TABLE IV
THERMAL DECOMPOSITION OF $Na_4HP_3O_{10}\cdot H_2O$

Step of heating curve	% total H_2O loss			
	Theory	Experiment		
1 → 3	33	36	39	40
3 → 4	17	17	18	15
4 → 5	50	47	43	45
1 → 5	100	100	100	100

water molecules per mole, indicating that the original 1.5-hydrate is somewhat unstable to air drying. The weight loss in the initial step was smaller when samples were air dried for long periods before ignition.

The thermogravimetric curve for $Na_5P_3O_{10}\cdot 6H_2O$, shown in Fig. 1 for comparison, is not characterized by stable intermediate compositions such as those found for the corresponding acid salts.

Acknowledgment.—The authors appreciate the assistance of Mr. L. G. Fauble of Monsanto's Kearny Plant with the ion-exchange analyses. Helpful comments were made by Mr. J. S. Metcalf and Dr. R. R. Irani.

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Phosphorus Complexes of Group III Acids. I. Boron Acids and 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

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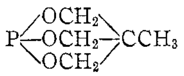
One to one complexes of the bicyclic phosphite, $CH_3C(CH_2O)_3P$, have been prepared with the acids BH_3, B_3H_7, $B(CH_3)_3$, and BF_3. The compound $CH_3C(CH_2O)_3PBH_3$ has a melting point of 199° and a measured dipole moment of 8.60 ± 0.05 D. This is in good agreement with a value estimated using additive bond moments. Trimethylamine will remove BH_3 groups from the complex to give $CH_3C(CH_2O)_3P$ and $(CH_3)_3NBH_3$. ΔH for the process: $CH_3C(CH_2O)_3P_{(s)} + B(CH_3)_{3(g)} = CH_3C(CH_2O)_3PBH_{3(s)}$ is estimated to be -14.4 ± 0.5 kcal./mole on the basis of pressure–temperature data. Comparable data for the complex $(CH_3)_3NB(CH_3)_3$ give an approximate value of -25 kcal./mole. The foregoing values suggest that $CH_3C(CH_2O)_3P$ is a weaker base toward both BH_3 and $B(CH_3)_3$ than is trimethylamine.

Introduction

The synthesis of the bicyclic phosphite ester



4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane first was reported by Verkade and Reynolds.[1] The caged structure of this molecule should lead to rather unusual behavior as a ligand and some of its rather striking transition metal chemistry has been reported by Verkade and Piper.[2] It was felt that complexes of this phosphite ester with reference acids such as BH_3, BF_3, $B(CH_3)_3$, and B_3H_7 would be of interest for two reasons. First, the consistent coördination pattern of these electron acceptors should lead to simple one to one adducts, uncomplicated by any variations in coördination number. Secondly, much already has been published in this area and comparisons with earlier work are readily available.[3-7]

Experimental

Preparation of $CH_3C(CH_2O)_3P$.—The phosphite, $CH_3C(CH_2O)_3P$, was prepared by a reaction first reported by Wadsworth and Emmons[8] but described in detail by Newman.[9] One mole of 2-hydroxymethyl-2-methyl-1,3-pro-

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(1) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

(2) J. G. Verkade and T. S. Piper in "Advances in the Chemistry of the Coordination Compounds," S. Kirshner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 634.

(3) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).

(4) R. W. Parry and T. C. Bissot, *ibid.*, **78**, 1524 (1956).

(5) R. W. Parry, G. Kodama, and C. E. Nordman, WADD Tech. Rept. 60-262, Univ. of Michigan, April, 1960.

(6) T. Reetz, *J. Am. Chem. Soc.*, **82**, 5039 (1960).

(7) F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

(8) W. S. Wadsworth and W. D. Emmons, Abstracts, 138th National Meeting, American Chemical Society, New York, N. Y., p. 97-P.

(9) M. S. Newman, private communication.

panediol was mixed with one mole of trimethyl phosphite and allowed to stand with frequent shaking at room temperature. At the end of the third day a homogeneous and colorless solution was formed. At the end of ten days methyl alcohol and excess trimethyl phosphite were distilled from the reaction mixture at room temperature at 0.05 mm. pressure. The pasty residue was heated to 100° at 0.05 mm. and the phosphite sublimed into a water-cooled wide-bore condenser. The yield was 85%. The product was resublimed *in vacuo* and stored in a desiccator over $CaCl_2$.

Diborane.—Commercially available diborane (Callery Chemical Company) was purified by trap distillation. The vapor pressure of the purified material was in the range 225–228 mm. at $-111.6°$. Deuteriodiborane was prepared from LiD and BF_3 in the presence of $AlCl_3$ and a trace of $LiAlD_4$.[10]

Boron Trimethyl.—Boron trimethyl was prepared and purified by the method of Brown from BF_3 and CH_3MgBr.[11]

Tetraborane.—Tetraborane was obtained as a by-product in the purification of diborane which had been stored at room temperature for several months under 1 to 5 atm. pressure. The vapor pressure of the purified material at 0° was 388 ± 1 mm.

Trimethylamineborane, $(CH_3)_3NBH_3$.—The authors wish to thank the Callery Chemical Company for the generous gift of the sample of trimethylamineborane used in this investigation. The material was sublimed once before use.

Trimethylamine.—Commercially available trimethylamine (Eastman, white label) was stored in a steel cylinder over CaH_2 and distilled directly into the apparatus.

Preparation of Tetrahydropyran.—Tetrahydropyran was prepared by hydrogenating 250 g. of 3,4-dihydropyran (Eastman, yellow label) under 75 atm. hydrogen pressure for 1.5 hr. Freshly prepared W-5 grade Raney nickel[12] (10 g.) was used as the catalyst. An 88% yield based on hydrogen absorption was realized. The crude product was filtered from the catalyst and bromine water added until the color due to free bromine remained for 2 hr. with constant shaking. Sodium hydroxide then was added to the mixture (while shaking) until the bromine color disappeared. The aqueous phase was separated and the organic layer washed 4 times with water and dried over anhydrous Na_2SO_4. The dried liquid was filtered and fractionally distilled from CaH_2. The portion boiling from 86–86.5° was retained.

Solvents.—Commercially available, reagent grade solvents were used. Ethers and hydrocarbons were dried over CaH_2 or $LiAlH_4$ and distilled.

Dioxane for dielectric constant measurements was purified in the manner described by Weaver, Shore, and Parry.[13] The index of refraction ($n^{25}D$) of the final distillate was 1.4198.

Benzene used in dielectric constant studies was purified as follows. Reagent grade benzene was slowly crystallized in an ice-bath and filtered when approximately half of the benzene had solidified. This procedure was repeated once and 10% water by weight added to the benzene thus obtained. The mixture was fractionally distilled and the benzene–water fraction boiling at 70° was retained. Water was removed by storage over anhydrous $CaSO_4$ for 24 hr. and by refluxing for 2 hr. over $LiAlH_4$. The benzene then was distilled from $LiAlH_4$. The fraction boiling at 80° was retained, stored over $LiAlH_4$, and redistilled in a vacuum line when needed. The index of refraction ($n^{25}D$) of the final distillate was 1.4978.

Boron Trifluoride.—Commercial boron trifluoride was purified by recovering the gas from the benzonitrile complex as described by Brown and Johannesen.[14]

Preparation of $CH_3C(CH_2O)_3PBH_3$.—The compound, $CH_3C(CH_2O)_3PBH_3$, was synthesized by several methods. The following low-temperature procedure gave the purest product in best yield. In a typical run, 1.0 g. of crude ligand (6.7 mmoles) was dissolved in anhydrous ether and filtered *in vacuo* to remove any insoluble impurities.[15] A sample of 3.7 mmoles of diborane was condensed onto the frozen solution at $-196°$ and the system warmed and stirred. As the solvent melted, a clear solution resulted. Around $-50°$ a fine white precipitate formed. After stirring for 0.5 hr. at room temperature, the system was filtered to remove the product, melting at 199° (uncorrected). A yield of 58% based on the ligand was realized. Attempted purification of this product by sublimation *in vacuo* at 125° or by recrystallization from mixed dioxane and dibutyl ether gave a material with a slightly lower melting point. Analyses were performed on the original product.

Anal. Calcd. for $BPO_3C_5H_{12}$: B, 6.68; C, 37.1; H, 7.47. Found: B, 6.59; C, 37.7; H, 7.49. Isopiestic molecular weight in methyl ether at 0°, calcd. for monomer: 162. Found: 152 ± 15.

Solutions in the range of 10^{-3} *M* in THF or CH_2Cl_2 were found to be non-conducting.

The dielectric constants of solutions of $CH_3C(CH_2O)_3PBH_3$ in dioxane were determined using a Sargent Model V oscillometer. The cell and cell holder were mounted in a metal can submerged in a thermostat at 25.00 ± 0.02°. The cell was calibrated with benzene and dioxane and measured dielectric constants of solutions of these two materials agreed well (±0.002) with values calculated from the composition of the solutions. The indices of refraction were measured with an Abbe refractometer on the same temperature control system as the oscillometer. The data observed for the solutions of the BH_3 complex are presented in Table I and Fig. 1.

The deutero compound, $CH_3C(CH_2O)_3PBD_3$, was prepared in the same manner as the normal compound except that B_2D_6 was substituted for B_2H_6.

Substitution of *n*-hexane for ether resulted in a product of similar purity. However, since the ligand dissolves slowly in *n*-hexane, solutions could not be frozen to condense the diborane and warmed at such a rate that complete solution was effected before reaction began. For this reason, the diborane was allowed to diffuse into the system

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[10] S. G. Shore, P. R. Girardot, and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 20 (1958).

[11] H. C. Brown, *ibid.*, **67**, 374 (1945).

[12] "Organic Syntheses," Coll. Vol. III, pp. 181–185.

[13] J. R. Weaver, S. G. Shore, and R. W. Parry, *J. Chem. Phys.*, **29**, 1 (1958).

[14] H. C. Brown and R. B. Johannesen, *J. Am. Chem. Soc.*, **72**, 2934 (1950).

[15] On long storage in a desiccator over $CaCl_2$ with intermittent exposure to the atmosphere when used, $CH_3C(CH_2O)_3P$ slowly hydrolyzes to form an ether-insoluble material which has been found by Barnes and Hoffman (private communication) to be $HOP(OCH_2)_2C(CH_3)CH_2OH$. In order to prevent formation of the ether-insoluble oxide ($CH_3C(CH_2O)_3P{=}O$) it was found necessary to scrupulously purify ethers of peroxides.

Table I

Dielectric Constants and Indices of Refraction of Solutions of $CH_3C(CH_2O)_3PBH_3$, in 1,4-Dioxane at 25°

x (Mole fraction $CH_3C(CH_2O)_3PBH_3$)	ϵ	n_D
0.00647	2.878	1.4201
.00294	2.514	1.4200
.000712	2.277	1.4198
.000652	2.271	1.4198
.000312	2.237	1.4198
.000000	2.209	1.4198
	$\frac{\partial \epsilon}{\partial x} = 104.1$	$\frac{\partial n_D}{\partial x} = 0.05$

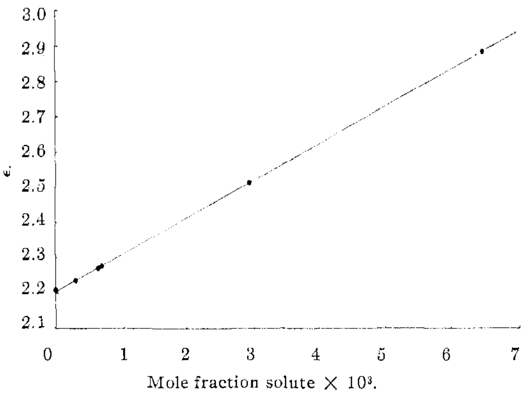

Fig. 1.—Dielectric behavior of solutions of $CH_3C(CH_2O)_3PBH_3$ in 1,4-dioxane.

against the pressure of the solvent vapor at room temperature.

The Debye–Scherrer X-ray powder pattern of $CH_3C(CH_2O)_3PBH_3$ was recorded with a 114.7-mm. camera using CuKα radiation and a Ni filter. The *d* values are listed in Table II.

Table II

Interplanar Spacings for the Compound $CH_3C(CH_2O)_3PBH_3$

d (Å.)	I^a	*d* (Å.)	I^a	*d* (Å.)
6.64	vvw	2.47	w	1.77
5.99	s	2.33	w	1.65
4.36	s	2.18	w	1.63
4.10	vw	2.05		1.61
3.53	w	2.00		1.59
2.99	vw	1.93		1.46
2.74	vw	1.89		1.42
2.61	vw	1.86		
2.52	w	1.82		

[a] s = strong, m = medium, w = weak, vw = very weak, vvw = very very weak.

Preparation of $CH_3C(CH_2O)_3PB_3H_7$.—The direct combination of $CH_3C(CH_2O)_3P$ (4.7 mmoles) with an excess of B_4H_{10} (6.04 mmoles) in a sealed tube of 60 cc. volume at room temperature resulted in a heterogeneous reaction system from which H_2, B_2H_6, B_4H_{10}, some higher boron hydrides, excess ligand, $CH_3C(CH_2O)_3PBH_3$, and $CH_3C(CH_2O)_3PB_3H_7$ were recovered. The solid mixture also contained a trace of an uncharacterized yellow fraction which was soluble in ether. A pure product was obtained by the method of Kodama, Parry, and Carter.[16] In a typical run 3.2 mmoles of B_4H_{10} were condensed onto 5 cc. of tetrahydropyran (THP), freshly distilled from $LiAlH_4$. The system was aged at 0° for 24 hr. before the volatile components (B_2H_6 and THP) were distilled at 0°. The solid residue was dissolved in 5 cc. of ether. An ether solution of ligand prepared by dissolving 0.5 g. (3.4 mmoles) of laboratory stock in 15 cc. of solvent (filtered to remove traces of insoluble impurities)[15] was added to the ether solution of B_3H_7–THP at room temperature. After a few seconds, a fine white precipitate formed which was washed twice with methyl ether to remove any monoborane complex. The product decomposed with some fusion at 167°.

Anal. Calcd. for $B_3PO_3C_5H_{16}$: B, 17.3; C, 32.0; H, 8.61. Found: B, 16.8; C, 32.2; H, 8.16.

The Debye–Scherrer X-ray powder pattern of $CH_3C(CH_2O)_3PB_3H_7$ was recorded in the same manner as was that of the BH_3 complex. The *d* values are listed in Table III.

Table III

Interplanar Spacing for the Compound $CH_3C(CH_2O)_3PB_3H_7$

d (Å.)	I^a	*d* (Å.)	I^a	*d* (Å.)	I^a
7.04	vw	4.40	w	2.25	vw
6.40	s	3.67	w	2.11	w
6.04	m	3.21	vvw	2.00	vw
4.96	vw	2.83	vw	1.92	vw
4.49	s	2.60	w	1.82	vvw

[a] See Table II for denotation of symbols.

Preparation of $CH_3C(CH_2O)_3PB(CH_3)_3$.—When boron trimethyl was condensed onto an ether solution of ligand, a white precipitate formed. While this precipitate could be isolated by filtering, attempts to remove the last traces of solvent by pumping resulted in the dissociation of the complex, leaving a very pure residue of $CH_3C(CH_2O)_3P$. The moist crystals could be sublimed slowly under a pressure of about 30 mm. of $B(CH_3)_3$ at room temperature to give well formed transparent crystals which became cloudy and crumbled as the pressure was reduced. The stoichiometry of the complex was established by dissolving a known weight of pure ligand (0.2845 g., 1.92 mmoles) in 5 cc. of dry $CHCl_3$ and observing the vapor tension of the system at −45° as known increments of $B(CH_3)_3$ were added. A plot of pressure *vs.* $B(CH_3)_3/CH_3C(CH_2O)_3P$ ratio is shown in Fig. 2.

The Complex $CH_3C(CH_2O)_3PBF_3$.—When boron trifluoride was added to an ether solution of the bicyclic phosphite at room temperature, no visible reaction occurred. Evaporation of such a solution left a pasty mass, retaining considerable ether from which some moist crystals could be sublimed *in vacuo* at 85°. These crystals hydrolyzed and melted when exposed to the low humidity of a helium-filled drybox. The direct reaction of BF_3 with the ligand in the

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(16) G. Kodama, R. W. Parry, and J. C. Carter, *J. Am. Chem. Soc.*, **81**, 3534 (1959).

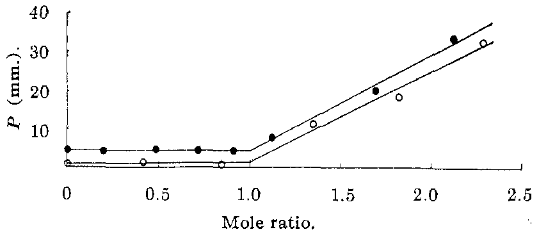

Fig. 2.—*P* (mm.) *vs.* mole ratio of $B(CH_3)_3/CH_3C(CH_2O)_3P$ (●) at −45° in $CHCl_3$; *P* (mm.) *vs.* mole ratio of $BF_3/CH_3C(CH_2O)_3P$ (○) at −78° in CH_2Cl_2.

absence of a solvent was vigorous at room temperature and resulted in an intractable paste.

Bulk quantities of a product of BF_3 and $CH_3C(CH_2O)_3P$ were prepared by passing BF_3 through a solution of the ligand in *n*-hexane at room temperature. A white precipitate formed which hydrolyzed and melted in the drybox. A sample was prepared by condensing 0.577 mmole of BF_3 onto a frozen solution of 0.577 mmole of $CH_3C(CH_2O)_3P$ in 5 cc. of hexane. After removal of the solvent at 0°, this material melted at 40–45° with decomposition and non-reversible evolution of some BF_3. It seems probable that the above reactions involve a rupture of the bicyclic ring system of the phosphite.

The stoichiometry of the BF_3 complex was established in the same manner as was that of the $B(CH_3)_3$ complex except that CH_2Cl_2 was used as a solvent at −78°. The results are shown in Fig. 2.

A solution of 0.133 mmole of $CH_3C(CH_2O)_3P$ in 24.7 cc. of ethyl ether was non-conducting, both before and after the addition of 0.131 mmole of BF_3.

Displacement Reactions.—Several systems were investigated to discern the feasibility of the reaction

$$(CH_3)_3NBH_3 + CH_3C(CH_2O)_3P = CH_3C(CH_2O)_3PBH_3 + N(CH_3)_3$$

Trimethylamine borane (6.2 mmoles) and the ligand (1.7 mmoles) were sealed together in an evacuated tube and heated to 125° for 36 hr. No trimethylamine was found in the mixture and the solid residue in $CHCl_3$ had an infrared spectrum typical of a mixture of the reactants with none of the bands unique to the phosphite complex.[17] In an attempt to take advantage of the difference in solubility of the two borane complexes, 4.1 mmoles of $(CH_3)_3NBH_3$ and 1.3 mmoles of $CH_3C(CH_2O)_3P$ were dissolved in 10 cc. of ethyl ether in a sealed vessel and heated to 80° for 24 hr. A small amount of $CH_3C(CH_2O)_3P{=}O$, arising from reaction between the ligand and traces of peroxides in the solvent, formed as a precipitate which was removed. No $N(CH_3)_3$ or $CH_3C(CH_2O)_3PBH_3$ could be isolated. The solid residue, dissolved in $CHCl_3$, again displayed the infrared spectrum of a mixture of the reactants. In THF results were no different. A mixture of 3.08 mmoles of $(CH_3)_3NBH_3$ and 3.33 mmoles of $CH_3C(CH_2O)_3P$ was dissolved in 20 cc. of THF and heated to 50° for 3 hr. under a helium atmosphere. No $N(CH_3)_3$ was evolved and fractional crystallization of the recovered solute in various solvents such as *n*-pentane and ether resulted in mixtures of the reactants in various ratios.

The reverse of the above reaction, $N(CH_3)_3 + CH_3C(CH_2O)_3PBH_3 = CH_3C(CH_2O)_3P + (CH_3)_3NBH_3$, proceeds to completion at room temperature, though slowly. A stock solution of 3.14 mmoles of $CH_3C(CH_2O)_3PBH_3$ in 25 cc. of THF was prepared in the drybox. A 10-cc. aliquot of this solution (1.26 mmoles) was treated with 2.11 mmoles of $N(CH_3)_3$ for 1.5 hr. at room temperature *in vacuo*. At the end of this time the volatile components, THF and $N(CH_3)_3$, of the mixture were removed at 0° and treated with 2.85 mmoles of HCl gas. The THF solution then was diluted with water and titrated with 1.82 milliequivalents of standard aqueous NaOH. This implies the consumption of 1.08 mmoles of $N(CH_3)_3$ and a similar quantity of $CH_3C(CH_2O)_3PBH_3$. The infrared spectrum of the solid residue dissolved in $CHCl_3$ was that of a mixture of the ligand, $CH_3C(CH_2O)_3PBH_3$, and $(CH_3)_3NBH_3$. Another 10-cc. aliquot of the $CH_3C(CH_2O)_3PBH_3$ stock solution was sealed into a tube of 60 cc. volume with 2.11 mmoles of $N(CH_3)_3$. After 60 hr. this reaction had gone to completion, as indicated by the consumption of $N(CH_3)_3$ and by the absence of bands due to the phosphite complex in the infrared spectrum of the non-volatile residue in $CHCl_3$.

Vapor Tension of $B(CH_3)_3$ over $CH_3C(CH_2O)_3P$.—Boron trimethyl was sealed in a tube with an excess of $CH_3C(CH_2O)_3P$. An attached manometer registered the pressure in the system relative to vacuum up to 1 atm. Above this pressure, measurement was made relative to atmospheric pressure in the reference arm of the manometer. A similar mercury manometer was used to measure atmospheric pressures simultaneously. Equilibrium conditions were obtained rapidly by allowing some of the phosphite to sublime in the enclosed boron trimethyl vapor. The entire system was thermostated in a water-bath controlled to ±0.01°. Corrections were made for the density of mercury at the various temperatures and for the stem of the reference arm of the monometer above the thermostat. The results are tabulated in Table IV and plotted in Fig. 3.

TABLE IV

PRESSURE-TEMPERATURE DATA FOR $CH_3C(CH_2O)_3PB(CH_3)_3$

Temp., °C.	Pressure, atm.
42.37	0.343
43.12	.347
43.64	.356
48.18	.482
52.11	.623
52.91	.664
57.59	.912
57.74	.919
59.49	1.130
63.73	1.457

Below 42°, equilibrium could not be established in a reasonable length of time (48 hr.). Above 65°, the complex was completely dissociated.

Results and Discussion

Two factors which may or may not be interdependent influence the donor ability of a ligand,

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[17] Spectral data for many of these compounds will be published in detail.

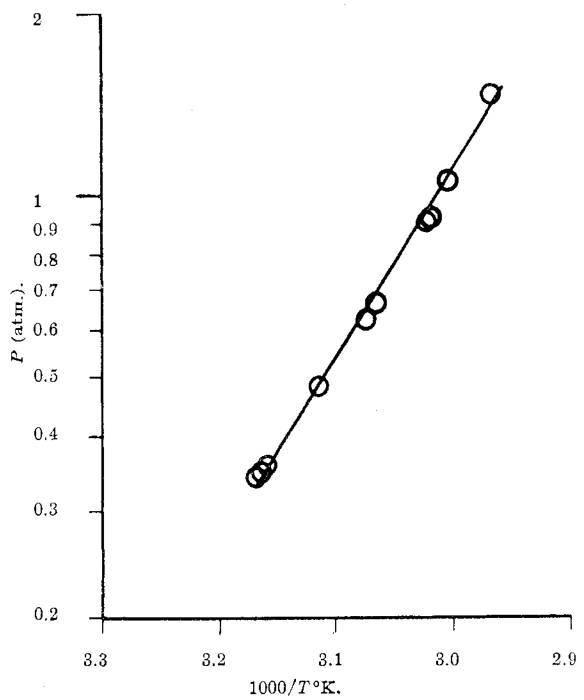

Fig. 3.—P (atm.) *vs.* $1000/T$ (°K.) for $CH_3C(CH_2O)_3PB(CH_3)_3$.

namely, the electron density and the steric requirements for coördination with a given acid. It cannot be ascertained how the unshared electron density varies among organic phosphites, but constraining the alkoxy groups to a fixed position as in the bicyclic phosphite substantially reduces the steric requirements for coördination over open-chain phosphites. In addition, constraint enhances the dipole moment of $CH_3C(CH_2O)_3P$ by more closely orienting the link moments to a common axis. The effect of these factors can be seen in the complexes discussed below.

The Borane Complex, $CH_3C(CH_2O)_3PBH_3$.—The unusually high melting point of the borane complex (199°) is in sharp contrast to those of the trialkyl phosphite boranes reported by Reetz[6]: a series of liquids or solids melting under 70°. Again, the complex does not sublime appreciably at temperatures below 125°. Further, the solubility of the complex differs from that of other borane complexes, being essentially insoluble in hydrocarbons, ethyl and *n*-butyl ethers, and liquid ammonia; moderately soluble in methyl ether and carbon disulfide; and readily soluble in chloroform, methylene dichloride, tetrahydrofuran, dioxane, and acetonitrile. These facts imply a large lattice energy for the complex, more in line with that of $(NH_2)_3PBH_3$[5] rather than the waxy, disordered trimethylamine borane[18] or the other trialkylphosphite boranes. Indeed, one would expect a large permanent electric moment leading to a strongly associated solid for this compound. The electric moment of $(CH_3)_3NBH_3$ is reported to be 4.69 D.[19] After subtracting 0.64 D. for the moment of the free amine[20] there is left 4.05 D. attributable to the BH_3 group and the perturbation of the donated electron pair. The corresponding considerations for H_3NBH_3 lead to the difference between 5.01 D.[19] and 1.46 D.,[20] or 3.55 D. Since the observed electric moment of the phosphite is 4.15 D.[21] one would expect a moment for $CH_3C(CH_2O)_3PBH_3$ to be somewhere in the vicinity of 7.7 to 8.2 D.

The dielectric data in Table I lead to an orientation polarization of $P_0 = 1511 \pm 15$ cc. when treated with the equation of Cohen–Henriquez.[22] This leads to a calculated electric moment of 8.60 ± 0.05 D., a number which agrees well enough with the predicted value when one considers the crude nature of the approximations involved in the prediction.

It is particularly interesting to note the deviations from additivity of the permanent electric moments for the borane and the oxide of $CH_3C(CH_2O)_3P$. Brown, Verkade, and Piper report the value of 7.10 D. for $CH_3C(CH_2O)_3P{=}O$[21] and 4.95 D. has been reported for $(CH_3)_3NO$.[23] Thus it is seen that

$$\mu_{CH_3C(CH_2O)_3P} + \mu_{(CH_3)_3NO} - \mu_{N(CH_3)_3} > \mu_{CH_3C(CH_2O)_3P{=}O}$$

since $4.15 + 4.95 - 0.64 > 7.10$, while

$$\mu_{CH_3C(CH_2O)_3P} + \mu_{(CH_3)_3NBH_3} - \mu_{N(CH_3)_3} < \mu_{CH_3C(CH_2O)_3PBH_3}$$

since $4.15 + 4.69 - 0.64 < 8.60$.

Since $CH_3C(CH_2O)_3P$ will not displace $N(CH_3)_3$ from $(CH_3)_3NBH_3$ (at least under the conditions investigated here) while $N(CH_3)_3$ will dis-

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(21) T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).

(22) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., Amsterdam, 1952, p. 302. Cohen–Henriquez equation

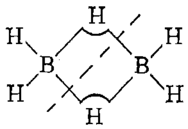
$$P = \frac{3M_1}{d_1(\epsilon_1 + 2)^2}\left[\frac{\partial \epsilon}{\partial x} - 2n_D(1)\frac{n_D}{x}\right]$$

where M_1, d_1, ϵ_1, and $n_D(1)$ refer to the molecular weight, density, dielectric constant, and index of refraction (sodium D line) of the solvent. Values for these properties at 25.0° were taken from the literature. The use of ϵ_1 instead of $n_D(1)$ in the term $(\epsilon_1 + 2)^2$ is necessary because of the permanent electric moment of the solvent. The use of n_D instead of n_∞ is of small consequence in light of the negligible value of $\partial n_D/\partial x$.

(23) See reference 20, p. 379.

place $CH_3C(CH_2O)_3P$ from $CH_3C(CH_2O)_3PBH_3$, the phosphite appears to be a weaker donor than $N(CH_3)_3$ with respect to BH_3.

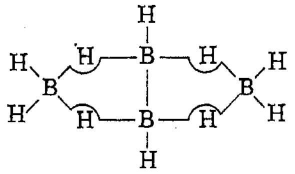
The reaction of $CH_3C(CH_2O)_3P$ with diborane classifies it as a symmetrical cleavage agent. That is, it cleaves the double hydrogen-bridge bond of diborane in a symmetrical fashion



$$+ 2CH_3C(CH_2O)_3P = 2CH_3C(CH_2O)_3PBH_3$$

It might be said that the course of this reaction in ether is a property of the solvent, since ethers are known to be symmetrical cleavage agents. However, the formation of the complex in a hydrocarbon medium establishes the phosphate as such an agent.

That $CH_3C(CH_2O)_3P$ is a symmetrical cleavage agent is seen also in its reaction with tetraborane in the absence of a solvent. While there were many side reactions, as shown by the wide variety of products identified in the system, the presence of some $CH_3C(CH_2O)_3PB_3H_7$ product suggests the reaction



$$+ 2\,CH_3C(CH_2O)_3P$$

$$= CH_3C(CH_2O)_3PBH_3 \quad + \quad CH_3C(CH_2O)_3PB_3H_7.$$

The Boron Trimethyl Complex, $CH_3C(CH_2O)_3PB(CH_3)_3$, and Its Heat of Dissociation.—The pressure–temperature data are tabulated in Table IV. Under the conditions employed here, the vapor pressure of the phosphite does not exceed 1 mm. and that of the $B(CH_3)_3$ complex is even less. It therefore was assumed that the vapor within the system was essentially pure $B(CH_3)_3$ and the data in Table IV were used to evaluate the parameters in the equation: $\log P = -\Delta H/2.303RT + b$. A least squares fit of the data afforded a value of $\Delta H_{\text{assoc}} = -14.4 \pm 0.5$ kcal./mole for the reaction

$$B(CH_3)_{3(g)} + CH_3C(CH_2O)_3P_{(s)} = CH_3C(CH_2O)_3PB(CH_3)_{3(s)}$$

Brown reports a value of -17.6 kcal./mole for the enthalpy of the reaction[3]

$$B(CH_3)_{3(g)} + N(CH_3)_{3(g)} = (CH_3)_3NB(CH_3)_{3(g)}$$

Since Brown's data cover a similar temperature range and since trimethylamine and its borane adduct have a symmetry similar to that of the complex in this investigation, it was felt that the data should afford some measure of comparison of donor strengths. However, our data refer to the reaction of a gas with a solid to produce another solid while all of Brown's species were gases. While data are lacking relative to the heats of sublimation of both the phosphite and its complex, it is possible to compare $CH_3C(CH_2O)_3P$ with $N(CH_3)_3$ in the solid phase. The heat of sublimation of $N(CH_3)_3$ can be obtained from the data of Aston and co-workers who report the heat of fusion as 1.564 kcal./mole and the heat of vaporization as 5.482 kcal./mole, or 7.0 kcal./mole for the heat of sublimation.[24]

The heat of sublimation of the complex, $(CH_3)_3NB(CH_3)_3$, can be estimated from Brown's data.[3] Brown reports the saturation pressure of this complex over a range of 0–65° and fits the data from 30 to 65° to the equation

$$\log P(\text{mm.}) = -3467/T + 11.949$$

Over the range from 65–100°, Brown reports data relative to the dissociation of the complex in the vapor phase and represents the equilibrium constant for this dissociation with the equation

$$\log K_P(\text{atm.}) = -3852/T + 9.998$$

From these data it is possible to correct the observed vapor pressures for the partial pressure of the dissociated species. Evans and co-workers have done this for the range of 6–35° and report a heat of sublimation for $(CH_3)_3NB(CH_3)_3$ of 13.0 kcal./mole.[25] However, we have found a noticeable curvature of the plot of $\log P_{\text{corr}}$ *vs.* $1/T$ for this system and conclude that a more appropriate value for comparison with $CH_3C(CH_2O)_3PB(CH_3)_3$ would be obtained from the same temperature interval (*i.e.*, 40–65°). Over this latter range we have calculated from Brown's data the heat of sublimation of $(CH_3)_3NB(CH_3)_3$ as 14.5 kcal./mole.

We then can say for the reaction

$$N(CH_3)_{3(s)} + B(CH_3)_{3(g)} = (CH_3)_3NB(CH_3)_{3(s)}$$

$$\Delta H = -17.6 + (7.0 - 14.5) \text{ kcal./mole} = -25.1 \text{ kcal./mole}$$

While there may be some error associated with the value for the heat of sublimation of the amine

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(24) J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen, and H. F. Zuhr, *J. Am. Chem. Soc.*, **66**, 1171 (1944).

(25) W. H. Evans, D. D. Wagman, and E. J. Prosen, Natl. Bur. Standards (U.S.) Rept. No. 4943, 1953.

complex, it seems certain that this quantity must be greater than that of the free amine and that ΔH for the above reaction must be less than -17.6 kcal./mole. Thus it can be said that relative to $B(CH_3)_3$, $CH_3C(CH_2O)_3P$ is a weaker donor than $N(CH_3)_3$ by several kilocalories.

CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES
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Coördination Compounds of Ethylenimine with Cobalt(III), Chromium(III), Palladium(II), Platinum(II), and Platinum(IV)

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The synthesis of inert coördination compounds with ethylenimine (aziridine) as ligand is described. Stable complexes of cobalt(III), chromium(III), palladium(II), platinum(II), and platinum(IV) have been prepared and identified. The properties of the complexes are discussed briefly.

Introduction

In a previous paper[1] the authors described complexes formed by ethylenimine with metal ions whose complexes belong to the "labile" or rapid replacement class. The aim of the present research was to prepare inert complexes with the same ligand. By the use of direct synthesis or of substitution methods, it was possible to prepare such compounds with Co(III), Cr(III), Pt(II), Pt(IV), and Pd(II). Aside from the interest in the complexing properties of this unusual amine, the inert complexes are of importance as potential agents in cancer chemotherapy.

Experimental

Analyses were made by Dr. S. M. Nagy, Massachusetts Institute of Technology, or by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. The symbol Az for ethylenimine (aziridine) will be used.

Reagents.—The ethylenimine was purchased from the Borden Chemical Co., Leominster, Mass. It was dried over sodium, distilled from potassium hydroxide pellets, and stored in a refrigerator; boiling point, 55.5°. All the salts and solvents were of reagent grade. Distilled water was used through all the preparations.

Infrared Spectra.—It is known that ethylenimine is not a very stable compound, being rather easily hydrolyzed or polymerized with concurrent ring opening. On account of the relatively severe conditions (use of acid media or oxidation with air or chlorine) employed in the preparation of some of the complexes here described, it was necessary to check the presence of the three-membered ring in the products by infrared analysis. A Perkin–Elmer model 137 spectrophotometer was used to obtain spectra of all of the prepared compounds in potassium bromide disks. As a guide on infrared spectra of ethylenimine we used the work of Hoffman, Evans, and Glockler[2]; they observed and assigned the frequencies of infrared bands both in the gas and in the liquid phase. Bands corresponding to those described in that work were found and identified in our compounds, the most useful one for the purpose of qualitative analysis being a strong band occurring at 880–890 cm.$^{-1}$ and assigned to the deformation of the Az-ring. Such a band was found in all of the described compounds, thus confirming the elemental analysis. The infrared spectra will not be reported herein, since a complete study of the infrared spectra of ethylenimine complexes is in progress.

***cis*-Chlorobis-(ethylenediamine)-ethyleniminecobalt-(III) Chloride Hydrate, $[Co(C_2H_8N_2)_2(C_2H_5N)Cl]Cl_2 \cdot H_2O$.**—To a slurry of 7 g. of acid-free *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride[3] in 10 ml. of ice-cold water was added 2 g. of Az. The dark red solution thus obtained was left in a refrigerator to crystallize overnight. On the following day the purple-red crystals were filtered by suction, washed with ethanol and ether, and dried over $CaCl_2$. More of the compound was obtained by addition of ethanol to the mother liquor. The complex was recrystallized from water–ethanol.

Anal. Calcd.: C, 20.79; H, 6.69; N, 20.21; Cl, 30.69. Found: C, 21.14; H, 6.83; N, 19.70; Cl, 31.03.

Bis-(ethylenediamine)-diethyleniminecobalt(III) Bromide, $[Co(C_2H_8N_2)_2(C_2H_5N)_2]Br_3$.—To 3 g. of ice-cold Az was added in very small portions 1 g. of *trans*-dibromobis-(ethylenediamine)-cobalt(III) bromide,[4] taking care that each portion had dissolved before adding the next one. The yellow solution was left at ice-temperature for a few hours, then by addition of ethanol and ether a yellow powdery compound was obtained. The complex was recrystallized from water–ethanol, filtered by suction, washed with

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[1] T. B. Jackson and J. O. Edwards, *J. Am. Chem. Soc.*, **83**, 355 (1961).

[2] H. T. Hoffman, Jr., G. E. Evans, and G. Glockler, *ibid.*, **73**, 3028 (1951).

[3] A. Werner, *Ber.*, **34**, 1733 (1901); *Inorg. Syntheses*, **2**, 222 (1946).

[4] A. Werner, *Ber.*, **44**, 111 (1911).