

The Donor Properties of Positively Charged Ligands. Pseudo-tetrahedral Co^{II} and Ni^{II} Complexes Containing Mono-quaternized Ditertiary Phosphines

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The halide salts of the mono-quaternized ditertiary phosphines, 1,2-bis(diphenylphosphino)ethane and 1,1-bis(diphenylphosphino)methane, abbreviated as $(\text{PCH}_2\text{CH}_2\text{P}^+)$ and (PCH_2P^+) respectively, react under anhydrous conditions with the cobalt(II) and nickel(II) halides, forming crystalline compounds of stoichiometry $\text{MX}_2 \cdot (\text{PCH}_2\text{CH}_2\text{P}^+)\text{X}$ and $\text{MX}_2 \cdot (\text{PCH}_2\text{P}^+)\text{X}$, where $\text{M} = \text{Co}^{\text{II}}$ and Ni^{II} and $\text{X} = \text{Cl}, \text{Br}, \text{I}$. On the basis of their vibrational and $d-d$ electronic spectra, magnetic properties, and X-ray powder diffraction patterns, these compounds are formulated as the high-spin, four-coordinate species $[\text{MX}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ and $[\text{MX}_3(\text{PCH}_2\text{P}^+)]$, having a pseudo-tetrahedral stereochemistry with C_{3v} symmetry.

Introduction

Complexes of positively charged amines with transition metal ions have been extensively investigated,¹⁻⁷ but only a few examples of complexes in which a « soft » donor positive-ion ligand is coordinated to metal ions have been reported.⁸⁻¹¹ In our systematic study of the donor properties of positively charged ligands we have prepared and investigated a novel series of cobalt(II) and nickel(II) complexes containing mono-quaternized ditertiary phosphines. The potential donor properties of positively charged phosphines appeared to be particularly interesting in view of the extreme versatility of P-donor ligands with non-transition elements, as well as with transition elements in a variety of oxidation states and stereochemistries. The positive-ion ligands $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}^+(\text{C}_6\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)$ and $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}^+(\text{C}_6\text{H}_5)_2$

$(\text{CH}_2\text{C}_6\text{H}_5)$, abbreviated as $(\text{PCH}_2\text{CH}_2\text{P}^+)$ and (PCH_2P^+) respectively, were first chosen for this study because parallel work on positively charged N-donor ligands has shown that when two CH_2 groups or less are interposed between the ligating atom and the positively charged site, the positive charge has a more marked effect on the donor properties of the ligand.¹ The metal ions Co^{II} and Ni^{II} appeared to be particularly suitable since their relatively low tendency to π -backdonation should allow a direct comparison of the properties of positively charged P-donor and N-donor ligands.

Results and Discussion

The chlorides, bromides, and iodides of cobalt(II) and nickel(II) react with the cation-phosphines $(\text{PCH}_2\text{CH}_2\text{P}^+)$ and (PCH_2P^+) , as described in the Experimental Section, to form crystalline compounds of stoichiometry $\text{MX}_2 \cdot (\text{PCH}_2\text{CH}_2\text{P}^+)\text{X}$ and $\text{MX}_2 \cdot (\text{PCH}_2\text{P}^+)\text{X}$.

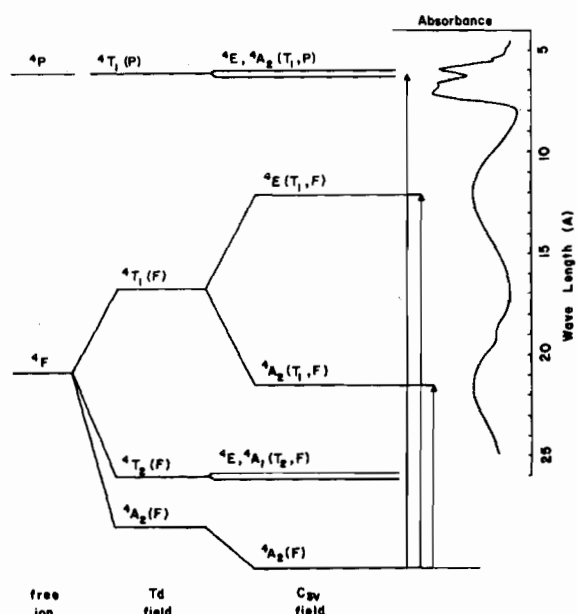


Figure 1. $d-d$ electronic spectrum (reflectance) of $[\text{CoCl}_2(\text{PCH}_2\text{CH}_2\text{P}^+)]$, compared with the energy level diagram for a d^7 metal ion in cubic field of C_{3v} symmetry (Ref. 15).

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Since these compounds are either insoluble or solvate extensively in solvents suitable for conductivity and spectral studies, their investigation was limited to solid state properties.

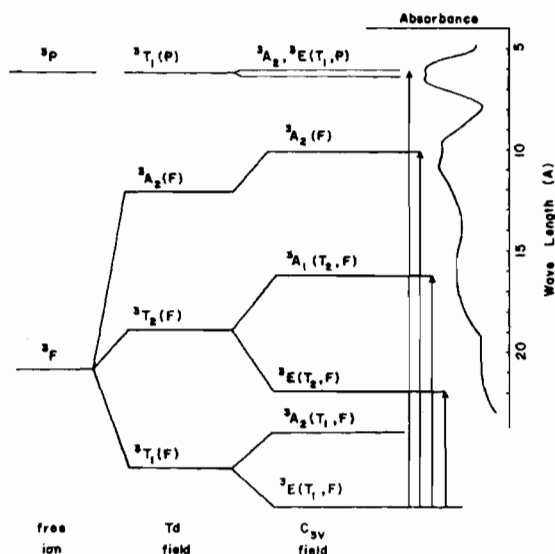


Figure 2. *d-d* electronic spectra (reflectance) of $[\text{NiCl}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$, compared with the energy level diagram for a d^8 metal ion in cubic field of C_{3v} symmetry (Ref. 15).

The *d-d* electronic spectra of the compounds, $\text{MX}_2 \cdot (\text{PCH}_2\text{CH}_2\text{P}^+)\text{X}$ and $\text{MX}_2 \cdot (\text{PCH}_2\text{P}^+)\text{X}$, shown in Figures 1 and 2, somewhat resemble those of the well known, tetrahedral tetrahalometallates, $[\text{CoX}_4]^{2-}$ and $[\text{NiX}_4]^{2-}$,^{12,13} and are virtually identical with those of the four-coordinate, high-spin, pseudo-tetrahedral anions $[\text{MX}_3(\text{C}_6\text{H}_5)_3\text{P}^+]^-$.¹⁴ The observed absorptions are assigned as shown in Tables I and II, assuming a pseudo-tetrahedral crystal field of C_{3v} ¹⁵ symmetry.

Thus the cation-phosphine, as well as the three halide ions, X, are coordinated to the central metal ion in the compounds of stoichiometry $\text{MX}_2 \cdot (\text{PCH}_2\text{CH}_2\text{P}^+)\text{X}$ and $\text{MX}_2 \cdot (\text{PCH}_2\text{P}^+)\text{X}$, which can be formulated as non-ionic, mononuclear species, $[\text{MX}_3(\text{L}^+)]$, similar to the complexes of the mono-quaternized ditertiary amine, 1,4-diazabicyclo[2.2.2]octonium.⁴ This formulation is in agreement with the values of the room temperature magnetic moments of the complexes, which are within the ranges usually observed for tetrahedrally coordinated Co^{II} and Ni^{II} , the moments of the Ni^{II} complexes being somewhat lower than those of the corresponding $[\text{NiX}_4]^{2-}$ anions, very likely as a result of the lower symmetry of the crystal field.

The vibrational spectra of the $[\text{MX}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ complexes consist essentially of the characteristic absorptions of the « free » cation-phosphine. The spectra are rather complicated, showing the many strong absorptions expected for compounds containing five non-equivalent phenyl groups. While a detailed assignment of the observed absorptions is not relevant to the present work, the spectra are useful in excluding the presence of possible phosphine-oxide impurities (no strong new absorptions being observed in the $\text{P}=\text{O}$ region). For the corresponding complexes of the (PCH_2P^+) ligand, the vibrational spectra again consist essentially of the characteristic absorptions of the free ligand. In addition, a strong absorption centered at 1708 cm^{-1} , with partly resolved maxima at 1714 and 1704 cm^{-1} , indicates the presence of acetone in the metal complexes obtained by crystallization from this solvent. In fact the « free » ligand halides $(\text{PCH}_2\text{P}^+)\text{X}^-$ also crystallize from acetone as an acetone-solvate (the $\text{C}=\text{O}$ stretching vibration appearing as a strong band at 1708 cm^{-1}). Since the *d-d* electronic spectra of these acetone-containing metal complexes are virtually identical with those without acetone, the presence

Table I. Colors and *d-d* Electronic Absorptions of Co^{II} Complexes Containing Positively Charged P-Donor Ligands

Complex and Color ^a	<i>d-d</i> Electronic Absorptions ^b ($\text{cm}^{-1} \times 10^{-3}$) and Assignments. ^c			
	${}^4\text{A}_2, {}^4\text{E}(\text{T}_1, \text{P})$		${}^4\text{E}(\text{T}_1, \text{F})$	${}^4\text{A}_1(\text{T}_1, \text{F})$
$[\text{CoCl}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ blue	15.1 (14.3, 15.1, 16.8, 18.7 sh)		8.2	4.7
			$\Delta = 3,500 \text{ cm}^{-1}$	
$[\text{CoBr}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ blue	14.6 (13.9, 14.6, 15.7, 17.6 sh, 19.3 sh)		7.8	4.5
			$\Delta = 3,300 \text{ cm}^{-1}$	
$[\text{CoI}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ yellow-green	13.5 (12.9, 13.5, 13.9)		7.6	4.4
			$\Delta = 3,200 \text{ cm}^{-1}$	
$[\text{CoCl}_3(\text{PCH}_2\text{P}^+) \cdot (\text{CH}_3)_2\text{CO}]$ blue	15.1 (14.5, 16.4, 15.7 sh, 16.9 sh)		8.0	4.7
			$\Delta = 3,200 \text{ cm}^{-1}$	
$[\text{CoBr}_3(\text{PCH}_2\text{P}^+) \cdot (\text{CH}_3)_2\text{CO}]$ blue	14.6 (13.9, 14.6, 15.7, 17.5 sh, 19.2 sh)		7.7	4.6
			$\Delta = 3,100 \text{ cm}^{-1}$	
$[\text{CoI}_3(\text{PCH}_2\text{P}^+) \cdot (\text{CH}_3)_2\text{CO}]$ chartreuse-brown	13.8 (13.3, 14.3)		7.4	4.5
			$\Delta = 2,900 \text{ cm}^{-1}$	

^a $\text{PCH}_2\text{CH}_2\text{P}^+ = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}^+(\text{C}_6\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)$; $\text{PCH}_2\text{P}^+ = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}^+(\text{C}_6\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)$. ^b From diffuse reflectance spectra. The values given are the midpoints of the absorption bands. Partly resolved maxima are given in parentheses. ^c The assignments follow the energy level diagram of Reference 15 for a d^7 system in a cubic field of C_{3v} symmetry. The symbol in parentheses indicates the parent term in T_d symmetry.

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Table II. Colors and *d-d* Electronic Absorptions of Ni^{II} Complexes Containing Positively Charged P-Donor Ligands

Complex and Color ^a	<i>d-d</i> Electronic Absorptions ^b (cm ⁻¹ × 10 ⁻³) and Assignments. ^c			
	³ E(T ₁ , F) →			
	³ A ₂ , ³ E(T ₁ , P)	³ A ₂ (F)	³ A ₁ (T ₂ , F)	³ E(T ₂ , F)
[NiCl ₃ (PCH ₂ CH ₂ P ⁺)] blue	15.9 (15.4, 16.5)	9.5 (9.3, 10.3)	6.1	4.5
[NiBr ₃ (PCH ₂ CH ₂ P ⁺)] turquoise	15.0 (14.6, 15.7)	9.4 (9.0, 9.7)	6.0	4.5
[NiI ₃ (PCH ₂ CH ₂ P ⁺)] brown	14.0	9.3	6.0	4.5
[NiCl ₃ (PCH ₂ P ⁺)] blue	15.9 (15.1, 16.7)	9.1 (9.1, 9.6)	6.1	5.0
[NiCl ₃ (PCH ₂ P ⁺)] · (CH ₃) ₂ CO greenish-blue	15.6	9.1 (9.1, 10.1)	6.1	5.0
[NiBr ₃ (PCH ₂ P ⁺)] · (CH ₃) ₂ CO green	14.5	9.2 (8.9, 9.7)	6.1	4.9
[NiI ₃ (PCH ₂ P ⁺)] · (CH ₃) ₂ CO brown	13.0	9.0	6.1	4.9

^a PCH₂CH₂P⁺ = (C₆H₅)₂PCH₂CH₂P⁺(C₆H₅)₂(CH₂C₆H₅); PCH₂P⁺ = (C₆H₅)₂PCH₂P⁺(C₆H₅)₂(CH₂C₆H₅). ^b From diffuse reflectance spectra. The values given are the midpoints of the absorption bands. Partly resolved maxima are given in parentheses. ^c The assignments follow the energy level diagram of Reference 15 for a *d*⁸ system in a cubic field of C_{3v} symmetry. The symbol in parentheses indicates the parent term in T_d symmetry.

of acetone in these compounds can be explained on the basis of the lattice requirements associated with the cation-phosphine (C₆H₅)₂PCH₂P⁺(C₆H₅)₂(CH₂C₆H₅). A significant feature in the vibrational spectra of the chloro-complexes is the presence in the far infrared region of a new medium-strong split absorption assigned to the metal-chlorine stretching vibrations: [CoCl₃(PCH₂CH₂P⁺)], 322, 312 cm⁻¹; [NiCl₃(PCH₂CH₂P⁺)] 313, 282 cm⁻¹; [CoCl₃(PCH₂P⁺)], 324, 314 cm⁻¹; [NiCl₃(PCH₂P⁺)], 322, 302 cm⁻¹. The presence of two rather than only one M-Cl absorption in this region is consistent with the C_{3v} symmetry assigned to the complexes, for which both the symmetric and the antisymmetric M-Cl stretching modes are infrared active. As is generally observed for tetrahedral and pseudo-tetrahedral complexes, the M-Cl stretching vibrations appear at somewhat higher frequencies for Co^{II} than for Ni^{II}.

The X-ray powder diffraction patterns of the Co^{II} and Ni^{II} complexes of each cation-phosphine ligand and each halide are virtually identical and indicate that the complexes are isomorphous, as may be expected from the analogous stereochemical assignments based on the *d-d* electronic spectra and from the close similarity of the vibrational spectra.

The complexes [MX₃(PCH₂CH₂P⁺)] and [MX₃(PCH₂P⁺)] are virtually insoluble in non-polar organic solvents and are decomposed by water and other strong donor solvents. Nitromethane appears to be one of the few solvents in which the [MX₃(PCH₂CH₂P⁺)] complexes dissolved slightly, retaining at least in part their identity; the [MX₃(PCH₂P⁺)] complexes are also soluble in acetone and dichloromethane. The *d-d* electronic spectra of all these solutions show the existence of a solvation equilibrium; the solvate species still have a pseudo-tetrahedral coordination with C_{3v} symmetry, similar to the original solid complex, but the spectra indicate partial replacement of the P-donor ligands by nitromethane.

On the basis of the evidence obtained, the [MX₃(PCH₂CH₂P⁺)] and [MX₃(PCH₂P⁺)] complexes may be considered to have a zwitter-ion structure in which the positive charge of the quaternized phosphorus

atom of the ligand is separated from the center of negative charge of the (MX₃⁻) moiety. The high thermal stability of these complexes and their low solubility in non-polar solvents, as compared with the ready solubility of the similar [MX₂L₂] complexes of uncharged phosphines, may be attributed to a high lattice energy arising from the favorable intermolecular interactions of the (P⁺) and (MX₃)⁻ sites of neighboring complex units in the lattice.

A significant result of the study of this novel series of complexes, [MX₃(L⁺)], is that the presence of the positive charge on the phosphine-cation ligand, although it undoubtedly contributes to the stability of the complexes and favors their formation by providing the suitable 1:3 metal-to-halide ratio, has very little influence on the ligating character of the P donor atom. In fact, the *d-d* electronic spectra of the corresponding metal complexes of the (PCH₂CH₂P⁺) and (PCH₂P⁺) ligands are virtually superposable, even though in the latter ligand the P donor atom is separated from the positive site by only a single CH₂ group. Also, the *d-d* electronic spectra of the complexes [CoBr₃(PCH₂CH₂P⁺)] and [CoBr₃(PCH₂P⁺)] are extremely similar to that of the complex [CoBr₃{P(C₆H₅)₃}]⁻, in which the P donor atom belongs to the uncharged triphenylphosphine ligand. These observations parallel those of our work on the pseudo-tetrahedral complexes of positively charged tertiary amines, where it was found, for example, that the spectra of [NiCl₃(L⁺)] (where L⁺ is a monoquaternized ditertiary amine) and of [NiCl₃(pyridine)]⁻ are virtually superposable. It may be concluded however surprising this may be, that the position of a donor atom in the spectrochemical and nephelauxetic series is not appreciably sensitive to the presence of a localized positive site on the ligand—at least for complexes of high-spin metal ions which act essentially as *sigma*-acceptors. Now it appears likely that to observe a direct electronic influence of the positive charge on the ligating ability of a donor atom, one must consider either complexes in which the positive charge of the ligand is partly delocalized on the ligating atom itself, or complexes in which the metal

ion is capable of strong π -backdonation to a positively charged ligand.

Experimental Section

Starting Materials. 1,2-bis(diphenylphosphino)ethane and 1,1-bis(diphenylphosphino)methane were obtained from STREM chemicals. Anhydrous cobalt(II) halides and nickel(II) chloride and bromide were used without further purification. An anhydrous solution of NiI_2 was prepared by repeatedly washing the hexahydrate $[\text{Ni}(\text{H}_2\text{O})_6]\text{I}_2$ with dichloromethane until pure pale-green crystals were obtained, and then refluxing these for 5 min in ethanol containing 30% triethylorthoformate.

Analytical reagent grade or spectrograde solvents were used in the preparation of the ligands and complexes.

Preparation of the Ligands. 1-diphenylphosphino, 2-benzylidiphenylphosphonium-ethane bromide, $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}^+(\text{C}_6\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)]\text{Br}^-$, was prepared by treating the parent diphosphine (1.00 g) in acetone (25 ml) with the stoichiometric quantity of benzylbromide (0.44 g). The white solid which separated after several hours was washed with acetone and recrystallized by dissolving it in isobutyl alcohol and reprecipitating with hexane (yield, 1.05 g). The pure product was obtained as white needles, m.p. 240-245°. *Anal.* Calcd. for $\text{C}_{33}\text{H}_{31}\text{P}_2\text{Br}$: C, 69.60; H, 5.45; Br, 14.04. Found: C, 70.22; H, 5.75; Br, 14.40. The compound is sparingly soluble in methanol and ethanol, very slightly soluble in acetone, and insoluble in non-polar solvents and water. The infrared spectrum of the compound closely resembles that of the parent diphosphine and shows the absence of phosphine-oxide impurities. Absorption maxima (cm^{-1}): 3070vw, 3055vw, 3040sh, 3005vw, 2985vw, 2880w, 2845w, 2730w, 1600w, 1595 w, 1495s, 1485s, 1455m, 1435vs (triplet), 1406m, 1338w, 1310w, 1280w, 1260w, 1195w, 1175w, 1150w, 1114vs, 1070w, 1025w, 995m, 930w, 870w, 845s, 832m, 806m, 765m, 755vs, 735vs, 720vs, 695vs, 670w, 580w, 522s, 503s, 488s, 480s, 464m, 435w, 408m, 350m, 340w, 326m.

1-diphenylphosphino, 1-benzylidiphenylphosphonium-methane bromide, $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}^+(\text{C}_6\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)]\text{Br}^-$ was prepared similarly to the ethane analog. The compound was obtained as white needles, m.p. 230-235°. *Anal.* Calcd. for $\text{C}_{32}\text{H}_{29}\text{P}_2\text{Br}$: C, 69.20; H, 5.26, Br, 14.39. Found: C, 69.54; H, 5.91; Br, 14.40. The infrared spectrum of the compound showed the absence of phosphine-oxide impurities. Absorption maxima (cm^{-1}): 3070 vw, 3046 vw, 3030 vw, 3000 vw, 2900 vw, 2885 w, 2854 w, 2780 vw, 2740 vw, 708 m sharp (C=O stretching of acetone), 1600 vw, 1595 vw, 1495 s, 1485 s, 1464 m, 1440 vs, 1414 w, 1365 s, 1228 m, 1150 w, 1128 m, 1112 m, 1070 w, 1030 w, 1000 vw, 870 s, 816 s, 790 w, 780 w, 755 w, 742 vs, 720 vw, 710 vw, 695 s, 530 w, 518 w, 505 w, 490 w, 474 w, 454 w, 365 vw, 328 vw. The compound is very slightly soluble in water; moderately soluble in methanol and

ethanol, sparingly soluble in acetone and tetrahydrofuran, insoluble in non-polar solvents. When the compound is recrystallized from acetone, an acetone solvate is obtained, as shown by the presence of a sharp strong absorption at 1708 cm^{-1} in the infrared spectrum.

The corresponding chloride, obtained similarly by monoquaternization of the diphosphine with benzylchloride, closely resembles the bromide salt in its properties.

Preparation of the Complexes. $[\text{NiCl}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$, $[\text{NiBr}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ and $[\text{NiI}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$. The bromo-complex was prepared by adding a slight excess of NiBr_2 in ethanol-triethylorthoformate (10%) solution to a warm suspension of the ligand bromide in acetone and triethylorthoformate (10%). The mixture was gently warmed for 10 min; the bright turquoise crystalline precipitate which formed was filtered, washed with an acetone-triethylorthoformate (10%) mixture, and dried *in vacuo*. Yield, 95%, calculated on the ligand. *Anal.* Calcd. for $\text{C}_{33}\text{H}_{31}\text{P}_2\text{Br}_3\text{Ni}$: Ni, 7.45; Br, 30.42; C, 50.30; H, 3.97. Found: Ni, 7.51; Br, 29.80; C, 50.93; H, 4.20. The compound decomposes above 280° and is paramagnetic, with $\mu_{\text{eff}} = 3.54$ B.M. at room temperature. The infrared spectrum is very similar to that of the free ligand bromide. The complex is insoluble in ethanol, methanol, acetone and non-polar solvents; it dissolves slightly, with partial solvation, in some polar solvents (e.g. nitromethane, dimethylformamide, acetonitrile), and in contact with water the complex decomposes with the separation of the insoluble white ligand bromide.

The chloro-complex, $[\text{NiCl}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$, (fine blue crystals) was prepared as described for the bromo-complex, using as the starting materials the ligand bromide, nickel(II) chloride, and a ten-fold excess of LiCl . *Anal.* Calcd. for $\text{C}_{33}\text{H}_{31}\text{P}_2\text{Cl}_3\text{Ni}$: Ni, 8.97; Cl, 16.20. Found: Ni, 9.0; Cl, 16.18. The iodo-complex $[\text{NiI}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ (dark brown powder) was obtained similarly using as the starting materials the ligand bromide, an anhydrous solution of nickel(II) iodide and a ten-fold excess of LiI . *Anal.* Calcd. for $\text{C}_{33}\text{H}_{31}\text{P}_2\text{I}_3\text{Ni}$: Ni, 6.32; I, 40.98. Found: Ni, 6.02; I, 41.3. The solubility patterns and infrared spectra of these complexes were identical to those of the bromo-complex. The infrared spectrum of the chloro-complex, however, showed two additional absorptions, at 313 (s) and 282 (m) cm^{-1} , which are assigned to the two expected Ni-Cl stretching vibrations. $[\text{CoCl}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$, $[\text{CoBr}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ and $[\text{CoI}_3(\text{PCH}_2\text{CH}_2\text{P}^+)]$ were prepared similarly to corresponding Ni^{II} complexes, except that the cobalt(II) halides were dissolved in a mixture of acetone-triethylorthoformate (10%). The bromo-complex obtained as a blue crystalline powder decomposes above 270° , is paramagnetic at room temperature (μ_{eff} , 4.50 B.M.) and has the same infrared spectrum and solubility pattern as the corresponding Ni^{II} complex. *Anal.* Calcd. for $\text{C}_{33}\text{H}_{31}\text{P}_2\text{Br}_3\text{Co}$: Co, 7.48; Br, 30.41. Found: Co, 7.25; Br, 30.95. The chloro-complex (fine blue needles), and the iodo-complex (chartreuse-brown powder) were obtained similarly. *Anal.* Calcd. for $\text{C}_{33}\text{H}_{31}\text{P}_2\text{Cl}_3\text{Co}$: Co, 9.00; Cl, 16.24. Found: Co,

9.30; Cl, 16.56. Calcd. for $C_{33}H_{31}P_2I_3Co$: Co, 6.34; I, 40.97. Found: Co, 6.08; I, 41.50. The infrared spectrum of the chloro-complex shows two medium-strong absorptions at 322 and 312 cm^{-1} , which are not present in either the free ligand or the bromo- and iodo-complexes, and are assigned to the Co—Cl stretching vibrations.

$[NiCl_3(PCH_2P^+)]$, $[NiBr_3(PCH_2P^+)]$, $NiI_3(PCH_2P^+)$ were obtained as the solvates, usually with 1 mole of acetone. The chloro-complex was prepared by the dropwise addition, with stirring, of a saturated solution of $NiCl_2$ in acetone-triethylorthoformate (10%) to a warm suspension of the ligand chloride in the same solvent. The ligand gradually dissolved as the Ni^{II} solution was added. From the clear greenish-blue solution, well-formed greenish-blue crystals separated after several hours. *Anal.* Calcd. for $[NiCl_3(PCH_2P^+)] \cdot CH_3COCH_3 = C_{35}H_{35}OP_2Cl_3Ni$: Ni, 8.43; Cl, 15.27. Found: Ni, 8.70; Cl, 15.00. The complex does not lose acetone on heating at 100° for 1 day; it decomposes above 250°. It is insoluble in non-polar solvents; moderately soluble with extensive solvation in acetone, nitromethane, tetrahydrofuran and other polar solvents. In highly polar solvents such as water, methanol, and ethanol the complex decomposes completely. The infrared spectrum of the complex is almost identical to that of the acetone solvate of the parent ligand chloride, except that the strong absorption arising from the C=O stretching vibration of the acetone is split into a doublet, with maxima at 1714 and 1704 cm^{-1} . (No appreciable shift of the midpoint of the band was observed). Also, two new strong absorptions appear at 322 and 302 cm^{-1} , which are assigned to the Ni—Cl stretching modes. The bromo-complex (bright-green prisms) was prepared similarly from the ligand bromide and nickel(II) bromide in acetone-triethylorthoformate solution. *Anal.* Calcd. for $C_{35}H_{35}OP_2Br_3Ni$: Ni, 70.07. Found: Ni, 6.85. The iodo-complex (dark greenish-brown prisms) was obtained in a similar manner from the ligand bromide and nickel(II) iodide in the presence of ten-fold excess of lithium iodide. *Anal.* Calcd. for $C_{35}H_{35}OP_2I_3Ni$: Ni, 6.05; Found: Ni, 5.85. $[NiCl_3(PCH_2P^+)]$ was obtained free from acetone by reacting the ligand chloride, in the presence of a ten-fold excess of LiCl, in a mixture of tetra-

hydrofuran and triethylorthoformate. Deep blue well-formed prisms separated after several days at room temperature. *Anal.* Calcd. for $C_{32}H_{29}P_2Cl_3Ni$: Ni, 9.19; Cl, 16.65. Found: Ni, 9.09; Cl, 16.78. The infrared spectrum of the blue crystals showed no absorption in the C=O stretching region; otherwise it was identical with that of the greenish-blue solvate $[NiCl_3(PCH_2P^+)] \cdot (CH_3)_2CO$.

$[CoCl_3(PCH_2P^+)]$ (fine bright blue needles) and $[CoBr_3(PCH_2P^+)]$ (well-formed blue prisms) were obtained as acetone solvates similarly to the corresponding nickel(II) complexes which they closely resemble in solubility, thermal stability and infrared spectra. *Anal.* Calcd. for $C_{35}H_{35}OP_2Cl_3Co$: Co, 8.45; Cl, 15.20. Found: Co, 8.39; Cl, 15.55. Calcd. for $C_{35}H_{35}OP_2Br_3Co$: Co, 7.10; Br, 28.87. Found: Co, 6.95; Br, 28.99. Calcd. for $C_{35}H_{35}OP_2I_3Co$: Co, 6.07. Found: Co, 6.28. In the infrared spectrum of the chloro-complex the Co—Cl stretching vibrations appear as a strong broad absorption with partly resolved maxima at 324 and 314 cm^{-1} .

Physical Characterization of the Complexes. *Vibrational spectra* were recorded in the 4000-250 cm^{-1} range, using a Perkin-Elmer Model 521 Spectrophotometer equipped with a dry-air purge. Samples were examined both in Nujol and in hexachlorobutadiene mulls, using CsBr plates. *d-d Electronic spectra* of solid samples were recorded with a Cary Model 14 Spectrophotometer (30,000-4,000 cm^{-1} range) equipped with a diffuse reflectance attachment. Transmission spectra of nitromethane solutions were obtained using chlorobenzene and dichloromethane as solvents. *X-ray powder diffractographs* were taken using nickel-filtered $CuK\alpha$ radiation. *Magnetic susceptibilities* were measured by the Gouy method for powdered samples at room temperature. Diamagnetic corrections from Pascal's tables were used in the calculation of μ_{eff} .

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