ Intensity statistics indicated an acentric space group in each case; therefore, $P2_12_12_1$ was chosen. The atomic scattering factors are those calculated by Cromer and Mann,⁹ atomic scattering factors for hydrogen are from Stewart, Davidson, and Simpson,¹⁰ and the anomalous scattering corrections for Ni and Co are from ref 11.

(E) Structure Solution and Refinement. 1. $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$. The position of the nickel atom was determined from a three-dimensional Patterson map. A series of electron-density calculations gave the phosphorus coordinates and finally those of all atoms except hydrogen. Least-squares refinement proceeded in the following steps.

(a) Anisotropic temperature factors were used for the heavy atoms (nitrogen and carbon atoms were isotropic), and hydrogen atom contributions were neglected, which resulted in 10.3 reflections per variable, and *R* = 0.060 and *R*_w = 0.104.

(b) Mixed-temperature factors were used (nitrogen and carbon atoms isotropic); hydrogen atom contributions were included (*C*-*H* distance assumed 1.08 Å), which gave *R* = 0.056 and *R*_w = 0.092. The minimized function was $\sum w(|F_o| - |F_c|)^2$, in which *w* is the weight assigned to the *F*_o values. A block-diagonal approximation was used. Weights of the type 1/ σ gave worse uniformity of $\langle w(\Delta F)^2 \rangle$ than weights $w = (F_o/50)^2$ if $|F_o| \leq 50$ and $w = (50/F_o)^2$ if $|F_o| > 50$. Therefore, the latter weighting scheme was used. A difference map, which was calculated after step b, was flat with electron-density differences in the range $\pm 0.3 \text{ e } \text{Å}^{-3}$ except in areas where fluorine atoms were indicated; here the differences were 2–3 times larger. The final conventional *R* factor was 0.056, and the *R*_w factor was 0.092.

2. $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$. The position of the cobalt ion was determined from a three-dimensional Patterson map. A series of electron-density calculations gave the phosphorus and chlorine coordinates and finally those of all atoms including the hydrogen atoms. Least-squares calculations were performed in the following steps.

(a) Anisotropic temperature factors were used for the heavy atoms (*O*, *N*, *C*, and *B* were isotropic), and contributions of hydrogen atoms

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were neglected, which resulted in 14.7 reflections per variable, and $R = 0.063$ and $R_w = 0.101$.

(b) Anisotropic temperature factors were used; contributions of the H atoms were neglected, which resulted in 8.47 reflections per variable, and $R = 0.054$ and $R_w = 0.085$. After this step, the positions of the hydrogen atoms were determined from a difference map. One additional peak was identified as the oxygen atom of a water molecule. A deficiency of electron density about 5 times the background value of the cobalt site and an excess of electron density about 3 times the background value at the chlorine site were also noted.

(c) Anisotropic temperature factors were used for all atoms except hydrogen. Contributions of the H atoms were included; however, the hydrogen atom coordinates were not refined. Scattering factors for Co^{2+} and Cl^- were used, which resulted in 7.63 reflections per variable, and $R = 0.041$ and $R_w = 0.058$.

(d) Anisotropic temperature factors for all atoms except hydrogen were used; coordinates of all atoms (including hydrogen) and population parameters and thermal parameters for hydrogen in the water molecule were refined, which resulted in 5.91 reflections per variable, and $R = 0.031$ and $R_w = 0.047$.

The validity of step d was tested by Hamilton's test of statistical significance.¹² It was found significant on a confidence level better than 0.005. The facts that no coordinate of any hydrogen atoms diverged during the refinement, that all hydrogen atoms have reasonable temperature coefficients, and that C-H and N-H bond lengths have values within acceptable limits also support the validity of this step. The refinement was performed with block-diagonal methods; the minimized function was $\sum w(|F_o| - |F_c|)^2$, in which w is the weight assigned to the F_o values. Weights of the type $1/\sigma$ gave worse uniformity of $\langle w(\Delta F)^2 \rangle$ than weights $w = (F_o/40)^2$ if $|F_o| \leq 40$ and $w = (40/F_o)^2$ if $|F_o| > 40$. Therefore, the latter weighting scheme was used.

Results and Discussion

Synthesis and Characterization. The major objectives of this study were to prepare nickel(II) and cobalt(II) N_2P_2 complexes and to convert them into complexes of macrocyclic ligands. Although we had isolated good yields of the planar complex $[\text{Ni}(2,3,2\text{-N}_2\text{P}_2)](\text{PF}_6)_2$ from solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with added PF_6^- ,¹³ the analogous reactions with the 3,3,3- N_2P_2 ligand provided good yields of the five-coordinate complex $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$. We have been able to show that $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]^+$ and $[\text{Ni}(3,3,3\text{-N}_2\text{P}_2)]^{2+}$ are present in solution in about an 8:1 ratio. Similar equilibria between four- and five-coordinate nickel(II) chloride complexes of polydentate phosphine ligands have been observed previously.^{14,15} Separation and isolation of the planar complex $[\text{Ni}(3,3,3\text{-N}_2\text{P}_2)](\text{PF}_6)_2$ was achieved by column chromatography on basic alumina using nitromethane as the eluant.

Since few planar cobalt(II) complexes have been isolated and characterized, particularly when halide ions are present in solution, we attempted to prepare the planar $[\text{Co}(3,3,3\text{-N}_2\text{P}_2)]^{2+}$ cation from cobalt acetate. It proved difficult to isolate a definitive solid from the resultant solutions; however, after a methanol solution sat in the refrigerator several weeks, a few X-ray-quality red-brown crystals formed. As discussed above, these crystals proved to be the five-coordinate chloride complex $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$. The chloride ion probably remained as an impurity from the tetradentate ligand synthesis, which involved $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ as one of the reagents; the BF_4^- ion had been added to the cobalt acetate solution to aid the isolation of crystals.

Electronic absorption spectra, magnetic susceptibility, and conductivity measurements on the nickel(II) complex all indicate a low-spin, square-pyramidal cation. In DMF solution, $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$ has two absorptions at 24 100 cm^{-1} (ϵ

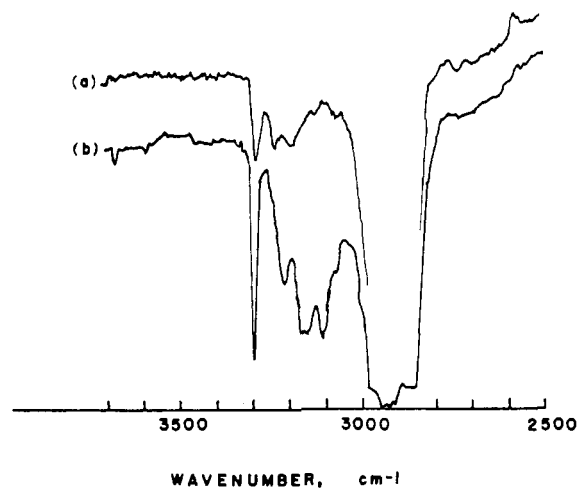


Figure 1. Infrared spectra of (a) $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4$ and (b) $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$ as Nujol mulls.

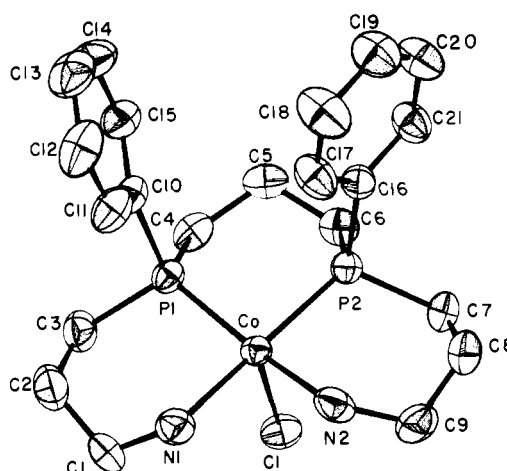


Figure 2. ORTEP drawing of the structure of the square-pyramidal cation $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]^+$, showing the atom-numbering scheme.

530) and 18 200 cm^{-1} (shoulder). The transmission spectrum of the finely ground solid also shows these same two peaks. The conductivity of the complex in DMF is 72 $\text{mhos cm}^2 \text{mol}^{-1}$ (a uni-univalent electrolyte), and its μ_{eff} is 0.58 μ_B .

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of both the four- and the five-coordinate cations, $[\text{Ni}(3,3,3\text{-N}_2\text{P}_2)]^{2+}$ and $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]^+$, suggest that only one geometric isomer (either the meso or the *dl* pair) is present in each solution. The $^{31}\text{P}\{^1\text{H}\}$ resonance of $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]^+$ occurs at -5.2 ppm in CD_3NO_2 ; the X-ray structure determination has shown this compound to be the meso isomer. The 90-MHz $^1\text{H}\{^{31}\text{P}\}$ spectrum shows that the phenyl protons are clearly separated into two multiplets (δ 8.2 and 7.5) with an intensity ratio of 2:3. The lower-field multiplet is assigned to the two hydrogen atoms that are ortho to the phosphorus atom.

The infrared spectra of both the cobalt and the nickel five-coordinate complexes suggest N-H hydrogen bonding; i.e., the NH_2 stretching frequencies are broadened and shifted 100–200 cm^{-1} to lower energies, as compared to those of normal coordinated amine ligands (Figure 1). The X-ray results, discussed below, also indicate N-H-Cl hydrogen bonding.

Descriptions of the Structures. Two single-crystal X-ray determinations have confirmed nearly identical square-pyramidal structures for both the nickel(II) and the cobalt(II) $[\text{MCl}(3,3,3\text{-N}_2\text{P}_2)]^+$ cations. The structure of the cobalt(II) cation is shown in Figure 2 along with the atomic numbering scheme used for both complexes. Positional and thermal parameters for the heavy atoms in these complexes are given

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Table II. Positional Parameters and Their Estimated Standard Deviations for $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]\text{PF}_6$

atom	x	y	z
Ni	0.0889 (1)	0.0278 (1)	0.1840 (1)
P1	0.0637 (2)	0.1001 (1)	0.3528 (3)
P2	0.0223 (2)	-0.0535 (1)	0.3049 (3)
P3	0.4980 (3)	0.2548 (2)	0.1817 (4)
C1	0.2580 (2)	-0.0137 (2)	0.2862 (3)
F1	0.5454 (6)	0.2707 (5)	0.3252 (10)
F2	0.4506 (10)	0.2369 (6)	0.0394 (10)
F3	0.3982 (6)	0.2567 (7)	0.2525 (11)
F4	0.4864 (7)	0.3344 (4)	0.1468 (11)
F5	0.5983 (8)	0.2554 (7)	0.1104 (11)
F6	0.5128 (10)	0.1759 (5)	0.2143 (11)
N1	0.1466 (6)	0.0999 (5)	0.0603 (10)
N2	0.0804 (7)	-0.0317 (5)	0.0106 (10)
C1	0.2128 (9)	0.1542 (6)	0.1140 (14)
C2	0.1659 (8)	0.2048 (6)	0.2105 (13)
C3	0.1459 (8)	0.1730 (6)	0.3516 (12)
C4	0.0807 (8)	0.0686 (6)	0.5282 (11)
C5	0.0250 (8)	0.0041 (6)	0.5693 (12)
C6	0.0507 (9)	-0.0577 (6)	0.4863 (13)
C7	0.0587 (10)	-0.1399 (7)	0.2497 (14)
C8	0.0393 (13)	-0.1520 (9)	0.0883 (18)
C9	0.1105 (11)	-0.1051 (8)	0.0089 (16)
C10	-0.0544 (8)	0.1394 (6)	0.3467 (11)
C11	-0.0898 (9)	0.1635 (6)	0.2229 (12)
C12	-0.1769 (9)	0.1962 (6)	0.2163 (13)
C13	-0.2313 (10)	0.1992 (7)	0.3336 (16)
C14	-0.1970 (11)	0.1760 (8)	0.4564 (15)
C15	-0.1089 (9)	0.1458 (6)	0.4649 (13)
C16	-0.1064 (7)	-0.0559 (6)	0.2974 (12)
C17	-0.1534 (9)	-0.0110 (7)	0.2112 (14)
C18	-0.2529 (11)	-0.0100 (8)	0.2072 (16)
C19	-0.3028 (10)	-0.0573 (7)	0.2884 (15)
C20	-0.2569 (10)	-0.1005 (7)	0.3729 (15)
C21	-0.1580 (9)	-0.1014 (7)	0.3812 (14)

Table III. Positional Parameters and Their Estimated Standard Deviations for $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$

atom	x	y	z
Co	0.0898 (1)	0.0272 (1)	0.1854 (1)
P1	0.0624 (1)	0.1050 (1)	0.3520 (1)
P2	0.0242 (1)	-0.0521 (1)	0.3205 (1)
C1	0.2459 (1)	-0.0050 (1)	0.2755 (1)
F1	0.4965 (4)	0.3311 (2)	0.1533 (5)
F2	0.5207 (4)	0.2472 (3)	0.3119 (5)
F3	0.4039 (4)	0.2423 (3)	0.1603 (12)
F4	0.5477 (6)	0.2267 (3)	0.0876 (7)
Ow	0.5830 (5)	0.0931 (4)	0.3358 (9)
N1	0.1439 (3)	0.0995 (2)	0.0484 (4)
N2	0.0865 (3)	-0.0393 (2)	0.0126 (4)
B	0.4902 (5)	0.2612 (3)	0.1776 (8)
C1	0.2069 (4)	0.1566 (3)	0.0944 (7)
C2	0.1601 (4)	0.2071 (2)	0.1925 (7)
C3	0.1436 (3)	0.1794 (2)	0.3427 (6)
C4	0.0795 (3)	0.0782 (2)	0.5371 (5)
C5	0.0230 (3)	0.0154 (3)	0.5851 (5)
C6	0.0512 (3)	-0.0504 (3)	0.5119 (5)
C7	0.0606 (4)	-0.1398 (2)	0.2741 (6)
C8	0.0472 (4)	-0.1555 (3)	0.1148 (6)
C9	0.1118 (4)	-0.1142 (3)	0.0209 (6)
C10	-0.0554 (3)	0.1448 (2)	0.3452 (5)
C11	-0.0912 (4)	0.1666 (3)	0.2146 (5)
C12	-0.1798 (5)	0.1986 (3)	0.2086 (7)
C13	-0.2321 (4)	0.2080 (3)	0.3324 (9)
C14	-0.1979 (4)	0.1857 (3)	0.4594 (8)
C15	-0.1094 (4)	0.1550 (3)	0.4677 (6)
C16	-0.1046 (3)	-0.0555 (2)	0.3098 (5)
C17	-0.1513 (4)	-0.0129 (3)	0.2152 (6)
C18	-0.2494 (4)	-0.0147 (3)	0.2043 (7)
C19	-0.3006 (4)	-0.0600 (3)	0.2877 (7)
C20	-0.2553 (4)	-0.1039 (3)	0.3814 (7)
C21	-0.1568 (3)	-0.1015 (3)	0.3938 (6)

in Tables II and III. Selected bond lengths and angles are presented in Tables IV-IX. Tables of observed and calculated

Table IV. Bond Lengths (Å) within the Cation^a $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]^+$

Ni-N1	2.006 (10)	Ni-N2	2.036 (11)
Ni-P1	2.178 (4)	Ni-P2	2.168 (4)
N1-C1	1.49 (2)	N2-C9	1.48 (2)
C1-C2	1.50 (2)	C9-C8	1.55 (2)
C2-C3	1.52 (2)	C8-C7	1.60 (2)
C3-P1	1.82 (1)	C7-P2	1.82 (1)
P1-C4	1.82 (1)	P2-C6	1.80 (1)
C4-C5	1.52 (2)	C6-C5	1.48 (2)
P1-C10	1.83 (1)	P2-C16	1.81 (1)
C10-C11	1.38 (2)	C16-C17	1.37 (2)
C11-C12	1.38 (2)	C17-C18	1.40 (2)
C12-C13	1.37 (2)	C18-C19	1.39 (2)
C13-C14	1.36 (2)	C19-C20	1.33 (2)
C14-C15	1.37 (2)	C20-C21	1.40 (2)
C15-C10	1.38 (2)	C21-C16	1.40 (2)
Ni-Cl	2.699 (7)		

^a The number in parentheses is the estimated standard deviation in the last significant figure.

Table V. Bond Angles (Deg) within the Cation^a $[\text{NiCl}(3,3,3\text{-N}_2\text{P}_2)]^+$

P1NiP2	89.1 (2)	N1NiN2	85.4 (4)
P1NiN1	94.1 (3)	P2NiN2	90.9 (3)
NiN1C1	121.9 (8)	NiN2C9	122.0 (9)
N1C1C2	113.3 (10)	N2C9C8	111.5 (12)
C1C2C3	112.2 (10)	C9C8C7	106.8 (13)
C2C3P1	115.7 (8)	C8C7P2	111.8 (10)
C3P1C4	100.3 (5)	C7P2C6	100.5 (6)
P1C4C5	116.6 (8)	P2C6C5	116.0 (9)
C4C5C6	112.8 (10)		
NiP1C10	112.9 (4)	NiP2C16	115.4 (4)
C3P1C10	105.1 (5)	C7P2C16	104.2 (6)
C4P1C10	106.7 (5)	C6P2C16	105.0 (6)
C10C11C12	121.0 (11)	C16C17C18	120.6 (12)
C11C12C13	118.6 (12)	C17C18C19	118.6 (13)
C12C13C14	120.8 (13)	C18C19C20	120.6 (13)
C13C14C15	120.8 (13)	C19C20C21	121.8 (13)
C14C15C10	119.3 (12)	C20C21C16	118.6 (12)
C15C10C11	119.3 (11)	C21C16C17	119.8 (11)
N1NiCl	93.9 (3)	N2NiCl	100.9 (3)
P1NiCl	93.3 (1)	P2NiCl	88.3 (2)

^a The number in parentheses is the estimated standard deviation in the last significant figure.

Table VI. Bond Lengths (Å) within the Cation^a $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]^+$

Co-N1	2.036 (5)	Co-N2	2.060 (5)
Co-P1	2.194 (4)	Co-P2	2.183 (3)
N1-C1	1.476 (7)	N2-C9	1.483 (7)
C1-C2	1.488 (8)	C9-C8	1.491 (8)
C2-C3	1.519 (9)	C8-C7	1.531 (9)
C3-P1	1.831 (5)	C7-P2	1.814 (6)
P1-C4	1.822 (6)	P2-C6	1.829 (6)
C4-C5	1.513 (7)	C6-C5	1.490 (7)
P1-C10	1.825 (5)	P2-C16	1.815 (5)
C10-C11	1.385 (7)	C16-C17	1.370 (7)
C11-C12	1.391 (9)	C17-C18	1.383 (8)
C12-C13	1.382 (10)	C18-C19	1.373 (9)
C13-C14	1.351 (11)	C19-C20	1.372 (9)
C14-C15	1.379 (8)	C20-C21	1.390 (8)
C15-C10	1.388 (8)	C21-C16	1.392 (7)
Co-Cl	2.430 (3)		

^a The number in parentheses is the estimated standard deviation in the last significant figure.

structure-factor amplitudes, positional and thermal parameters for hydrogen atoms, and least-squares planes are available as supplementary material, along with tables of bond lengths and angles for the PF_6^- and BF_4^- anions.

The coordination geometry for each cation is virtually the same, except for the metal-halogen distance ($\text{Ni-Cl} = 2.699$

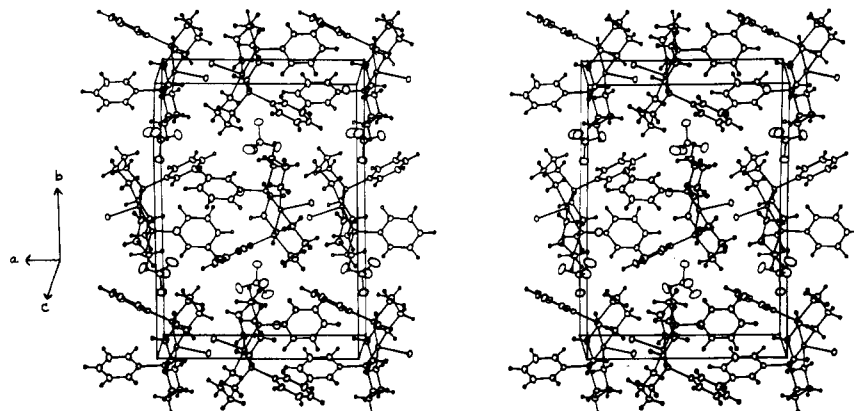


Figure 3. Stereoscopic view of the crystal packing for $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$.

Table VII. Bond Angles (Deg) within the Cation^a $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]^+$

P1CoP2	89.5 (2)	N1CoN2	86.4 (2)
P1CoN1	92.7 (2)	P2CoN2	90.7 (2)
CoN1C1	123.3 (4)	CoN2C9	123.7 (3)
N1C1C2	113.5 (5)	N2C9C8	113.6 (4)
C1C2C3	114.2 (4)	C9C8C7	113.2 (5)
C2C3P1	114.3 (4)	C8C7P2	112.4 (3)
C3P1C4	100.6 (2)	C7P2C6	101.1 (2)
P1C4C5	116.0 (3)	P2C6C5	114.2 (3)
C4C5C6	113.6 (4)		
CoP1C10	114.9 (2)	CoP2C16	114.5 (2)
C3P1C10	103.7 (2)	C7P2C16	103.6 (2)
C4P1C10	105.7 (2)	C6P2C16	105.2 (2)
C10C11C12	119.6 (5)	C16C17C18	120.7 (5)
C11C12C13	120.0 (6)	C17C18C19	119.7 (6)
C12C13C14	120.4 (6)	C18C19C20	120.6 (5)
C13C14C15	120.4 (6)	C19C20C21	119.7 (5)
C14C15C10	120.5 (5)	C20C21C16	119.9 (5)
C15C10C11	119.1 (5)	C21C16C17	119.4 (4)
N1CoCl	93.1 (2)	N2CoCl	97.7 (1)
P1CoCl	94.9 (1)	P2CoCl	90.2 (1)

^a The number in parentheses is the estimated standard deviation in the last significant figure.

(7) Å and Co-Cl = 2.430 (3) Å). All three six-membered chelate rings in each complex are in the chair conformation. Dihedral angle calculations (Supplementary Table XI) show the close similarities in the ring conformations of the two complexes. The in-plane metal-ligand distances are in good agreement with the values reported by Sacconi¹⁴ for the N_2P_2 donor set in the low-spin, square-pyramidal complexes $[\text{MBr}(\text{PNNP})]^+$, where M = Co(II) or Ni(II) and PNNP is the ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{PPh}_2$. The basal plane metal-ligand bond distances in Sacconi's complexes are as follows:¹⁴ Co-P = 2.22 (1) (average), Ni-P = 2.21 (1) (average), Co-N = 2.03 (3) (average), Ni-N = 2.00 (2) (average), Ni-Br = 2.807 (4), and Co-Br = 2.534 (6) Å.

It is interesting that the nickel-halide bond distance is 0.27 Å longer than the cobalt-halide distance in both Sacconi's and our complexes. The longer metal-halogen bond distances for the nickel complexes can be rationalized qualitatively by a simplified MO scheme. The effect of an elongated axial M-Cl bond is to decrease the antibonding character of the electrons in the molecular orbital that is primarily d_{z^2} . Thus, a low-spin nickel(II) complex, with two electrons in the d_{z^2} orbital, would be expected to experience more metal-ligand electron-electron repulsion and to display a M-Cl bond distance longer than that of a low-spin cobalt(II) complex, which would have only one electron in the metal d_{z^2} orbital.

Even though molecular models indicate that our 3,3,3- N_2P_2 ligand is sufficiently flexible to form either a trigonal-bipyramidal or a square-pyramidal structure, both the nickel(II)

Table VIII. Hydrogen Bond Lengths (Å) within the Cation^a $[\text{CoCl}(3,3,3\text{-N}_2\text{P}_2)]^+$

C1-H1A	1.07 (5)	C9-H9A	0.87 (8)
C1-H1B	0.86 (7)	C9-H9B	1.05 (6)
C2-H2A	1.01 (5)	C11-H11	0.92 (7)
C2-H2B	0.87 (7)	C12-H12	1.06 (6)
C3-H3A	0.97 (5)	C13-H13	0.96 (7)
C3-H3B	1.06 (6)	C14-H14	0.96 (9)
C4-H4A	0.93 (4)	C15-H15	0.90 (7)
C4-H4B	0.83 (5)	C17-H17	1.05 (6)
C5-H5A	0.94 (6)	C18-H18	0.90 (12)
C5-H5B	0.95 (5)	C19-H19	1.01 (6)
C6-H6A	0.95 (5)	C20-H20	0.98 (7)
C6-H6B	1.05 (5)	C21-H21	0.94 (6)
C7-H7A	1.02 (6)	N1-H41	0.81 (5)
C7-H7B	1.04 (4)	N1-H42	0.94 (6)
C8-H8A	1.03 (5)	N2-H51	0.87 (5)
C8-H8B	0.99 (4)	N2-H52	0.83 (5)

^a The number in parentheses is the estimated standard deviation in the last significant figure.

Table IX. Contact Distances for Atoms Involved in Hydrogen Bonding

complex	bond	bond length, ^a Å	bond angle, ^b deg	X...H, Å
Co	N1-H41...F1	3.1	171	2.3
Co	N1-H42...Cl	3.5	167	2.57
Co	N2-H52...Cl	3.34	160	2.55
Ni	N1-H ^c ...F4	3.27		
Ni	N1-H ^c ...F5	3.31		
Ni	N1-H ^c ...Cl	3.40		
Ni	N2-H ^c ...Cl	3.26		

^a The distance between the hydrogen-bonded atoms N and F or N and Cl. ^b The angle of NHF or NHCl with H as the central atom. ^c The hydrogen atoms were not located in the X-ray analysis.

and cobalt(II) complexes adopt comparable square-pyramidal structures in the crystals. Sacconi found that the *tripod* ligand $\text{Et}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, having the same N_2P_2 donor set, yielded high-spin, trigonal-bipyramidal Co(II) complexes,³ whereas the *open-chain* tetradentate ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{PPh}_2$ forms low-spin square-planar Co(II) complexes,^{2,14} similar to our 3,3,3-NPPN ligand. Thus, subtle changes in the nature of the tetradentate ligands can exhibit dramatic effects on the structure and the resultant spin state of the metal complex, particularly when the donor set is close to the magnetic-crossover region. Both Sacconi's and our results indicate that open-chain tetradentate ligands containing an N_2P_2 donor set favor the low-spin, square-planar structure for both nickel(II) and cobalt(II) regardless of whether the bridging carbon chains contain two or three methylene groups. The tripod geometry of the ligand

$\text{Et}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ apparently induces the trigonal-bipyramidal structure onto cobalt in that case.

Figure 3 is a stereoscopic view showing the molecular packing of the cobalt complex. The hydrogen atoms were refined for the cobalt structure, and they are included in the stereoscopic view. The unit-cell dimensions of the nickel and cobalt complexes are similar except for an elongation of the c axis (0.34 Å) in the nickel complex. This elongation of the c axis is attributed to the increased metal-halogen bond length in the nickel complex. The positional parameters of comparable atoms in both structures are very similar, even to the position of the boron and phosphorus atoms of the anions. The position of F1 in the cobalt complex is close to the position of F4 in the nickel complex; the anions in both complexes are located above the plane defined by the four donor atoms, near N1 and close to the phenyl rings.

A water molecule is located near amine proton H51 in the cobalt complex. The N2-H51-O angle is 159° with a contact distance of 3.08 Å between N2 and oxygen. The H51-O distance is 2.25 Å, which is sufficiently close for hydrogen bonding. Since only very weak O-H absorption bands were observed in the infrared spectrum of the cobalt complex when it was stored in a dry N_2 atmosphere, we assume that the H_2O molecule became entrapped in the lattice during a long exposure to the laboratory atmosphere before the X-ray data collection began. There was no X-ray evidence, and only very weak infrared evidence, of water in the nickel complex.

Hydrogen bonding of the amine protons appears to be prominent in both the nickel and cobalt complexes. The number of amine stretching vibrations can be explained on the basis of hydrogen-bonding contact distances between the N-H protons and the halogen atoms near them (Table IX).

The sums of the van der Waals radii for the sets of atoms H, F and H, Cl are 2.5 and 3.0 Å, respectively; thus, the X...H

distances determined here and reported in Table IX indicate the presence of intermolecular hydrogen bonding in the solid state. The infrared spectrum of the cobalt complex shows two vibrations at 3240 and 3190 cm^{-1} that arise from N-H hydrogen bonding, whereas the nickel complex shows three bands at 3210, 3160, and 3110 cm^{-1} (Figure 1). One possible reason for the difference in the number of absorption bands may be the fact that the N1 proton in the nickel complex is about equidistant from F4 and F5, whereas only one fluorine atom (F1) is near N1 in the cobalt complex. The hydrogen-fluorine contact distance with either F4 or F5 is estimated to be ~ 2.4 Å, which is within hydrogen-bonding limits. The sharp infrared band at 3290 cm^{-1} that is observed for both metal complexes is assigned to the amine proton H51, which does not participate in any hydrogen bonding.

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Registry No. $[\text{NiCl}(\text{3,3,3-N}_2\text{P}_2)]\text{PF}_6$, 81447-13-4; $[\text{CoCl}(\text{3,3,3-N}_2\text{P}_2)]\text{BF}_4 \cdot 0.8\text{H}_2\text{O}$, 81447-16-7; $\text{3,3,3-N}_2\text{P}_2$, 71734-66-2; $\text{Ph}(\text{H})\text{-PCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, 13822-50-9; 1,3-dichloropropane, 142-28-9.

Supplementary Material Available: Listings of structure factor amplitudes ($\times 10$), positional and thermal parameters for the hydrogen atoms, thermal parameters for nonhydrogen atoms, least-squares planes, and bond lengths and angles for the anions (50 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of $[(t\text{-C}_4\text{H}_9\text{NC})_2\text{Pd}((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2)_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$, a Compound with Two Monodentate Diphosphine Ligands

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$[(t\text{-C}_4\text{H}_9\text{NC})_2\text{Pd}(\text{dpm})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$ (dpm is bis(diphenylphosphino)methane) has been prepared by the successive addition of *tert*-butyl isocyanide, dpm, and sodium tetraphenylborate to bis(benzonitrile)palladium dichloride, by the addition of *tert*-butyl isocyanide, dpm, and sodium tetraphenylborate to $(\text{dpm})\text{PdCl}_2$ and by the addition of *tert*-butyl isocyanide and sodium tetraphenylborate to $[\text{Pd}_2(\mu\text{-dpm})_2(\mu\text{-I})(\text{CH}_3)\text{I}][\text{BF}_4]$. The structure of $[(t\text{-C}_4\text{H}_9\text{NC})_2\text{Pd}(\text{dpm})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$ has been determined by X-ray crystallography. It crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell of dimensions $a = 13.554(12)$ Å, $b = 14.172(8)$ Å, $c = 14.658(8)$ Å, $\alpha = 113.58(5)^\circ$, $\beta = 111.39(5)^\circ$, and $\gamma = 97.00(6)^\circ$. Full-matrix least-squares refinement yielded $R = 7.9\%$. The palladium is planar with trans isocyanide and trans, monodentate dpm ligands.

Introduction

Bis(diphenylphosphino)methane (dpm) has been extensively used as a bridging ligand.¹⁻³ In this form, it is remarkable for the variability in the metal-metal separation which it

spans.⁴ Compounds in which this diphosphine acts as a chelating ligand are also known.⁵⁻⁸ We have recently reported on a case of the bridge to chelate transformation.⁹

Complexes containing monodentate bis(diphenylphosphino)methane ligands are known but are currently less

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