the acceptor. The sulfur and selenium atoms contain empty 3d and 4d orbitals, respectively. It is reasonable to assume that back donation of pπ halogen electrons to the 3d orbitals of sulfur (4d of selenium) can take place, which will result in an increase in the $X \rightarrow I_2$ interaction. This $p\pi_I \rightarrow d\pi_X$ back donation is impossible in phosphine oxides because of the lack of a dπ orbital on the oxygen atom. Thus, there can be no enhancement in the oxygen-coordinated complexes by back donation of pπ electrons from the iodine molecule.

The much greater stability of the iodine complex of triphenylarsine as compared with that of triphenylarsine oxide (Table III) can be explained in essentially the same way. In the triphenylarsine complex, in addition to the $As \rightarrow I_2$ interaction, $p\pi_I \rightarrow d\pi_{As}$ back-bonding can occur, thereby enhancing the $As–I_2$ interaction. In the arsine oxide, interaction with iodine occurs at the oxygen atom and back-bonding is again impossible because of the nonavailability of 3d orbitals in the oxygen atom.

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Contribution from the Chemical Laboratory,
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The Addition Compounds of Some Phosphines with Boron Trifluoride, Borane, and Trimethylboron

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Saturation pressures and equilibria in the vapor phase have been investigated by a manometric method for the addition compounds of tetramethylenephosphine, $(CH_2)_4PH$, with BF_3, borane, and $B(CH_3)_3$, of pentamethylenephosphine, $(CH_2)_5PH$, with BF_3 and $B(CH_3)_3$, and of triethylphosphine with BF_3. The high degree of dissociation in the vapor phase of the cyclic phosphine addition compounds with BF_3 and with $B(CH_3)_3$ makes a quantitative investigation experimentally difficult. The composite thermodynamic and volatility data indicate the donor ability sequence tetramethylenephosphine > pentamethylenephosphine.

Introduction

In contrast to the extensive investigations of the relative base strengths of saturated open-chain and cyclic compounds containing nitrogen, oxygen, and sulfur as the heteroatom, comparatively few studies have been made on the electron-donating ability of the phosphines. Particularly sparse are quantitative thermodynamic data. Results have been reported for the interaction of trimethylphosphine and dimethylphosphine with BF_3[2] and with $B(CH_3)_3$,[3] the corresponding methylphosphine and phosphine adducts being too unstable to permit quantitative comparison. Also, for several methyl-, ethyl-, and vinyl-substituted phosphines it has been found[4] that the donor strength toward $B(CH_3)_3$ is $C_2H_5(CH_3)_2P > (CH_3)_3P > (CH_2{=}CH)(CH_3)_2P \gg (C_2H_5)_3P > (CH_2{=}CH)_3P$. The determination of p$K_a$ values for a number of substituted phosphines[5] shows a base strength sequence of tertiary > secondary > primary phosphine.

No work at all on the donor properties of the cyclic phosphines has been reported in the literature, and only recently has the synthesis of the saturated five- and six-membered ring compounds[6,7] been achieved. The cyclic compounds are of special interest because a ring size effect has been demonstrated to exist. Thus, for cyclic ethers, the order of donor ability toward methanol-*d* or chloroform[8,9] and toward iodine[10] is four- > five- > six- > three-membered ring. For the cyclic sulfides toward iodine[11,12] a different order is observed, five- > six- > four- > three-membered ring. In the case of the cyclic imines there is some question as to whether the maximum in donor strength occurs for the four-membered ring[13] or the five-membered ring.[14]

In this work, a study was undertaken of the donor strengths toward several Lewis acids of the five- and the six-membered ring cyclic phosphines, the only two currently available saturated cyclic compounds.

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[1] Taken in part from the Ph.D. thesis of Harris L. Morris, The University of Michigan, Dec 1965.

[2] E. A. Fletcher, Doctoral Dissertation, Purdue University, 1952.

[3] S. Sujishi, Doctoral Dissertation, Purdue University, 1949.

[4] H. D. Kaesz and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6213 (1960).

[5] W. A. Henderson and C. A. Streuli, *ibid.*, **82**, 5791 (1960).

[6] A. B. Burg and P. J. Slota, *ibid.*, **82**, 2148 (1960).

[7] M. Braid, Doctoral Dissertation, Temple University, 1962.

[8] S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).

[9] S. Searles, M. Tamres, and E. R. Lippincot, *ibid.*, **75**, 2775 (1953).

[10] (a) Sr. M. Brandon, M. Tamres, and S. Searles, *ibid.*, **82**, 2129 (1960); (b) M. Tamres and Sr. M. Brandon, *ibid.*, **82**, 2134 (1960).

[11] J. D. McCullough and D. Mulvey, *ibid.*, **81**, 1291 (1959).

[12] M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962).

[13] H. C. Brown and M. Gerstein, *J. Am. Chem. Soc.*, **72**, 2926 (1950).

[14] S. Searles, M. Tamres, F. Block, and L. A. Quaterman, *ibid.*, **78**, 4917 (1956).

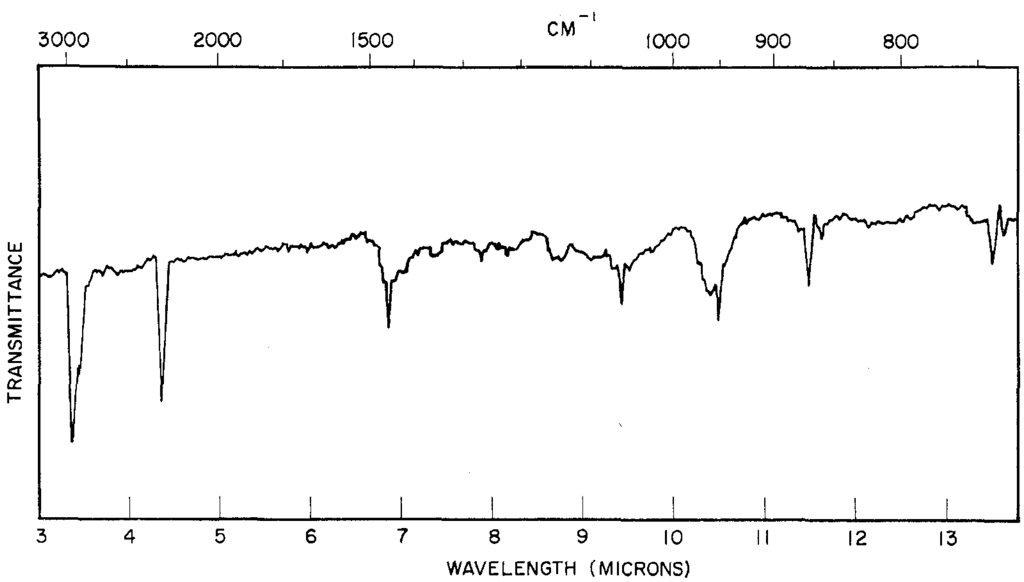

Figure 1.—Infrared spectrum of pentamethylenephosphine.

Experimental Section

Apparatus and Procedure.—The manometric system employed, which incorporated the use of a constant temperature manostat,[15] and the techniques for measuring known quantities of reagents as well as the saturation pressures and melting points of the adducts,[15,16] have been described previously. The special problems associated with the manometric study of weak complexes also have been discussed.[17]

Materials.—Triethylphosphine was prepared by the method of Hibbert[18] as modified by Mann and Wells.[19] However, ethyl bromide was used in place of ethyl chloride and the higher boiling solvent, tetrahydrofuran, was employed rather than diethyl ether which is usually used. The vapor pressure observed for the purified material agreed with the literature[20] values of 3.8 and 14.1 mm at 0 and 25°, respectively.

A pure sample of tetramethylenephosphine was generously supplied by Dr. Anton B. Burg of the University of Southern California. It was actually prepared by Dr. Ross I. Wagner, using a method[21] different from the one reported in the literature by Burg and Slota,[6] which involved the reaction of $Cl(CH_2)_4Cl$ with $NaPH_2$ in refluxing ammonia. Vapor pressures taken on this sample were in excellent agreement with published results: calculated, Trouton constant = 22.9 ± 0.1 eu, bp (extrapolated) 104.8 ± 1.3°; lit.[6] Trouton constant = 22.1 eu, bp (extrapolated) 105.4°. The purity was further confirmed by the agreement of its infrared spectrum with that in the literature.[6]

A small sample of pentamethylenephosphine was kindly furnished by Dr. Edgar Howard, Jr., of Temple University. The saturated six-membered ring phosphine was synthesized using the method reported by Braid.[7] Reproducible vapor pressures of this sample were obtained after a few brief exposures of the phosphine to the vacuum pump with the temperature maintained at −30.6°. The following data were obtained for the liquid [t (°C), p (mm)]: 21.3, 9.5; 25.5, 12.1; 30.5, 15.9; 35.6, 20.7; 41.0, 26.9; 45.6, 34.0; 48.1, 38.1; 50.6, 42.2; 54.1, 50.0; 56.7, 56.1; 59.4, 62.3; 62.3, 71.0; 64.4, 76.6; 67.9, 89.3; 71.4, 102.1. A least-squares treatment of the data gave $\log P = -2086/T + 8.069$. The extrapolated boiling point was determined as 128.9 ± 2.5°, which is a little higher than that reported by Braid.[7] The Trouton constant was calculated as 23.7 ± 0.2 eu.

It was not found possible to determine the melting point using the Stock-type falling rod apparatus[22] because the pure phosphine appeared glassy over a substantial temperature range. Therefore, the melting point was determined by equating the vapor pressures of the solid and liquid cyclic phosphine. The vapor pressures for the solid are [t (C°), p (mm)]: −22.9, 0.4; −15.3, 0.8; −6.6, 1.6; 0.0, 2.5; 3.1, 3.1; 7.1, 4.0; 8.7, 4.5; 12.9, 5.8; 16.1, 7.1; 18.3, 8.3. The data follow the equation $\log P = -2260/T + 8.666$.

A melting point of 17.3° was obtained using this procedure. It was noted visually that pentamethylenephosphine froze to a glassy solid which appeared to melt at *ca.* 21°, although partial melting occurred at lower temperatures. These results are consistent with Braid's[7] reported value of 19°. The infrared spectrum taken on a gas sample after purification is shown in Figure 1.

The boron trifluoride, commercially available from The Matheson Co., Inc., was purified by the method described by Brown and Johannesen.[23] The vapor pressures observed for the purified material have been reported in an earlier paper[17] and are in good agreement with those calculated from literature values.[24]

Crude diborane obtained commercially from the Callery Chemical Co. was passed through a −126° trap to remove decomposition products and was stored at −196°. The observed vapor pressure of diborane was 129.5 mm at −119.0° (lit.[25] 129 mm) and 223.5 mm at −111.8° (lit.[25] 223 mm).

Trimethylboron was prepared and purified by the method previously described by Brown[26] using methyl iodide instead of methyl bromide. The purification procedure, as noted elsewhere,[27] was found to be quite tedious. The infrared spectrum taken for the gas was in perfect agreement with that published.[28] The vapor pressure for trimethylboron was 30.5 mm at −78.5° (lit.[29] 30.3 mm), 86.5 mm at −63.5° (lit.[29] 85.8 mm), 210.0 mm at −48.0° (lit.[29] 211.6 mm), and 245.5 mm at −45.2° (lit.[29] 245.0 mm).

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(15) D. E. McLaughlin and M. Tamres, *J. Am. Chem. Soc.*, **82**, 5618 (1960).

(16) D. E. McLaughlin, M. Tamres, and S. Searles, *ibid.*, **82**, 5621 (1960).

(17) H. L. Morris, N. I. Kulevsky, M. Tamres, and S. Searles, *Inorg. Chem.*, **5**, 124 (1966).

(18) H. Hibbert, *Ber.*, **39**, 160 (1906).

(19) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 702 (1938).

(20) H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, **32**, 681 1936.

(21) R. I. Wagner, personal communication.

(22) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 183.

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

(24) V. E. Pohland and W. Harlos, *Z. Anorg. Allgem. Chem.*, **207**, 242 (1932).

(25) A. Stock and E. Kuss, *Ber.*, **56**, 789 (1923).

(26) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).

(27) J. G. Verkade and C. W. Heitsch, *Inorg. Chem.*, **2**, 512 (1963).

(28) W. J. Lehmann, C. O. Wilson, and I. Shapiro, *J. Chem. Phys.*, **28**, 777 (1958).

(29) A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921).

Table I

Phosphine Adducts of Boron Trifluoride, Borane, and Trimethylboron

Adduct	Melting range, °C	Ratio[a] (cc of adduct / cc of tensimeter)	$\log P = (-A/T) + B$		Bp,[b] °C	Trouton constant,[b] eu
			A	B		
Triethylphosphine–BH_3	65 to 67	0.308[c]	2729	8.505	212.0 ± 15.1	25.7 ± 0.9
		Pumping method	3325	9.949	197.3 ± 3.7	32.3 ± 0.3
Tetramethylenephosphine–BF_3	−5.2 to −4.8	0.308[c]	2555	9.797	96.2 ± 3.5	31.7 ± 0.3
		Pumping method	2634	10.034	95.1 ± 2.3	32.7 ± 0.2
Pentamethylenephosphine–BF_3	−3.0 to −2.5	Pumping method	2612	10.093	89.0 ± 4.0	33.0 ± 0.4
Tetramethylenephosphine–BH_3	−66 to −65	Pumping method	2659	8.135	233.0 ± 9.4	24.0 ± 0.5
Tetramethylenephosphine–$B(CH_3)_3$	−15.1 to −14.2	0.308[c]	2557	10.187	76.8 ± 3.8	33.4 ± 0.4
		Pumping method	2632	10.413	76.3 ± 3.4	34.5 ± 0.4
Pentamethylenephosphine–$B(CH_3)_3$	−12.5 to −12.0	Pumping method	2495	10.225	66.5 ± 1.8	33.6 ± 0.2

[a] Ratios are given for the matched sample method. The quantity of adduct is expressed as cc of gas at STP. [b] Given with standard error. [c] Tensimeter volume range of 46 to 47 cc.

Results and Discussion

Saturation Pressures.—Two methods generally are used to prepare 1:1 adducts: (A) a matched sample method in which equal quantities of donor and acceptor are measured out, and (B) a pumping method in which the more volatile component is added in excess, and the excess is pumped off. It was pointed out in a previous paper[17] that the saturation pressures were not reproducible for the weak sulfide–BF_3 adducts when the pumping method was utilized. However, this was not the case for the phosphine adducts, where both methods gave similar results. The saturation pressure equations determined from a least-squares fit of the data[30] for the adducts of the phosphines with BF_3, BH_3, and $B(CH_3)_3$ are summarized in Table I, together with the calculated boiling points and Trouton constants. Included also are the melting point data for the adducts.

The saturation pressures of tetramethylenephosphine–BH_3 are relatively low, and attempts to take measurements above 85° produced deviation from the linear log P *vs.* $1/T$ plot. The deviation was on the high side and became larger with increasing temperature. This is most likely due to diborane decomposition, as residual pressures were subsequently observed at −196°.

Dissociation Data.—The pertinent experimental conditions for the dissociation data measurements are summarized in Table II. The difficulties encountered in measuring small differences in dissociation pressures, discussed previously for sulfide adducts,[17] are present here also. The extreme case is that observed for pentamethylenephosphine–BF_3, in which the change in dissociation pressure was less than 0.05 mm over nearly a 30° temperature interval. The experimental data[30] reflect these small differences in that several inversions in the dissociation pressures were observed as a function of temperature, and many data points were taken to improve the statistical evaluation.

Table II

Experimental Conditions for the Adducts of Phosphines with Boron Trifluoride and Trimethylboron

Adduct	Run	Temp range, °C	Sum of component press, mm at 0°	Range in adduct press, mm at 0°
Triethylphosphine–BF_3	1	143.2–168.6	37.25	3.39–2.12
	2	141.5–165.7	30.67	2.46–1.59
Tetramethylenephosphine–BF_3	1	57.4–87.3	46.92	0.82–0.67
	2	60.2–86.3	61.36	1.29–1.09
Pentamethylenephosphine–BF_3	1	59.2–86.6	61.17	1.11–1.07
Tetramethylenephosphine–$B(CH_3)_3$	1	42.4–69.1	61.60	0.34–0.13
	2	43.8–64.1	60.64	0.32–0.13
Pentamethylenephosphine–$B(CH_3)_3$	1	40.2–68.9	62.26	0.40–0.29

The volatilities of triethylphosphine–BF_3 and of tetramethylenephosphine–BH_3 are much lower than those of the cyclic phosphines with BF_3 and with $B(CH_3)_3$. Consequently, much higher temperatures had to be employed for the vapor phase dissociation studies of the former. Tetramethylenephosphine–BH_3 is of such low volatility, *e.g.*, ~5 mm at 85°, that extremely small concentrations of components had to be measured out for dissociation studies. It was observed that the adduct remained completely associated in the vapor phase at temperatures up to 150°, although the dissociation pressures finally increased at still higher temperatures. The apparent lack of decomposition at temperatures near 150° would be in accord with the absence in the vapor phase of appreciable amounts of B_2H_6, which is not stable at these temperatures.

It was observed for the tetramethylenephosphine–BF_3 adduct that condensation with subsequent revaporization resulted in lower dissociation pressures (corrected to 0°) and, therefore, lower dissociation constants at a given temperature. As long as the adduct was kept in the vapor phase (above *ca.* 50°), the dissociation pressures randomly determined as a function of temperature were reproducible. The effect

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(30) The original data have been deposited as Document No. 9067 with the A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $2.50 for photoprints, or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

of condensation on the dissociation measurements of tetramethylenephosphine–BF_3 is similar to that reported for thiacyclopentane–BF_3.[17] When the individual species were mixed and permitted to remain in the condensed phase for a substantial period of time before entering the vapor phase, the measured dissociation constant was found to be quite low. Subsequent condensation and revaporization of the adduct resulted in still lower dissociation constants (increasing $\Delta G°$). But at each of these stages, a study of the temperature dependence of the equilibrium constant gave a similar $\Delta H°$. These results point out the danger of relying solely on an observed linear plot of log K *vs.* $1/T$, even if the result for $\Delta H°$ is in an expected range, as yielding a valid set of thermodynamic data. Precautions should be taken to check for decomposition in the condensed phase. On long standing at room temperature in a sealed tube, evidence of polymerization of tetramethylenephosphine–BF_3 was quite apparent.

Decomposition in the vapor phase as well as in the condensed phase was observed for the triethylphosphine–BF_3 addition compound, but only to a very slight extent, becoming more pronounced at temperatures above 170°. The same observation in the vapor phase for the BF_3 adducts of trimethylphosphine and of dimethylphosphine was reported by Fletcher,[2] who claimed that the former could not be prepared pure from the starting materials and that the decomposition of the latter was so rapid that a dissociation constant at only a single temperature could be determined for each mixture of components.

These general observations of the BF_3 adducts with phosphines differ somewhat from those found previously with sulfides.[17] The adducts with dimethyl and diethyl sulfides seemed stable in both the vapor and condensed phases, whereas the cyclic sulfide adducts underwent decomposition in the condensed phase. It is interesting to note that decomposition was not observed for the five- and six-membered cyclic ethers with BF_3.[16]

Toward other Lewis acids, *e.g.*, $B(CH_3)_3$ and BCl_3, different decomposition trends are observed. The cyclic phosphine–$B(CH_3)_3$ adducts appear to be stable, as do the sulfide–BCl_3 adducts,[17] whereas ethers in the presence of BCl_3 decompose quite readily in the liquid phase.[31–33]

Thermodynamic Results.—The thermodynamic data for triethylphosphine–BF_3, compared with those for trimethylphosphine–BF_3[2] ($\Delta H° = 18.9$ kcal/mole, $\Delta S° = 45.3$ eu, $\Delta G_{100}° = 1.99$ kcal/mole), show that the former is less stable, indicating the presence of steric interaction with the ethyl groups. This effect is even more pronounced when $B(CH_3)_3$ is the reference acid.[4]

In the case of the BF_3 adducts, both triethyl- and trimethylphosphine show substantially higher stability than do tetramethylene- and pentamethylenephosphine, which are secondary phosphines. Comparison with the data obtained by Fletcher[2] for dimethylphosphine–BF_3 ($\Delta H° = 14.7$ kcal/mole, $\Delta S° = 44.1$ eu, $\Delta G°_{1400} = -1.74$ kcal/mole) indicates that his enthalpy and entropy values seem to be quite high, especially since the free energy change is in the same range as that for the cyclic phosphine–BF_3 adducts. Fletcher's results were based on only three data points and, consequently, are more likely to be in doubt.

Toward $B(CH_3)_3$, trimethylphosphine[3,4] shows greater stability than do tetramethylene- and pentamethylenephosphine, but this trend apparently is reversed in the case of triethylphosphine as a result of steric interaction. All of the thermodynamic data for tetramethylenephosphine are in closer argeement with those reported by Sujishi[3] for dimethylphosphine–$B(CH_3)_3$ ($\Delta H° = 11.4$ kcal/mole, $\Delta S° = 35.1$ eu, $\Delta G°_{100} = -1.69$ kcal/mole). The data for the $\Delta H°$ and $\Delta S°$ values for the cyclic phosphines are higher than those for the corresponding BF_3 adducts (Table III), although the latter are more associated at comparable temperatures. This may reflect a difference in the steric requirements of these Lewis acids.

TABLE III

THERMODYNAMIC DISSOCIATION DATA FOR ADDITION COMPOUNDS OF PHOSPHINES WITH BORON TRIFLUORIDE, BORANE, AND TRIMETHYLBORON

Adduct	Run	$\Delta H°$,[a] kcal/mole	$\Delta S°$,[a] eu	$\Delta G°_{60}$, kcal/mole
Triethylphosphine–BF_3	1	9.5 ± 0.3	18.8 ± 0.7	1.49[b]
	2	9.4 ± 0.3	18.8 ± 0.8	1.49[b]
Tetramethylenephosphine–BF_3	1	2.5 ± 0.1	7.5 ± 0.4	−0.02
	2	2.3 ± 0.2	7.2 ± 0.4	−0.06
Pentamethylenephosphine–BF_3		1.1 ± 0.1	3.6 ± 0.2	−0.15
Tetramethylenephosphine–BH_3		No dissociation up to 150°		
Tetramethylenephosphine–$B(CH_3)_3$	1	8.4 ± 0.2	29.3 ± 0.7	−1.42
	2	9.1 ± 0.5	31.8 ± 1.5	−1.47
Pentamethylenephosphine–$B(CH_3)_3$		3.1 ± 0.2	12.3 ± 0.7	−1.03

[a] Given with standard error. [b] At 150°.

Thermodynamic data for tetramethylenephosphine–BH_3 were not possible to obtain because of its low volatility and apparent lack of dissociation in the vapor phase. These general features, however, lend support to BH_3 being a much stronger acid than BF_3 toward phosphines, in agreement with the behavior noted for these acids toward donors in the second row of the periodic table.[34]

Ring Size Effect.—As pointed out in the study with sulfides,[17] thermodynamic data for highly dissociated

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(31) J. Grimley and A. K. Holliday, *J. Chem. Soc.*, 1212 (1954).

(32) J. D. Edwards, W. Gerrard, and M. F. Lappert, *ibid.*, 1470 (1955).

(33) H. L. Morris, Doctoral Dissertation, University of Michigan, 1965.

(34) T. D. Coyle, H. D. Kaesz, and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 2989 (1959).

adducts are based on measurements of small differences between large numbers, and omission of one or two data points from the log K *vs.* $1/T$ plot could affect $\Delta H°$ by as much as 1 kcal/mole. The check on duplicate runs on the tetramethylenephosphine adducts (Table III) is gratifying, considering the difficulty of the measurements. In view of this agreement, the single runs with the pentamethylenephosphine adducts are considered reliable. Duplicate measurements were not run, the choice having been made to use the very limited supply of this compound to make single runs with two different reference acids. The composite thermodynamic data indicate that tetramethylenephosphine is a better donor than pentamethylenephosphine.

Besides the over-all thermodynamic data, the criterion of relative volatilities of adducts with comparable molecular weight has been used as a means to determine relative donor abilities.[35] On this basis, one also could conclude (Table I) that, as donors, tetramethylenephosphine > pentamethylenephosphine.

Table IV lists available thermodynamic dissociation data of five- and six-membered ring donors containing oxygen, sulfur, nitrogen, and phosphorus. Regardless of the heteroatom and, for the limited number of cases investigated, regardless of the acceptor, the general trend is that the five- is a better donor than the six-membered ring. These results reflect the dependence of donor strength on ring size[8,9] and on the nature of the heteroatom in the ring.[12]

TABLE IV

THERMODYNAMIC DISSOCIATION DATA FOR ADDITION COMPOUNDS OF FIVE- AND SIX-MEMBERED RING DONORS WITH BORON TRIFLUORIDE AND TRIMETHYLBORON

Adduct	Ref	$\Delta H°$,[e] kcal/mole	$\Delta S°$,[e] eu	$\Delta G°$, kcal/mole
Tetrahydrofuran–BF_3	*a*	16.8	36.6	3.15[f]
Tetrahydropyran–BF_3	*a*	15.4	34.6	2.51[f]
Thiacyclopentane–BF_3	*b*[g]	5.2 ± 0.4	18.5 ± 1.3	−0.91[h]
Thiacyclohexane–BF_3	*b*	1.5 ± 0.1	5.9 ± 0.3	−0.44[h]
Tetramethylenephosphine–BF_3	*c*[g]	2.4 ± 0.2	7.4 ± 0.3	−0.04[h]
Pentamethylenephosphine–BF_3	*c*	1.1 ± 0.1	3.6 ± 0.2	−0.15[h]
Pyrrolidine–$B(CH_3)_3$	*d*	20.4	43.5	4.19[f]
Piperidine–$B(CH_3)_3$	*d*	19.7	45.0	2.86[f]
Tetramethylenephosphine–$B(CH_3)_3$	*c*[g]	8.7 ± 0.4	30.6 ± 1.5	−1.45[h]
Pentamethylenephosphine–$B(CH_3)_3$	*c*	3.1 ± 0.2	12.3 ± 0.7	−1.03[h]

[a] Ref 16. [b] Ref 17. [c] This research. [d] Ref 13. [e] Given with standard error. [f] At 100°. [g] Average values reported. [h] At 60°.

Since in no case studied to date is there a systematic increase in donor ability with increasing ring size, an interpretation of donor strength based solely on reorganization energy[36] (which is dependent upon bond angles) is not sufficient. Direct measurement of bond angles for the methylphosphines in the vapor phase[37,38] also makes the concept of reorganization energy less tenable as the major factor in influencing donor ability.

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(35) H. C. Brown and H. Pearsall, *J. Am. Chem. Soc.*, **67**, 1765 (1945).

(36) J. H. Gibbs, *J. Chem. Phys.*, **22**, 1460 (1954).

(37) L. S. Bartell and L. O. Brockway, *ibid.*, **32**, 512 (1960).

(38) L. S. Bartell, *ibid.*, **32**, 832 (1960).