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

$$\begin{array}{l} CH_3\ \text{agent} + (CH_3)_2NPX_2 \rightarrow (CH_3)_2NP(CH_3)_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow (CH_3)_2NPX_2 \\ (CH_3)_3P \xleftarrow[\text{agent}]{CH_3} (CH_3)_2PX + XP[N(CH_3)_2]_2 \rightarrow \text{addnl reactions} \end{array}$$

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 byproduct,[10] $(CH_3)_2NH_2CN$, was expected to complicate the cleavage of $(CH_3)_2NP(CH_3)_2$ as shown in the equation

$$\begin{array}{l} (CH_3)_2NP(CH_3)_2 + HCN \rightleftarrows (CH_3)_2PCN + (CH_3)_2NH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \uparrow\downarrow HCN \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad (CH_3)_2NH_2CN \end{array}$$

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]

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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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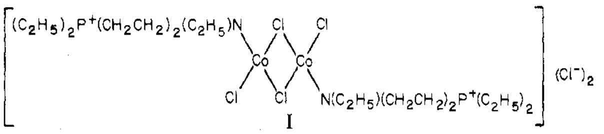
at 296°K: $\chi_M = 9199.6 \times 10^{-6}$, $\chi_M^{cor} = 9431.1 \times 10^{-6}$, $\mu_{eff} = 4.72$ BM. Specific conductance [6.84×10^{-4} *M* (mononuclear unit) in purified absolute ethanol at 25°]: 5.38×10^{-5} ohm^{-1} cm^{-1}. Visible spectrum (reflectance, kK): 15.3 max, 16.8 s, sh, 17.9 w, sh, 20.2 vw, sh, 22.9 w.

Results and Discussion

When bis(2-chloroethyl)ethylamine hydrochloride was treated with diethylphosphine, using the method of Issleib[10] for the conversion of a 2-chloroethylamine to a 2-diethylphosphinoethylamine function, cyclization took place to give the substituted hexahydro-1,4-azaphosphorinum ring system. The product, hexahydro-1,4,4-triethyl-1,4-azaphosphorinium chloride, was isolated as its hydrochloride monohydrate. The analysis, melting point, solubility, and acidity of the compound are in accord with its formulation as a tertiary ammonium quaternary phosphonium salt. The ^{31}P nmr position is in the typical range for quaternary phosphonium salts[11] and indicates somewhat less shielding in the six-membered nitrogen-containing ring than in the simple tetraethylphosphonium ion. The infrared absorptions characteristic of the protonated tertiary amine and of water disappeared on conversion to the coordinated base in its cobalt(II) complex.

The free base $(C_2H_5)N(CH_2CH_2)_2P^+(C_2H_5)_2Cl^-$ can act as a ligand through nitrogen and might be compared to triethylamine.[12] Both of these form 1:1 complexes with cobalt(II) chloride, which contain pseudotetrahedrally coordinated cobalt(II) by the common criteria of ligand field spectrum and magnetic moment. Thus, both have the typically structured $^4A_2 \rightarrow {}^4T_1(P)$ (T_d) absorption, at 15.3 kK for the cationic ligand and at 16.0 kK for triethylamine.[12] The room-temperature magnetic moments of the cobalt complexes are 4.72 BM for the cationic ligand and 4.52 BM for triethylamine.[12] Both criteria indicate a somewhat smaller contribution to the average ligand field from the cationic ligand than from the uncharged amine, which is reasonable.

For the complex $CoCl_2 \cdot N(C_2H_5)_3$ to contain four-coordinate cobalt, it must be formulated as a dichloro-bridged dinuclear complex,[12] with negligible magnetic interactions at room temperature. The cationic ligand complex may be formulated similarly, as illustrated in structure I.



I

Alternatively, a nonelectrolyte zwitterionic structure $[L^+CoCl_3^-]$ might be considered. Such a structure has been reported for tetrahedral cobalt(II) complexes of various aminoaminium,[13] aminophosphonium,[14,15] and phosphinophosphonium[16] cationic ligands.

These zwitterionic complexes have a small degree of electrolytic conductance in polar solvents, due to partial solvolysis. In contrast, the complex reported here is highly conducting in absolute ethanol without a significant change in the absorption spectrum on dissolution.[17] A molar conductance of 157 ohm^{-1} cm^{-2} mol^{-1} is calculated for the dinuclear complex, well in excess of values for 1:1 electrolytes or for cobalt(II) chloride itself in this solvent.[18]

Registry No. $(C_2H_5)N(CH_2CH_2)_2P^+(C_2H_5)_2$ Cl^-, 36609-76-4; $[Co_2(L)_2Cl_4]Cl_2$, 36655-07-9.

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An X-Ray Photoelectron Spectroscopy Study of *N,N'*-Ethylenebis(benzoylacetoniminato)cobalt(II) and Its Oxygen and Nitric Oxide Adducts

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The nature of the bonding of molecular oxygen to metals in natural systems has long been of interest. Recent studies of coboglobin, hemoglobin with the iron replaced by cobalt, have shown that the cobalt-oxygen bond is quite similar to the iron-metal bond in hemoglobin.[1] Esr studies of various 1:1 cobalt-oxygen complexes have shown that the complexes may best be described as Co^{III}-O_2^- complexes,[2] that is, a superoxide ligand coordinated to a formally cobalt(III) species. The purpose of the studies reported here was to measure and compare the X-ray photoelectron spectra of Co(benacen) [benacen = *N,N'*-ethylenebis(benzoylacetonimine)] and its oxygen adduct in order to test the latter's formulation as a Co(III) complex. For similar reasons we have also examined the nitric oxide adduct of Co(benacen).

Experimental Section

All complexes were prepared by literature methods, the complex Co(benacen)pyO_2 [py = pyridine] by the method of Landels and Rodley,[3] the complex Co(benacen)NO by the method of Tamaki, *et al.*,[4] and the complex Co(benacen)pyNO_2 by the method of Clarkson and Basolo.[5]

The photoelectron spectra were taken on an AEI ES 100B spectrometer with an aluminum X-ray source (Kα = 1486.6 eV).

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