Table VIII. Electron Exchange Rate Constants for Sm(II), Yb(II), and Eu(II)

Reaction	k_{obsd},[a] M^{-1} sec^{-1}	$k = k_{\text{act}}$,[a] M^{-1} sec^{-1}	k_{11},[b] M^{-1} sec^{-1}	K_{12}	k_{22}(calcd), M^{-1} sec^{-1}
$Ru(NH_3)_6{}^{3+}$ + Sm(II)	3.5×10^6	3.6×10^6	8.2×10^2	9.2×10^{27}	5×10^{-12}
$Ru(NH_3)_6{}^{3+}$ + Yb(II)	5.7×10^5	5.6×10^5	8.2×10^2	1.5×10^{21}	3×10^{-9}
$Ru(NH_3)_6{}^{3+}$ + Eu(II)	1.1×10^2	1.1×10^2	8.2×10^2	9.6×10^8	1×10^{-7}

[a] At $\mu \to 0$. [b] T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_{\text{act}}} = \frac{1}{k_{\text{diff}}} \qquad \text{(II)}$$

The activation-controlled rate constant (k_{act}) is the one calculated by eq I. The diffusion-controlled rate constant (k_{diff}) was calculated using the Debye equation.[27]

The value obtained is 1.1×10^8 M^{-1} sec^{-1}. As this calculated value is given for zero ionic strength, the observed values k_{obsd} for $RuNH_3{}^{3+}$ were corrected accordingly using Davies' equation[28] (Table VIII); thus, only k_{act} for Sm(II) was corrected by eq II (Table VIII). The calculated values of k_{22} (Table VIII) show that the rate of electron transfer between the lanthanide ions is very slow and reflect the fact that the exchanging electron of these ions is in an f orbital. The k_{22} value for the Eu(II)-Eu(III) couple is in good agreement with that of Meier and Garner.[29]

Knowing the k_{22} value, it is possible to calculate the specific rate constants of the Ln(II) ions studied with the $Co(NH_3)_6{}^{3+}$ complexes. Assuming a value of 1×10^{-9} M^{-1} sec^{-1} for the exchange reaction of the $Co(NH_3)_6{}^{3+}$-$Co(NH_3)_6{}^{2+}$ couple,[4] the values obtained are 33, 3, and 2×10^{-4} M^{-1} sec^{-1} for Sm(II), Yb(II), and Eu(II), respectively. The result obtained for Eu(II) is in agreement with the accepted value.[9] These low values corroborate the fact that in the pulse radiolytic measurements these reactions could not be followed.

Registry No. Table I RF^{2+}, 36126-23-5; RCl^{2+}, 15156-18-0; RBr^{2+}, 14591-65-2; RI^{2+}, 14972-83-9; $RN_3{}^{2+}$, 14283-04-6; $RCNS^{2+}$, 15663-42-0; ROH^{2+}, 18885-27-3; RH_2O^{3+}, 13820-81-0; $RNH_3{}^{3+}$, 13820-83-2; $[Co(en)_3]^{3+}$, 14977-29-8; RCN^{2+}, 14216-98-9. Table II $RuCl^{2+}$, 36273-18-4; $RuBr^{2+}$, 36273-19-5; RuI^{2+}, 36273-20-8; $RuOH^{2+}$, 36388-18-8; RuH_2O^{3+}, 36273-21-9; $RuNH_3{}^{3+}$, 36273-22-0. Eu, 7440-52-0; Yb, 7440-64-4; Sm, 7440-19-9.

Acknowledgments. The authors wish to thank Miss A. Amozig for the preparation and the analysis of the complexes and Mr. Y. Ogdan for his careful operation of the linear accelerator.

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[28] C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

[29] D. J. Meier and C. S. Garner, *J. Phys. Chem.*, 56, 853 (1952).

Notes

Contribution from the Department of Chemistry, The University
of Texas at Arlington, Arlington, Texas 76010

Preparation of Dimethylaminodimethylphosphine and Cleavage to Dimethylcyanophosphine by Hydrogen Cyanide[1]

Edward A. Dietz, Jr., and Donald R. Martin*

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The compound $(CH_3)_2PCN$ has been prepared recently by the action of AgCN on $(CH_3)_2PCl$ in acetonitrile.[2] The success of the reactions of HX (where X is Cl, Br, or I) with $(CH_3)_2NP(CH_3)_2$ to produce the corresponding alkylhalophosphines[3,4] suggested the analogous cleavage by HCN

$$(CH_3)_2NP(CH_3)_2 + 2HCN \rightarrow (CH_3)_2PCN + (CH_3)_2NH_2CN$$

Present work utilizing ^1H nmr data and vacuum-line manipulation shows that this reaction proceeds as written providing good yields of the cyanophosphine. Dialkylaminophosphines can be obtained by the alkylation of dialkylaminochlorophosphines with Grignard reagents,[3,5] alkylaluminum compounds,[6] or organolithium reagents;[7,8] however, the only reported synthesis of $(CH_3)_2NP(CH_3)_2$ employed CH_3MgBr and $(CH_3)_2NPCl_2$.[3] We have found this procedure to be optimum after studying the reactions of the methylating agents CH_3MgX (where X is Cl, Br, or I) and CH_3Li with either $(CH_3)_2NPCl_2$ or $(CH_3)_2NPBr_2$.

Experimental Section

General Information. All reactions were conducted under either high-vacuum conditions or a dry nitrogen atmosphere using anhydrous, freshly purified materials. Infrared spectra were recorded using a Beckman Model 257 spectrophotometer operating from 4000 to 625 cm^{-1}. Proton magnetic resonance data were obtained with a Varian Associates T-60 nmr spectrometer at 37° using tetramethylsilane dissolved in the sample for reference.

Materials. Diethyl ether solutions of CH_3MgBr and CH_3Li and a tetrahydrofuran solution of CH_3MgCl were supplied by Alfa Inorganics, while CH_3MgI was prepared by standard methods. Hydrogen cyanide prepared from KCN and H_2SO_4 was purified by vacuum fractionation using −63, −78, −83, and −196° cold traps. Pure HCN was retained at −83° as indicated by infrared, vapor pressure, and molecular weight data.

Dimethylaminodichlorophosphine.[3] To 267 g of PCl_3 dissolved in 164 g of pyridine and 650 ml of Et_2O at 0° was slowly added, with stirring, a solution of 90 g of $(CH_3)_2NH$ in 300 ml of Et_2O. The $(CH_3)_2NPCl_2$ was isolated by distillation under reduced pressure followed by distillation under atmospheric pressure. The boiling range of the product was observed to be 149-152°. *Anal.* Calcd for

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[1] The authors are grateful for the support of this research by The Robert A. Welch Foundation.

[2] C. E. Jones and K. J. Coskran, *Inorg. Chem.*, 10, 1536 (1971).

[3] A. B. Burg and P. J. Slota, Jr., *J. Amer. Chem. Soc.*, 80, 1107 (1958).

[4] A. B. Burg and R. I. Wagner, U. S. Patent 2,934,564 (1957); *Chem. Abstr.*, 54, 18437 (1960).

[5] K. Issleib and W. Seidel, *Chem. Ber.*, 92, 2681 (1959).

[6] L. Maier, *Helv. Chim. Acta*, 47, 2129 (1964).

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Table I.[a] Preparations of Dimethylaminodimethylphosphine

Reaction	Halophosphine	Methylating agent	Work-up	$(CH_3)_2NP(CH_3)_2$ yields, %	
				Run 1	Run 2
1	$(CH_3)_2NPCl_2$	CH_3Li	Warm to room temp, filter ppt, add 15 ml of diglyme to filtrate, then distil	26	16
2	$(CH_3)_2NPBr_2$	CH_3Li	Same as 1	9	10
3	$(CH_3)_2NPCl_2$	CH_3MgI	Warm to room temp, reflux for 1 hr, add 100 ml of diglyme, filter ppt, then distil filtrate	28	27
4	$(CH_3)_2NPBr_2$	CH_3MgI	Warm to room temp, add 100 ml of diglyme, filter ppt, then distil filtrate	0	0
5	$(CH_3)_2NPCl_2$[b]	CH_3MgBr	Warm to room temp, reflux for 1.5 hr, filter ppt, add 15 ml of diglyme to filtrate, then distil	38	30
6	$(CH_3)_2NPBr_2$	CH_3MgBr	Same as 3	Trace	Trace
7	$(CH_3)_2NPCl_2$	CH_3MgCl	Same as 5	12	15
8	$(CH_3)_2NPBr_2$	CH_3MgCl	Same as 3	Trace	2

[a] All reactions were conducted at −25° using 0.125 mol of halophosphine in 160 ml of Et_2O and 0.25 mol of methylating agent. Except for reactions 1, 2, and 4 which gave yellow solutions and solids, all systems produced colorless solutions and white precipitates. [b] This reaction served as a model for the others so an additional run was carried out yielding 37% $(CH_3)_2NP(CH_3)_2$.

$(CH_3)_2NPCl_2$ (Volhard method after hydrolysis at 0°): Cl, 48.6. Found: Cl, 48.3.

Dimethylaminodibromophosphine.[7] Following the above methods, a mixture containing 637 g of PBr_3, 650 ml of Et_2O, and 189 g of pyridine was allowed to react with 108 g of $(CH_3)_2NH$ in 300 ml of Et_2O. The product was isolated by distillation at 0.6 ± 0.2 mm with a boiling range of 27.5-29.0°. *Anal.* Calcd for $(CH_3)_2NPBr_2$ (Volhard method after hydrolysis at 0°): Br, 68.1. Found: Br, 67.8.

Synthesis of Dimethylaminodimethylphosphine. The reaction of $(CH_3)_2NPBr_2$ with CH_3Li will be described as an example of the reactions presented in Table I.

To a 500-ml three-necked flask equipped with a Dry Ice condenser, dropping funnel, and stirrer was added a solution of 0.125 mol (18 ml) of $(CH_3)_2NPBr_2$ in 160 ml of Et_2O. With very rapid stirring and the flask maintained at −25°, 110 ml of 2.3 *M* CH_3Li solution was added rapidly (5 min) to the flask. With continued stirring the mixture was allowed to warm to room temperature to yield a clear light yellow solution and a fine light yellow precipitate. The solid was filtered on a fine-porosity fritted funnel and washed with 150 ml of Et_2O. To the filtrate was added 30 ml of diglyme (to facilitate distillation) followed by distillation to isolate the product. The crude product was collected from 100 to 103° and afforded a 9.6% yield (1.25 g) based upon the phosphorus-containing reactant. Final purification of this product for further studies was conducted by a high-vacuum fractionation from a −30 to a −50° cold trap. The $(CH_3)_2NP(CH_3)_2$ was characterized and its purity determined from vapor pressure,[3] infrared,[6] nmr,[9] and molecular weight data.

Synthesis of Dimethylcyanophosphine. Hydrogen cyanide (5.15 mmol) was condensed with $(CH_3)_2NP(CH_3)_2$ (2.61 mmol), warmed to room temperature for 10 min, cooled to 0°, and then fractionated using 0, −23, and −196° cold traps. In the −23° trap was retained $(CH_3)_2PCN$ (prolonged distillation allows the product slowly to pass the −23° trap) which was refractionated through 0, −23, and −196° cold traps. The vapor pressure of the pure $(CH_3)_2PCN$ was 1.5 mm at 0° and 6.6 mm at 22.5°. The product from this reaction was 0.19 g, representing 84% of the $(CH_3)_2NP(CH_3)_2$. *Anal.* Calcd for $(CH_3)_2PCN$ (Liebig method after hydrolysis at 0°): CN, 29.9. Found: CN, 29.9.

The material trapped at −196° from the first fractionation was warmed to −63° and opened to a −196° trap to remove traces of volatile impurities from the $(CH_3)_2NH_2CN$. In the −196° trap 0.12 mmol of $(CH_3)_2NH$ (identified by its infrared spectrum) was found and the −63° trap contained $(CH_3)_2NH_2CN$ as indicated by a vapor pressure[10] of 25.2 mm at 0°. The $(CH_3)_2NH_2CN$ was condensed (−196°) onto 15 g of NaOH pellets and allowed to react at 0° for 20 min to remove the HCN component. The released amine (2.57 mmol) then was recovered by fractionation through at −63° trap to a −196° trap. (Dimethylamine was identified by its ir spectrum.)

In a similar reaction the $(CH_3)_2PCN$ was isolated and condensed to an nmr tube with CH_3CN-TMS. Its nmr spectrum was recorded and exhibited a doublet 1.46 ppm downfield from TMS with a coupling constant of 4.6 Hz in agreement with published values.[2] In additional reactions, yields as high as 92% were obtained.

Discussion

The reaction of $(CH_3)_2NPCl_2$ with CH_3MgBr studied by Burg and Slota[3] gave a maximum yield of 48% $(CH_3)_2NP(CH_3)_2$ (eq 1). These authors proposed that facile methylation at the P-N bond of product and reactant would lead to lowered yields of $(CH_3)_2NP(CH_3)_2$ by formation of $P(CH_3)_3$ and methylchlorophosphines (eq 2-4).

$$2CH_3MgBr + (CH_3)_2NPCl_2 \rightarrow (CH_3)_2NP(CH_3)_2 + 2BrMgCl \qquad (1)$$

$$(CH_3)_2NP(CH_3)_2 + CH_3MgBr \rightarrow (CH_3)_3P + BrMgN(CH_3)_2 \qquad (2)$$

$$CH_3MgBr + (CH_3)_2NPCl_2 \rightarrow CH_3PCl_2 + BrMgN(CH_3)_2 \qquad (3)$$

$$2CH_3MgBr + (CH_3)_2NPCl_2 \rightarrow (CH_3)_2PCl + ClMgBr + BrMgN(CH_3)_2 \qquad (4)$$

If these side reactions result from P-N bond attack by the methylating reagent, then other reagents might show different reactivity toward the P-Cl and P-N bonds and be reflected in the yield of $(CH_3)_2NP(CH_3)_2$. As shown in Table I the Grignard and CH_3Li reagents do show a change but indicate even greater P-N attack than with CH_3MgBr. Since the P-Br bond is weaker than the P-Cl bond, methylation of $(CH_3)_2NPBr_2$ would be expected to favor P-Br over P-N attack more than would be the case with $(CH_3)_2NPCl_2$. Surprisingly, the results indicate the contrary and suggest alternate side reactions based upon exchange phenomenon.

Reorganization reactions between mixtures of phosphorus compounds are common. In the case of the halo and dialkylamino groups in three-coordinate phosphorus species, the exchange has been shown to be rapid and random[6,7,11]

$$(CH_3)_2NP(C_2H_5)_2 + PCl_3 \rightarrow (C_2H_5)_2PCl + (CH_3)_2NPCl_2$$

This characteristic of phosphorus compounds suggested the sequence represented below as partly or totally accounting

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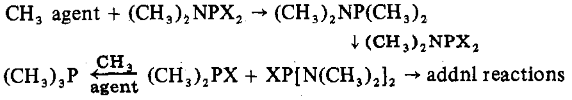
[9] H. Vahrenkamp and H. Noth, *J. Organometal. Chem.*, **12**, 281 (1968).

[10] Dimethylammonium cyanide has not been reported before; consequently, its properties were studied and will be published later. Pertinent to this discussion is the fact its vapor pressure at 0° is 25.0 mm with complete dissociation of the adduct in the vapor phase.

[11] J. R. Van Wazer and L. Maier, *J. Amer. Chem. Soc.*, **86**, 811 (1964).

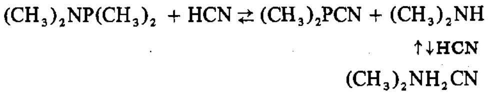
for the poor yields of $(CH_3)_2NP(CH_3)_2$ when methylating $(CH_3)_2NPCl_2$ or $(CH_3)_2NPBr_2$



$$\begin{array}{l} \mathrm{CH_3\ agent} + (\mathrm{CH_3})_2\mathrm{NPX_2} \rightarrow (\mathrm{CH_3})_2\mathrm{NP(CH_3)_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow (\mathrm{CH_3})_2\mathrm{NPX_2} \\ (\mathrm{CH_3})_3\mathrm{P} \xleftarrow[\text{agent}]{\mathrm{CH_3}} (\mathrm{CH_3})_2\mathrm{PX} + \mathrm{XP[N(CH_3)_2]_2} \rightarrow \text{addnl reactions} \end{array}$$

These types of reactions are consistent with present data which show the $(CH_3)_2NPBr_2$ system to be so reactive because of the weak P-Br bond that little $(CH_3)_2NP(CH_3)_2$ is obtained; whereas, the stronger P-Cl bond of $(CH_3)_2NPCl_2$ retards these side reactions slightly thus allowing for higher yields of $(CH_3)_2NP(CH_3)_2$.

The cleavage of $(CH_3)_2NP(CH_3)_2$ by HCN is synthetically useful and involves none of the contamination problems experienced with the cleavage by HCl.[3] Dissociation of the by-product,[10] $(CH_3)_2NH_2CN$, was expected to complicate the cleavage of $(CH_3)_2NP(CH_3)_2$ as shown in the equation



$$\begin{array}{l} (\mathrm{CH_3})_2\mathrm{NP(CH_3)_2} + \mathrm{HCN} \rightleftarrows (\mathrm{CH_3})_2\mathrm{PCN} + (\mathrm{CH_3})_2\mathrm{NH} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \uparrow\downarrow \mathrm{HCN} \\ \qquad\qquad\qquad\qquad\qquad\qquad (\mathrm{CH_3})_2\mathrm{NH_2CN} \end{array}$$

In this reaction the first mole of HCN cleaves $(CH_3)_2NP(CH_3)_2$ producing $(CH_3)_2NH$. The second mole of HCN removes $(CH_3)_2NH$ from the system. The cleavage was not affected by the dissociation of $(CH_3)_2NH_2CN$, however, and this was explained by nmr studies.

The cleavage reaction was observed with ^1H nmr spectroscopy by allowing various molar ratios of $HCN/(CH_3)_2NP(CH_3)_2$ (from 1/6 to 4) and $(CH_3)_2NH/(CH_3)_2PCN$ (from 1 to 2) to react. The product distributions then were found from the respective nmr signals which were independently found for each compound. These studies revealed that the cleavage of $(CH_3)_2NP(CH_3)_2$ proceeds almost totally with only 1 mol of HCN, while the product, $(CH_3)_2PCN$, reacts only slightly with $(CH_3)_2NH$ even at a 2/1 excess in contrast to other alkylhalophosphines. Thus, the second mole of HCN is not required but facilitates the reaction.

Registry No. $(CH_3)_2NP(CH_3)_2$, 683-84-1; HCN, 74-90-8; $(CH_3)_2PCN$, 31641-57-3.

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

A Novel Aminophosphonium Cationic Ligand and Its Cobalt(II) Chloride Complex[1]

Robert H. Marvich[2] and John T. Yoke*

Received March 30, 1972

Cationic ligands in metal complexes have been of continuing interest.[3] We report here a novel example of a saturated six-membered ring system, containing tertiary amine and quaternary phosphonium groups.[4] The cationic monodentate tertiary amine ligand hexahydro-1,4,4-triethyl-1,4-azaphosphorinium chloride and its cobalt(II) chloride complex are described.

Experimental Section

Air-sensitive materials were handled under nitrogen by Schlenk techniques.[5] Spectra were obtained with Cary 16, Beckman DK-2, and Perkin-Elmer 621 spectrophotometers. A Varian HA 100 spectrometer was used to obtain ^{31}P nmr spectra at 40.5 MHz. Magnetic susceptibility and conductivity measurements were made as previously described.[6] Chloride was determined by Mohr's method and cobalt was determined by potentiometric back-titration of potassium hexacyanoferrate(III). Equivalent weights were determined by potentiometric titration. Microanalyses were by Galbraith Laboratories, Knoxville, Tenn., and C. F. Geiger, Ontario, Calif.

Bis(2-chloroethyl)ethylamine Hydrochloride. A solution of 26.6 g (0.23 mol) of *N*-ethyldiethanolamine (Aldrich) in 30 ml of chloroform was added dropwise with stirring to a solution of 52.4 g (0.44 mol) of thionyl chloride in 100 ml of chloroform. The reaction mixture was heated at reflux for 1 hr and allowed to cool, and then 200 ml of ether was added. The white percipitate of bis(2-chloroethyl)ethylamine hydrochloride was filtered, washed with ether, and dried in air; mp 137-138°, lit.[7] 140-141°. It was not necessary to liberate the nitrogen mustard from its hydrochloride salt.

Diethylphosphine. Tetraethyldiphosphine disulfide was prepared[8] (68%) from ethylmagnesium bromide and thiophosphoryl chloride in ether, mp 74-77°, lit.[8] 76-77°. A 12.0-g (0.050-mol) quantity of tetraethyldiphosphine disulfide was suspended in 25 ml of freshly distilled diglyme in a flask fitted with a solids addition tube, stirrer, and a distilling head connected to a Schlenk receiving flask. The reaction flask was immersed in a cold water bath. Lithium aluminum hydride powder, 4.0 g, was slowly added to the stirred suspension under nitrogen. The reaction mixture was then maintained at 50° for 1 hr. The diethylphosphine[9] was then distilled (84-88°) into the ice-cooled receiving flask.

Hexahydro-1,4,4-triethyl-1,4-azaphosphorinium Chloride Hydrochloride Monohydrate. A 10.7-g (0.052-mol) quantity of bis(2-chloroethyl)ethylamine hydrochloride and 40 ml of chlorobenzene were added under nitrogen to 0.10 mol of diethylphosphine in the Schlenk flask, which was fitted with a condenser. The reaction mixture was maintained at reflux for 22 hr. The volatile solvent was then removed at a reduced pressure. The white solid residue was recrystallized in air from ethanol-ether, giving fluffy crystals, yield 7.3 g (52.5%); mp 268° dec. ^{31}P nmr (H_2O): −22.2 ppm *vs.* external H_3PO_4. Ir (Nujol) (cm^{-1}): 3470 vs (H_2O), 3400 vs (NH^+), 3230 m, 2450 s, 1620 s (H_2O), 1280 m, 1265 s, 1218 s, 1170 m (NH^+), 1105 s, 1050 s, 1035 m, 1025 m, 950 s, 935 s, 890 s, 830 s (NH^+), 815 s, 785 s, 745 m, 735 m. The compound is soluble in water and alcohol, slightly soluble in acetone, and insoluble in ether, chloroform, and hydrocarbons. *Anal.* Calcd for $C_{10}H_{24}NPCl_2 \cdot H_2O$: C, 43.17; H, 9.42; N, 5.03; P, 11.14; Cl, 25.5; equiv wt 278. Found: C, 43.45; H, 9.18; N, 5.14; P, 10.50; Cl, 25.9; equiv wt 296.

Cobalt(II) Chloride Complex. A solution of 7.74 mmol of sodium ethoxide in 20 ml of ethanol was added under nitrogen to 0.873 g (3.01 mmol) of hexahydro-1,4,4-triethyl-1,4-azaphosphorinium chloride hydrochloride monohydrate in a 50-ml Schlenk flask. A precipitate of sodium chloride formed. The mixture was heated to reflux briefly and then filtered through Celite into a solution of 0.692 g (5.33 mmol) of anhydrous cobalt(II) chloride in 35 ml of ethanol under nitrogen in a 50-ml Schlenk flask. The mixture was refluxed for 1 hr and filtered hot through Celite. The dark blue filtrate was cooled in an ice bath and filtered to give royal blue crystals of the complex. The product was dried *in vacuo* and stored under nitrogen; mp 199-200°. Ir (Nujol) (cm^{-1}): 1260 m, 1220 m, 1120 m, 1099 m, 1065 s, 1048 s, 1040 s, 952 m, 940 s, 885 m, 818 m, 780 s, 738 m. The compound is soluble in acetonitrile and hot alcohol, slightly soluble in cold alcohol, and insoluble in ether and hydrocarbons; it decomposes in water. *Anal.* Calcd for $CoCl_3C_{10}H_{23}NP$: Co, 16.67; Cl, 30.1; C, 33.97; H, 6.56; N, 3.96; P, 8.76. Found: Co, 16.70; Cl, 29.5; C, 33.46; H, 6.43; N, 4.06; P, 8.68. Magnetic susceptibility data (powder) (per mononuclear Co unit)

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(1) Presented at the 27th Northwest Regional Meeting of the American Chemical Society, Corvallis, Ore., June 1972.

(2) NSF Department Development Grant Postdoctoral Fellow.

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