Acknowledgments.—W. E. H. thanks the Continental Oil Co. for a fellowship and grant in support of this research, and the Woodrow Wilson Foundation, the National Science Foundation, and the Koppers Co. for fellowship support. The authors acknowledge their great debt to Professor Robert W. Parry for his association with certain preliminary portions of the work.

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Complexes of Ethylphosphine and Diethylphosphine with the Halides of Cobalt(II) and Zinc

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Received January 20, 1962

Calcium chloride does not react with ethylphosphine at 0° nor with diethylphosphine at 20°, but cobalt(II) and zinc halides give complexes of the types $CoX_2 \cdot C_2H_5PH_2$, $CoX_2 \cdot 2C_2H_5PH_2$, $CoX_2 \cdot 2(C_2H_5)_2PH$, $CoX_2 \cdot 4(C_2H_5)_2PH$, $ZnX_2 \cdot C_2H_5PH_2$, and $ZnX_2 \cdot 2(C_2H_5)_2PH$. These compounds are compared with the previously reported primary, secondary, and tertiary ethylamine complexes[2] and the triethylphosphine complexes.[3] The coördinating sequence $R_2PH > R_3P > RPH_2$ is observed, and interpreted in terms of a competition between polarized ion–dipole coördinate bonding and the energy required for expansion of the crystal lattice on coördination. Some spectral and magnetic data for the cobalt(II) complexes are presented.

Introduction

It has long been known that alkylation of phosphine by reaction of alkyl halides with phosphonium iodide in a sealed tube gives only tertiary phosphines and quaternary phosphonium salts unless zinc oxide is incorporated in the reaction mixture. Zinc oxide is converted into zinc iodide during the reaction, and in some manner the zinc iodide binds the primary and secondary alkylphosphine intermediates so that they subsequently can be obtained on hydrolysis of the reaction product.[4] This preparative method has been superseded in practice.[5] It was suggested that the primary and secondary phosphines were removed from the reaction zone by formation of double salts of their phosphonium iodides with zinc iodide. Another possibility could be formation of primary and secondary phosphine–zinc coördination compounds.

While tertiary phosphines are common ligands in coördination chemistry, very little work has been done with primary and secondary phosphines. Satisfactory preparative methods for these bases have been developed recently.[5] The compounds are toxic–probably very much so although no information seems to be available[6]—and have the foul odor and property of spontaneous inflammability characteristic of volatile organic phosphines.[7] They are strong reducing agents and have more protonic acidic character than amines, so that it may be expected that coördination reactions might be complicated by oxidation–reduction or dehydrohalogenation reactions.

Brown[8] has compared the base strengths toward trimethylborane of primary, secondary, and tertiary amines and phosphines in developing his well known theories of steric strain, and similar studies with other Group III alkyl reference acids have been reported. The compounds $AlCl_3 \cdot C_2H_5PH_2$[5,9] and $BF_3 \cdot (CH_3)_2PH$[10] have been described. There have been two reports on transition metal complexes. The compound $CoCl_2 \cdot C_2H_5PH_2$ was prepared[5,9] by treating anhydrous cobalt(II) chloride with an excess of ethylphosphine and then pumping off the unreacted base *in vacuo*. The compounds $CoCl_2 \cdot 4(C_2H_5)_2PH$

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[1] Abstracted from the Ph.D. Dissertation submitted by W. E. Hatfield to the Graduate College, University of Arizona, 1962.

[2] W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

[3] W. E. Hatfield and J. T. Yoke, *ibid.*, **1**, 475 (1962).

[4] A. W. Hofmann, *Ber.*, **4**, 430, 605 (1871).

[5] J. T. Yoke, G. Kodama, and R. W. Parry, to be published.

[6] T. W. Hale, Medical Advisory Committee, Manufacturing Chemists' Association, private communication.

[7] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, New York, N. Y., 1950, Chapter 2.

[8] H. C. Brown, *J. Chem. Soc.*, 1250 (1956).

[9] J. T. Yoke, Dissertation, University of Michigan, 1954.

[10] E. Fletcher, Dissertation, Purdue University, 1952.

and $CoBr_2 \cdot 4(C_2H_5)_2PH$ were obtained[11] by crystallization of the anhydrous components in absolute alcohol. Under these conditions, dicyclohexylphosphine gave only a 2:1 complex with Co(II). The nickel halides behaved similarly. Cr(III) gave 3:1 complexes but Fe(III) was reduced to Fe(II) which gave only 2:1 complexes.

In the present work, the reference acids calcium, cobalt(II), and zinc ions were used as examples of the 8, incomplete, and 18-electron configurations in an investigation of the coördinating abilities of mono- and diethylphosphine. Similar studies have been reported for the primary, secondary, and tertiary ethylamines[2] and for triethylphosphine and triethylarsine.[3]

Experimental

Reagents.—The preparation of the anhydrous metal halides has been described previously.[2]

Ethylphosphine was prepared by the reduction of diethyl ethylphosphonate (Virginia-Carolina Chemical Co., research sample, redistilled) with lithium aluminum hydride (Metal Hydrides Inc.) in diglyme (Ansul Chemical Co. ether no. 141, redistilled, b.p. 158–160° uncor.). By analogy with previous work,[5] the reactions are presumed to be

$$4C_2H_5P(O)(OC_2H_5)_2 + 5LiAlH_4 = LiAl(PHC_2H_5)_4 + 8H_2 + 4LiOC_2H_5 + 4Al(O)(OC_2H_5)$$

$$LiAl(PHC_2H_5)_4 + 4LiOC_2H_5 + 4Al(O)(OC_2H_5) + 16H_2O = 4C_2H_5PH_2 + 8C_2H_5OH + 5LiOH + 5Al(OH)_3$$

A 200-ml. quantity of diglyme and 10 g. (0.26 mole) of $LiAlH_4$ were placed in a 1-l. 3-neck flask fitted through standard taper joints with a dropping funnel with a pressure equalizing side arm, a mechanical stirrer, and a cold finger condenser leading to the atmosphere through a train consisting of a U trap immersed in liquid nitrogen, a safety trap, a mineral oil bubbler, and a sulfuric acid bubbler. The system was flushed with nitrogen, purified as described previously,[2] which entered through the top of the dropping funnel. A solution of 9.7 g. (0.060 mole) of diethyl ethylphosphonate in 50 ml. of diglyme was added over a period of 1 hr. The reaction mixture was allowed to stand overnight. It then was hydrolyzed by dropwise addition of a 50% solution of water in diglyme through the dropping funnel, with a stream of nitrogen passing through the apparatus. The ethylphosphine was swept into the U trap cooled in liquid nitrogen. After hydrolysis was complete, the reaction flask was warmed to drive over the final portions of ethylphosphine.

Stopcocks on each arm of the U trap then were closed and the trap was attached to the vacuum line by means of a standard taper joint. The crude product was fractionated in the vacuum system until a tensiometrically homogeneous middle portion was obtained whose vapor pressures over a range of temperatures agreed with the literature[5] values.

Since tertiary phosphines can be conveniently stored as their silver iodide complexes, an experiment was performed to see if ethylphosphine would make a similar compound. A solution of ethylphosphine in ether was shaken with a solution of silver iodide in aqueous potassium iodide. A precipitate did not form and after several days the stoppered flask contained a silver mirror and a black solid.

Diethylphosphine was prepared by the reduction of tetraethyldiphosphine disulfide with lithium aluminum hydride in diglyme following the method of Issleib and Tzschach.[12] Tetraethyldiphosphine disulfide was prepared by the reaction of ethyl magnesium bromide, prepared as described previously,[3] with thiophosphoryl chloride (Victor Chemical Co. research sample, redistilled). The reactions are taken to be

$$2P(S)Cl_3 + 6C_2H_5MgBr = (C_2H_5)_2P(S){-}P(S)(C_2H_5)_2 + MgBrCl + C_4H_{10}$$

$$2(C_2H_5)_2P(S){-}P(S)(C_2H_5)_2 + 3LiAlH_4 = LiAl[P(C_2H_5)_2]_4 + Li_2S + Al_2S_3 + 6H_2$$

$$LiAl[P(C_2H_5)_2]_4 + Li_2S + Al_2S_2 + 12H_2O = 4(C_2H_5)_2PH + 4H_2S + 3LiOH + 3Al(OH)_3$$

The Grignard reagent was prepared from 18 g. (0.75 g.-atom) of magnesium and 82 g. (0.75 mole) of ethyl bromide in 600 ml. of ether. With the reaction flask cooled in running water, a solution of 43 g. (0.25 mole) of thiophosphoryl chloride in 100 ml. of ether was added over a 6-hr. period. After standing overnight, the reaction mixture was brought to reflux for 1 hr., cooled, and hydrolyzed with 10% H_2SO_4 to give two clear layers. The ether portion was worked up in the usual way to give an oily product which crystallized on cooling. The tetraethyldiphosphine disulfide was recrystallized from acetone–water; yield 79%, m.p. 76°, lit. 76–77°.

A 24-g. quantity of this reagent, dissolved in the minimum amount of diglyme, was added over a period of 1 hr. to 10.0 g. of $LiAlH_4$ in 100 ml. of diglyme. The reaction mixture then was heated on a water bath for 1 hr. and stirred for 4 hr. at room temperature. It then was hydrolyzed with freshly boiled distilled water and the resulting mixture was allowed to stand overnight. An atmosphere of nitrogen was maintained at all stages of the reaction.

The reaction flask then was attached to the vacuum line and evacuated. Diethylphosphine and water distilled from the flask and were condensed in a liquid nitrogen-cooled finger. The frozen mixture was allowed to warm and melt, forming two liquid layers. The finger was rotated about a joint and the liquids flowed into a separatory vessel. The lower water layer was drained off, and the diethylphosphine was transferred through the vacuum system to a bulb containing anhydrous sodium sulfate as a drying agent.

The diethylphosphine then was fractionated in the vacuum system to give a tensiometrically homogeneous middle portion whose vapor pressure–temperature relation agreed with the previously reported values.[5]

Preparation and Study of Complexes.—The coördination reactions were observed in the course of an isothermal study of pressure as a function of composition in the base–salt systems. An excess of the pure alkylphosphine was

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[11] K. Issleib and G. Döll, *Z. anorg. allgem. Chem.*, **305**, 1 (1960).

[12] K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 704 (1959).

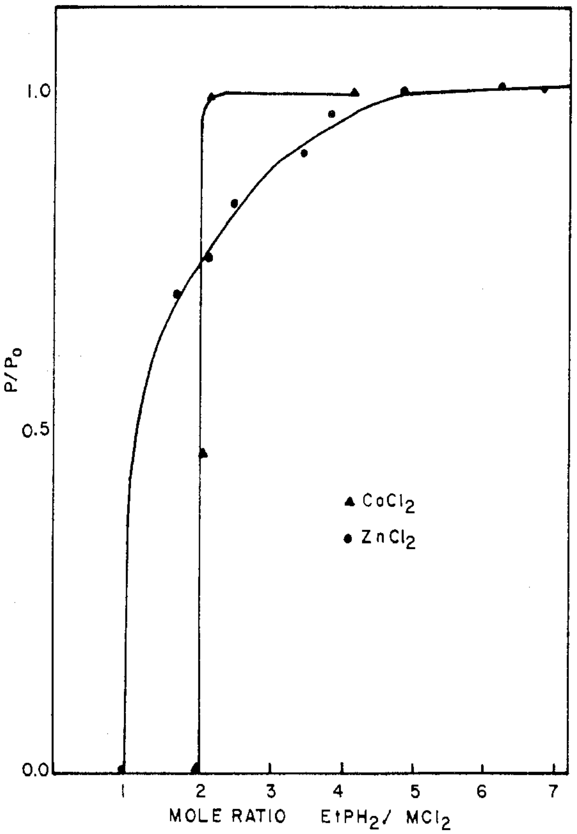

Fig. 1.—0.0° isotherm, ethylphosphine with $CoCl_2$ and $ZnCl_2$.

condensed onto a sample of each anhydrous metal halide in a tared tube attached to a high vacuum line. Portions of the volatile base then were removed by distillation in the vacuum system. The pressures were measured at 0.0° in the ethylphosphine systems and at 20.0° in the diethylphosphine systems. The details of the experimental method have been described.[2]

Calcium chloride and an excess of ethylphosphine, or of diethylphosphine, were equilibrated for several hours. Each base then could be quickly and quantitatively recovered, indicating that there was no complex formation in either case.

The 0.0° pressure–composition phase diagrams for the ethylphosphine systems with cobalt(II) and zinc chlorides are shown in Fig. 1.

Liquid ethylphosphine reacts quickly and vigorously with anhydrous cobalt(II) chloride, with a severalfold increase in the volume of the solid. The pressure of ethylphosphine becomes negligibly small at a base:salt mole ratio of 2.0, indicating the formation of the new compound dichlorobis-(ethylphosphine)-cobalt(II). *Anal.* Mole ratio $C_2H_5PH_2$:$CoCl_2$ found 1.98; % C found 19.0, calcd. 18.9; % H found 5.72, calcd. 5.55.[13] In agreement with the previous report,[5,9] it was found that one-half of the ethylphosphine content of this compound is easily removable by pumping, so as to give the complex $CoCl_2 \cdot C_2H_5PH_2$.

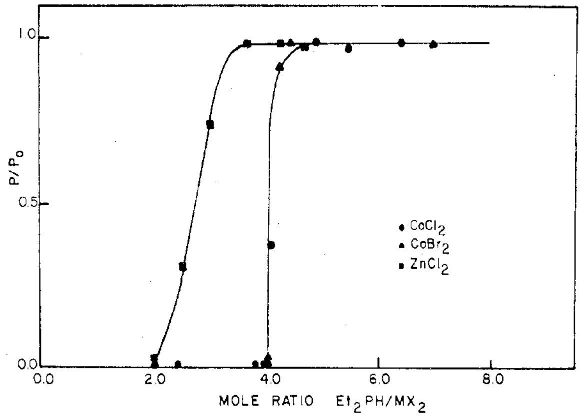

Fig. 2.—20.0° isotherm, diethylphosphine with $CoCl_2$, $CoBr_2$, and $ZnCl_2$.

However, after the 2:1 complex stood for some time this behavior could no longer be observed.

Anhydrous zinc chloride dissolves completely in an excess of liquid ethylphosphine, and the pressure of the system drops to a negligibly small value at a mole ratio of 1.0. The compound, dichloroethylphosphine-zinc(II), is soft, spongy, and doubtless di- or polymeric so as to contain tetracoördinate zinc. *Anal.* Mole ratio $C_2H_5PH_2$: $ZnCl_2$ found 0.99.

The 20.0° pressure–composition phase diagrams for the diethylphosphine systems with zinc chloride and cobalt(II) chloride and bromide are shown in Fig. 2.

Liquid diethylphosphine also reacts vigorously with anhydrous cobalt(II) halides with severalfold expansion of the solids. The isotherms indicate formation of the compounds dichloro- and dibromotetrakis-(diethylphosphine)-cobalt(II), agreeing with the solution work of Issleib and Döll.[11] These green compounds are unstable toward air. The chloride fumes when exposed to the air; the bromide does not fume but a sample showed signs of decomposition after storage for 2 days in a screw-cap bottle.

Although the dissociation pressure of $CoCl_2 \cdot 4(C_2H_5)_2PH$ is too small to be measured on a mercury manometer, it was found that a sample of the compound easily lost one-half of its content of diethylphosphine when the trap containing it was opened directly to the vacuum line pumping system at room temperature. In this way the new compound, $CoCl_2 \cdot 2(C_2H_5)_2PH$, a black-green paste, was obtained. *Anal.* Mole ratio $(C_2H_5)_2PH$:$CoCl_2$ found 2.06; % Cl found 21.0, calcd. 22.9.

Anhydrous zinc chloride dissolves completely in an excess of liquid diethylphosphine, and the pressure of this system drops to a negligible value at a base:salt mole ratio of 2.0. The product, dichlorobis-(diethylphosphine)-zinc(II), is a colorless oil. *Anal.* Mole ratio $(C_2H_5)_2PH$:$ZnCl_2$ found 1.95; % Cl found 20.7, calcd. 22.4.

Analytical.—Halide analyses were by the Volhard method. Values of the mole ratio base:salt were determined by weighing the tared reaction tube at the point at which the pressure became negligibly small, as described previously.[2]

Magnetic Moments and Spectra.—The room temperature magnetic susceptibility of $CoCl_2 \cdot 2C_2H_5PH_2$ was determined by the Gouy technique, and the magnetic moment was calculated as described previously.[2] A value

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(13) Carbon and hydrogen microanalyses by Alfred Bernhardt, Mikroanalytisches Laboratorium im Max Planck Institut für Kohlenforschung, Müllheim (Ruhr), Germany.

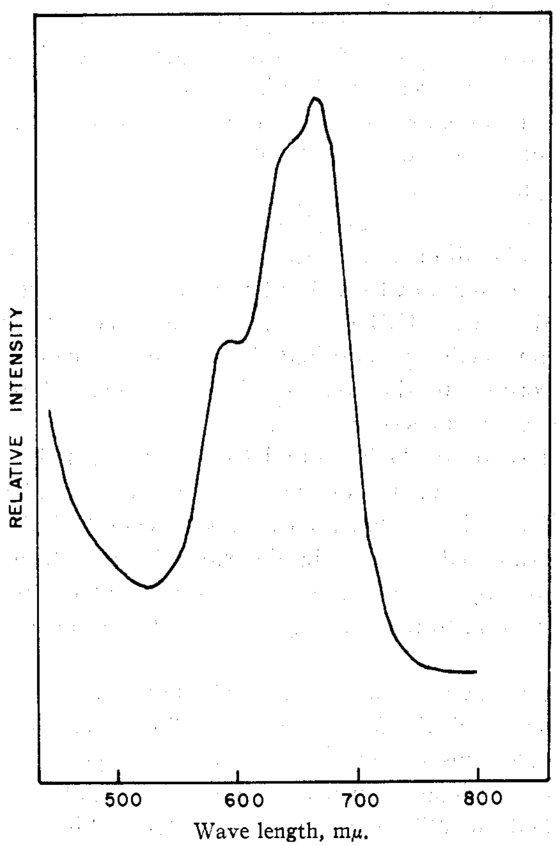

Fig. 3.—Spectrum of $CoCl_2 \cdot 2(C_2H_5)_2PH$ in benzene.

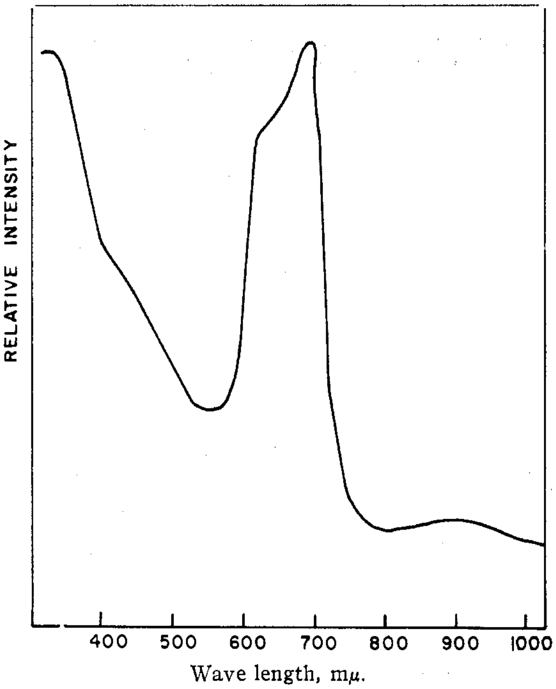

Fig. 4.—Reflectance spectrum of $CoCl_2 \cdot 2C_2H_5PH_2$.

for μ_{eff} of 4.30 B.M. was found. The absorption spectrum of a benzene solution of $CoCl_2 \cdot 2(C_2H_5)_2PH$ was obtained using a Cary Model 11 recording spectrophotometer and is shown in Fig. 3. The reflectance spectra were obtained as described previously[2] and are given for $CoCl_2 \cdot 2C_2H_5PH_2$ and for $CoBr_2 \cdot 4(C_2H_5)_2PH$, respectively, in Fig. 4 and 5.

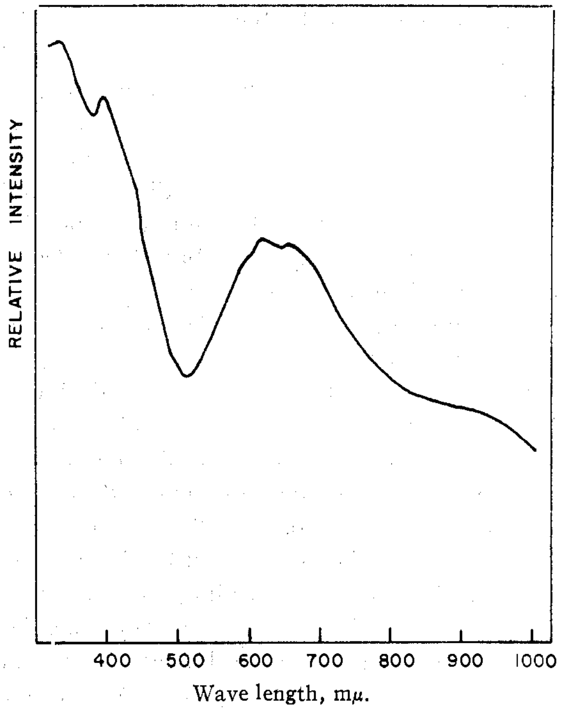

Fig. 5.—Reflectance spectrum of $CoBr_2 \cdot 4(C_2H_5)_2PH$.

Discussion

Calcium chloride does form a stable 2:1 complex with ethylamine,[2] as well as higher ethylamine complexes with appreciable dissociation pressures, but it does not react with ethylphosphine. Similarly, zinc chloride binds two molecules of ethylamine in a stable complex,[2] but only one molecule of ethylphosphine. The stoichiometry of coördination depends on lattice energy terms as well as on coördinate bond energy.[3] The smaller molar volume of ethylamine and its slightly higher permanent dipole moment (1.3 D. as opposed to 1.17 D. for ethylphosphine[14]) cause the amine to have a higher apparent coördinating tendency toward calcium and zinc chlorides. In the field of the poorly shielded d^7 cobalt(II) ion, the importance of the induced dipole contribution to the total dipole moment is greatly increased, allowing the much more polarizable ethylphosphine to become equivalent to ethylamine. This is seen in the fact that both bases give stable 2:1 complexes.

Increasing the degree of alkyl substitution on

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(14) R. W. Parry and R. N. Keller, "Chemistry of the Coordination Compounds," J. S. Bailar, ed., Reinhold Publishing Co., New York, N. Y., chapter 3.

nitrogen is unfavorable both in lowering the permanent and induced contributions to the total dipole moment in the ion–dipole attraction term and in increasing the molar volume and hence the energy required for expansion of the metal salt lattice. It was found[2] that with two ethyl groups on nitrogen cobalt(II) and zinc chlorides still give stable 2:1 complexes but that calcium chloride no longer reacts. With three ethyl groups on nitrogen, only cobalt(II) is coördinated and only 1:1 complexes are formed.

One would expect that increasing the degree of alkyl substitution on phosphorus would increase the ion–dipole attraction, since the permanent dipole moment is considerably increased and the large polarizability is only slightly decreased.[14] In opposition to this trend would be the increase in molar volume of the ethylphosphines, presumably appearing in the difference in lattice energies of the simple and complex salts rather than in lack of availability of the lone pair of electrons for donation.

This simple model is in excellent accord with the maximum in coördinating ability observed with substitution of two ethyl groups on phosphorus. It has been shown[3] that stable 2:1 complexes are the only compounds formed in the triethylphosphine–cobalt(II) halide systems. Ethylphosphine forms both 1:1 and 2:1 complexes. Thus, all three ethylphosphines form stable 2:1 complexes, but in addition diethylphosphine gives a 4:1 complex, seen in the phase diagram of the two component system and also prepared in solution by Issleib and Döll.[11]

The magnetic moments of 4.30 and 4.39 B.M. found for $CoCl_2 \cdot 2C_2H_5PH_2$ and $CoCl_2 \cdot 2(C_2H_5)_3P$,[3] and the absorption in the 600–700 mμ region observed for $CoCl_2 \cdot 2C_2H_5PH_2$, $CoCl_2 \cdot 2(C_2H_5)_2PH$, and $CoCl_2 \cdot 2(C_2H_5)_3P$,[3] suggest that cobalt(II) is tetrahedrally coördinated in these compounds, according to the considerations put forward by Cotton and his co-workers.[15]

Issleib and Döll[11] found $CoBr_2 \cdot 4(C_2H_5)_2PH$ to have a magnetic moment of 1.97 B.M. This value indicates that the Co(II) ion is octahedrally coördinated and can be described by the strong field approximation with allowance made for distortion to remove degeneracy in the e_g levels.

Acknowledgment.—W. E. H. thanks the Continental Oil Co. for a grant and fellowship in support of this research, and also the Koppers Co., the National Science Foundation, and the Woodrow Wilson Foundation for fellowship support.

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(15) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961), and references therein.