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Characterization of Complexes of Trimethyl Group 5A Bases with Simple Boron Lewis Acids¹

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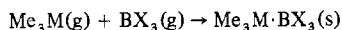
The compounds formed by the reaction of the group 5A Lewis bases trimethylphosphine, trimethylarsine, and trimethylstibine with the simple boron Lewis acids boron trifluoride, boron trichloride, boron tribromide, diborane, and trimethylborane have been characterized by ¹H NMR, ir-Raman spectroscopy, mass spectrometry, conductivity, tensimetric titration, gas-phase displacement reactions, and melting point determinations. The expected one-to-one adducts were formed in most cases; however, trimethylborane underwent no reaction with either trimethylarsine or trimethylstibine, and trimethylstibine reacted anomalously with diborane and boron trifluoride. In general, the relative order of adduct bond strengths as determined by gas-phase calorimetry² is supported by the results of these experiments. Under the conditions of these experiments, no evidence was found for salt formation or for ligand exchange in the adducts.

Introduction

The nature of the coordinate bond formed between tertiary derivatives of elements of group 3A, particularly those of boron, and tertiary derivatives of group 5A, particularly those of nitrogen and phosphorus, have been the object of continued interest and investigation.³ Conventional analytical tools such as vibrational and nuclear magnetic resonance spectroscopy⁴⁻¹⁰ have been used extensively in attempts to gain understanding of the nuances of the bonding in these classic Lewis acid-base adducts. Relatively few data exist for the adducts of the heavier group 5A congeners, arsenic^{11,12} and antimony.¹² We recently reported the results of a gas-phase calorimetric investigation² of trimethylphosphine, trimethylarsine, and trimethylstibine adducts with several simple boron Lewis acids. Table I summarizes the results of that study where

$$\Delta H_{\text{reacn}} = \Delta H_{\text{adduct formn}} + \Delta H_{\text{subl}}$$

for the reaction



where M = P, As, or Sb and X = F, Cl, Br, H, or Me. Reported herein is the characterization of these adducts by a wide variety of physical techniques. Of particular interest is a comparison of the relative adduct bond strengths as found previously by calorimetry in contrast to the order predicted by the methods used in the present investigation.

Experimental Section

All preparative work was carried out on a high-vacuum system using standard techniques.¹³ All acids and bases were prepared and purified as previously described.²

¹H NMR spectra were recorded on a Varian Associates XL-100-15 NMR spectrometer. All NMR samples were prepared by condensing the desired amount of acid and/or base into an NMR tube containing degassed benzene-*d*₆ or methylene chloride. Following the addition of the reactants, the tubes were flame sealed and removed from the high-vacuum system. All ¹H chemical shifts are reported with respect to internal tetramethylsilane.

The ir spectra were recorded from 3000 to 270 cm⁻¹ using a Perkin-Elmer Model 457 grating infrared spectrophotometer. The ir spectra of the adducts were recorded in Nujol or *n*-nonane mulls between CsI plates. Ir spectra of the uncomplexed acids and bases were recorded in a 10-cm gas-phase ir cell equipped with CsI windows. The Raman spectra were recorded from 1500 to 100 cm⁻¹ using a Jarrell-Ash Model 25-500 laser Raman spectrophotometer equipped with a Coherent Radiation Model 52-A argon ion laser. Raman adduct samples were prepared in sealed Pyrex glass capillary tubes. All vibrational spectra were obtained at ambient temperature.

The mass spectra of the adducts were obtained using a Varian MAT-311 mass spectrometer operating at 70 eV.

Conductivities were measured using a Leeds and Northrup conductivity bridge in conjunction with an inert-atmosphere conductivity cell.

Tensimetric titrations were carried out using a tensimeter fitted

Table I. Measured Enthalpies,^a ΔH_{reacn} (kcal/mol)

Base	BF ₃	BCl ₃	BBr ₃	BH ₃	B(CH ₃) ₃
(CH ₃) ₃ P	-45.5	-68.6	-122.3	-79.9 ^b	-41.0
(CH ₃) ₃ As	-20.4	-46.2	-81.2	-49.6 ^b	No reacn
(CH ₃) ₃ Sb	-4.2 ^c	-26.8	-19.8	-6.6 ^c	No reacn

^a For the reaction acid (g) + base (g) → adduct (s).²^b $\Delta H_{\text{reacn}} = -17.75$ kcal/mol [for $\frac{1}{2}\text{B}_2\text{H}_6 \rightarrow \text{BH}_3$: G. W. Mapes, S. A. Fridmann, and T. P. Fehlner, *J. Phys. Chem.*, **74**, 3307 (1970)]. ^c Anomalous reaction; not simple adduct formation (see text).

with greaseless high-vacuum Teflon stopcocks.¹⁴ The pressure was monitored by using a capillary-tube mercury manometer in conjunction with a cathetometer.

Gas-phase displacement reactions were performed by condensing a known quantity (~0.1 mmol) of the acid into a 250-ml bulb which was connected to a second 250-ml bulb via a high-vacuum Teflon stopcock. The arrangement was such that an equal quantity of base could be introduced into the second bulb. The stopcock connecting the two bulbs was then opened, allowing the gases to mix and react at ambient temperature, resulting in the solid adduct being distributed over a large surface area. An equimolar amount of the displacing reactant (either acid or base) was then introduced into the two-bulb apparatus. The progress of the reaction was monitored using gas-phase ir spectroscopy.

Melting point data were obtained in unsealed capillary tubes exposed to the atmosphere and are reported uncorrected.

Results and Discussion

A. NMR Spectra. The NMR chemical shift data for the methyl protons on the free and complexed Lewis bases are listed in Table II. The solubilities of the adducts studied proved to be very low in all common solvents. All reported data were obtained using saturated solutions. In the case of benzene-*d*₆, some of the methyl proton chemical shifts of the coordinated base were observed upfield of the chemical shift of the methyl protons of the uncoordinated base. From consideration of simplistic inductive effects, a downfield shift of the coordinated base would be predicted. Previous work has demonstrated that these unusual chemical shifts are due to anisotropic solvent effects.¹⁵ Such effects were neither expected nor observed in methylene chloride solvent. In all cases the spectra of the base protons were broadened considerably upon adduct formation, presumably due to the interaction with the quadrupolar boron nucleus. No new acid-base exchange phenomena on the NMR time scale were observed for the entire series of adducts. The two systems which undergo exchange, Me₃P·BMe₃ and Me₃P·BF₃, have been previously described.^{10,16} For the systems Me₃As + BMe₃ and Me₃Sb + BMe₃, ¹H NMR indicated that there was no reaction. Only resonances corresponding to free acid and free base were observed, with the chemical shift being invariant with both temperature and concentration. ¹¹B NMR spectra

Table II. NMR Data: Chemical Shifts of Lewis Base Methyl Protons

System	Benzene- d_6		Methylene chloride		J_{P-H} , Hz
	Chem shift ^a	Coord Chem shift ^b	Chem shift ^b	Coord chem shift ^b	
Me ₃ P	82		99		2.7
Me ₃ P·BF ₃	78 ^c		111 ^c		
Me ₃ P·BCl ₃	72	+10	200	-101	11
Me ₃ P·BBr ₃	65	+17	165	-66	9
Me ₃ P·BMe ₃	55 ^c		100 ^c		
Me ₃ P·BH ₃	67	+15	131.5	-32.5	14
Me ₃ As	78		94		
Me ₃ As·BF ₃	67.5	+10.5	94	0	
Me ₃ As·BCl ₃	65	+13	202	-106	
Me ₃ As·BBr ₃	67	+11	148	-54	
Me ₃ As + BMe ₃	78 ^d	0	94 ^d	0	
Me ₃ As·BH ₃	69	+9	225	-131	
Me ₃ Sb	59		75		
Me ₃ Sb + BF ₃	<i>e</i>		<i>e</i>		
Me ₃ Sb·BCl ₃	73	-14	140	-65	
Me ₃ Sb·BBr ₃	95	-36	114	-39	
Me ₃ Sb + BMe ₃	59 ^d	0	75 ^d	0	
Me ₃ Sb + B ₂ H ₆	<i>e</i>		<i>e</i>		

^a In Hz downfield from internal TMS. ^b Coordination chemical shift = (chemical shift reference) - (chemical shift of coordinated species) in Hz. ^c System exchanging; chemical shift dependent on concentration and temperature; see ref 10 and 16. ^d No reaction. ^e No base methyl protons observed for 1:1 stoichiometry.

were not obtained because of insufficient solubility of most of the adducts.

The use of NMR chemical shifts as a criterion for adduct bond strengths is at best tenuous.¹⁰ We find that for these compounds no correlation exists between the calorimetric data (Table I) and the ¹H NMR chemical shift using either benzene or methylene chloride solvents.

B. Vibrational Spectra. A comparison of the infrared (Table III) and Raman (Table IV) spectra of the adducts with the spectra of the uncomplexed acids and bases demonstrated vibrational frequency shifts characteristic of simple coordinate covalent bond formation. The peaks attributable to the vibrations of the trimethyl Lewis base species were shifted to slightly higher wave numbers, which is indicative of a shortening of the M-C bond with a concomitant change in the C-M-C bond angle due to decreased lone-pair repulsion upon coordination. All frequency shifts observed for the coordinated Lewis bases were quite small, on the order of 10–20 cm⁻¹. Cullen et al.¹⁷ have demonstrated that the *quaternization* of tertiary arsines resulted in shifts on the order of 50 cm⁻¹. The large vibrational frequency increase observed upon quaternization may be attributed to the higher oxidation state of the arsenic atom with the attendant increase in As-C bond strength. Clearly the tertiary bases in our study formed covalent adducts with the boron Lewis acids rather than quaternary salts.

All of the boron Lewis acids exhibited vibrational frequency shifts to lower wave numbers upon coordination. Such shifts occur typically when planar, sp²-hybridized boron Lewis acids coordinate and adopt an approximately sp³ tetrahedral configuration.⁴ The resultant changes in X-B-X bond angles and B-X bond strengths were observed as a sizable decrease (~100 cm⁻¹) in the frequencies of the associated vibrational modes.

By tentatively assigning the M-B symmetric stretch observed in the Raman spectra, approximate force constants for the M-B bonds were calculated. The values given in Table V were calculated via the simple harmonic oscillator approximation with the assumption that the observed M-B mode was a pure M-B stretching mode. The calculated M-B vibrational force constants correlate well with the observed ΔH_{reacn} values

Table III. Infrared Spectra (cm⁻¹) of Complexes^{a,b}

Me ₃ P·BF ₃	2960–2890 vs, 1470–1450 s, 1375 s, 1365 m, 1301 m, 955 m, 875 w, 787 m, 720 m, 530 m, 298 m
Me ₃ P·BCl ₃	2960–2890 vs, 1415 s, 1299 s, 1291 s, 1060 w, 985 s, 950 s, 798 w, 770 s, 725 s, 700 s, 660 s, 393 w, 292 w
Me ₃ P·BBr ₃	2960–2845 vs, 1410 w, 1310 w, 1290 m, 975 m, 945 m, 780 m, 760 m, 720 m, 640 w, 610 m, 320 vw
Me ₃ P·BMe ₃	2960–2845 vs, 1460 m, 1375 m, 1295 m, 1145 s, 942 s, 860 m, 745 w, 700 w, 355 w
Me ₃ P·BH ₃	^c 2960–2840 vs, 2395–2340 vs, 1455 s, 1375 s, 1291 m, 1135 m, 1068 m, 940 s, 883 m, 753 m, 708 m, 570 w
Me ₃ As·BCl ₃	2960–2840 vs, 2720 w, 1456 s, 1412 w, 1374 s, 1262 w, 1190 w, 915 m, 785 m, 635 m, 590 m
Me ₃ As·BBr ₃	2975–2860 vs, 2530 w, 1937 w, 1913 w, 1419 s, 1270 m, 918 vs, 845 w, 810 m, 679 s, 640 s, 602 s, 584 s, 291 w
Me ₃ As·BH ₃	^d 2975–2840 vs, 2400–2340 s, 2260 m, 1895 w, 1425 s, 1268 s, 1135 m, 1052 s, 900 s, 852 m, 620 w, 605 m, 490 w
Me ₃ Sb·BCl ₃	2920–2850 vs, 1460 s, 1375 s, 1265 m, 965 w, 860 m, 580 w, 520 w
Me ₃ Sb·BBr ₃	2930–2850 vs, 1460 s, 1375 s, 1300 w, 1150 w, 860 w, 610 w, 575 w

^a Tentative assignment of all vibrational modes may be found in D. C. Mente, Ph.D. Dissertation, Texas Tech University, 1975.

^b References for ir spectra of free acids and bases: BF₃, J. Vanderryn, *J. Chem. Phys.*, 30, 331 (1959); BCl₃, D. A. Daws and G. Bottger, *ibid.*, 34, 689 (1961); BBr₃, T. Wentink and V. H. Tiensuu, *ibid.*, 28, 826 (1958); BMe₃, W. J. Lehman, C. O. Wilson, Jr., and I. Shapiro, *ibid.*, 28, 777 (1958); B₂H₆, R. C. Taylor and A. R. Grimes, *Spectrochim. Acta*, 10, 419 (1958); PMe₃, M. Halmann, *ibid.*, 16, 407 (1960); AsMe₃, H. Sieberg, *Z. Anorg. Allg. Chem.*, 273, 161 (1953); SbMe₃, F. Ostwald, *Z. Anal. Chem.*, 197 309 (1963). ^c P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, 11, 553 (1972). ^d See ref 11.

Table IV. Raman Spectra (cm⁻¹)^{a,b}

Me ₃ P·BF ₃	1438 w, 766 s, 697 m, 680 m, 639 s, 315 m, 293 w, 269 m, 242 s
Me ₃ P·BCl ₃	1431 w, 790 s, 778 s, 680 m, 665 s, 300 s, 248 m, 210 s
Me ₃ P·BBr ₃	1410 w, 978 w, 789 s, 773 s, 677 s, 629 w, 319 s, 277 s, 264 m, 174 s, 147 s
Me ₃ P·BMe ₃	1437 m, 1033 w, 946 w, 841 w, 767 s, 708 s, 683 s, 467 s, 234 s, 222 s
Me ₃ P·BH ₃	^c 1428 w, 960 w, 762 s, 714 s, 662 s, 580 s, 520 w, 296 w, 276 s, 218 s, 161 s, 134 w
Me ₃ As·BF ₃	1424 w, 1305 w, 718 w, 658 s, 637 s, 595 s, 460 w, 181 s
MeAs·BCl ₃	1422 w, 1126 w, 704 w, 641 s, 601 s, 265 s, 183 s
Me ₃ As·BBr ₃	1422 m, 1128 m, 959 w, 676 s, 608 s, 468 w, 318 w, 296 w, 264 w, 221 m
MeAs·BH ₃	^d 1424 m, 1285 w, 1270 w, 1140 w, 635 s, 616 s, 497 s, 220 m, 171 s
Me ₃ Sb·BCl ₃	1409 w, 1243 w, 1223 w, 1204 w, 770 w, 719 w, 557 w, 514 s, 408 m, 305 w, 274 m, 264 w, 210 s, 157 s
Me ₃ Sb·BBr ₃	1408 m, 1236 w, 1226 w, 630 s, 620 s, 316 w, 281 w, 256 w, 180 s, 164 s, 130 m, 121 s
Me ₃ Sb + BF ₃	1405 w, 1228 w, 1223 w, 1202 w, 783 w, 570 vs, 523 w, 198 w, 153 vs
Me ₃ Sb + B ₂ H ₆	1255 w, 1235 w, 1214 w, 744 w, 586 s, 314 w

^a Tentative assignment of all vibrational modes may be found in D. C. Mente, Ph.D. Dissertation, Texas Tech University, 1975.

^b References for Raman spectra of free acids and bases: BF₃, J. Vanderryn, *J. Chem. Phys.*, 30, 331 (1959); BCl₃, D. A. Daws and G. Bottger, *ibid.*, 34, 689 (1961); BBr₃, T. Wentink and V. H. Tiensuu, *ibid.*, 28, 826 (1958); BMe₃, J. Goubeau and H. J. Becher, *Z. Anorg. Allg. Chem.*, 268, 1 (1952); B₂H₆, R. C. Taylor and A. R. Grimes, *Spectrochim. Acta*, 10, 419 (1958); Me₃P and Me₃As, E. J. Rosenbaum, D. J. Rosenbaum, D. J. Rubin, and C. R. Sandberg, *J. Chem. Phys.*, 8, 366 (1940); Me₃Sb, E. J. Rosenbaum and T. A. Ashford, *ibid.*, 7, 554 (1959). ^c P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, 11, 553 (1973). ^d See ref 11.

previously determined in our laboratory (Table I). While the general ordering of adduct stabilities (as measured calorimetrically) approximates the ordering of the strength of the adduct bonds (as measured by the force constants), there are

Table V. Calculated Vibrational Force Constants for Acid-Base Bond Symmetric Stretch^a

Adduct	Assigned peak	Calcd force const, mdyn/A
Me ₃ P·BF ₃	242	1.23
Me ₃ P·BCl ₃	248	2.43
Me ₃ P·BBr ₃	174	2.62
Me ₃ P·BMe ₃	234	1.04
Me ₃ P·BH ₃	571	2.33 ^b
Me ₃ As·BF ₃	181	0.81
Me ₃ As·BCl ₃	183	1.17
Me ₃ As·BBr ₃	221	2.32
Me ₃ As·BH ₃	497	1.81 ^c
Me ₃ Sb·BCl ₃	157	0.91
Me ₃ Sb·BBr ₃	121	0.86

^a Assignments based on comparison with spectra of uncomplexed acids and bases and ref 4 and 11. ^b Reference 4. ^c Reference 11.

minor relative differences. For example, the adduct which has the second greatest ΔH_{reacn} , i.e., Me₃As·BBr₃, has the fourth largest force constant. These apparent inconsistencies might arise from several sources. First, the measured ΔH_{reacn} values include ΔH_{subl} of the adducts. Although the variation among the ΔH_{subl} values is probably not great, it is possible that if the ΔH_{adduct} were measured directly rather than ΔH_{reacn} , small differences in the relative ordering of adduct stabilities might result. Second, the force constant data could be in error due to either misassignment of the M-B stretching mode or to the assumption that the M-B stretching mode is not mixing with other modes. Third, and most likely, there is no particular reason that the trend in complex stability should be in exactly the same order as the trend in M-B bond strengths.¹⁸ Variations in reorganization energies could easily explain minor variations in the ordering of complex stability.

Spectra for the systems Me₃As + BMe₃ and Me₃Sb + BMe₃ were superimpositions of the spectra for the uncomplexed reactants. The vibrational spectra for the systems Me₃Sb + BF₃ and Me₃Sb + B₂H₆ indicated that reaction had occurred but that the products were not simple acid-base adducts.

C. Mass Spectra. The mass spectra of the air-stable adducts Me₃P·BF₃, Me₃P·BCl₃, Me₃P·BBr₃, Me₃P·BH₃, Me₃P·BMe₃, Me₃As·BCl₃, Me₃As·BBr₃, Me₃As·BH₃, Me₃Sb·BCl₃, and Me₃Sb·BBr₃ have been observed and the major peaks with their assignments are given in Table VI. None of the mass spectra of halogen-containing adducts exhibited a parent peak, but all exhibited fragments containing an acid-base bond. The adducts containing the BH₃ and BMe₃ Lewis acid moieties exhibited parent peaks. Characteristic isotopic envelopes were observed for fragments containing boron, chlorine, or bromine atoms. Some weak ion peaks attributable only to M₄⁺ cage

Table VI. Mass Spectra of Complexes^a

+ ion	Me ₃ P·BF ₃	Me ₃ P·BCl ₃	Me ₃ P·BBr ₃	Me ₃ P·BMe ₃	Me ₃ P·BH ₃	Me ₃ As·BCl ₃	Me ₃ As·BBr ₃	Me ₃ As·BH ₃	Me ₃ Sb·BCl ₃	Me ₃ Sb·BBr ₃
Me ₃ M·BX ₃				<i>b</i>	<i>b</i>			<i>b</i>		
Me ₃ M·BX ₂		49	38	1	2	1	6	4	4	24
Me ₃ M·BX		11			19			3	3	63
Me ₃ M·B					17					35
Me ₂ M·BX ₂		4	2	2						
Me ₂ M·BX		11	1	2					81	
Me ₃ M	70	100	100	42	100	81	98	96	46	45
Me ₂ M	100	100	46	52	45	100	97	100	100	92
MeM	30			12		32	34	29	18	42
M·B					41					
BX ₃							23			
BX ₂	49	58	8	100		78	100		67	
BX		49								
X		36	62			14	19		15	100
M ₄				1	2	5	1	4	8	8
Me ₂ M						2	6	6		

^a Reported as percent ion intensity. ^b Observed, but less than 1% ion intensity.

and MMe₅⁺ ions were observed for some of the samples.

D. Conductivity Data. It has recently been shown^{19a} that some compounds which would be expected to be simple Lewis acid-base adducts are actually salts formed by ligand transfer. In order to ensure that salt formation was not occurring in the present study, we determined the conductivities of a representative set of adducts. The conductivities of the adducts Me₃P·BBr₃, Me₃As·BCl₃, and Me₃Sb·BBr₃ were measured in dry CH₂Cl₂ under an inert atmosphere. The very low conductivities observed (Table VII) in these experiments indicated that these species remained associated in CH₂Cl₂ and that no salt-like species or conductive dissociation products were present.^{19b}

E. Tensimetric Titrations. Tensimetric titrations were carried out on all combinations of Lewis acids and bases at 0° using either *n*-nonane or diglyme as solvents. The results were those expected for a 1:1 complexation reaction for all systems except the following: Me₃As·BF₃, Me₃As·BMe₃, Me₃Sb·BF₃, Me₃Sb·BMe₃, and Me₃Sb·BH₃. The adduct Me₃As·BF₃ is highly dissociated at low pressures² and the tensimetric titration indicated no observable adduct formation under the conditions of the experiment. Similar results were obtained for the Me₃As + BMe₃ and Me₃Sb + BMe₃ systems, indicating no reaction. The Me₃Sb + B₂H₆ system yielded anomalous results due to the formation of an uncharacterized white solid and hydrogen gas. The Me₃Sb + BF₃ system yielded a clear liquid which showed no break in the tensimetric titration curve and was therefore not a simple adduct.

F. Gas-Phase Displacement Reactions. The gas-phase displacement reactions were carried out by allowing the displacing reactant (either an acid or base) to come into contact with a thin layer of solid complex. By mixing boron acids with Me₃P·BX₃ solid adducts, the following sequence of adduct stabilities was demonstrated: Me₃P·BBr₃ > Me₃P·BH₃ > Me₃P·BCl₃ > Me₃P·BF₃ > Me₃P·BMe₃. Similarly for the Me₃As system the order is Me₃As·BBr₃ > Me₃As·BH₃ > Me₃As·BCl₃ and for Me₃Sb the order is Me₃Sb·BCl₃ > Me₃Sb·BBr₃.

Through experiments involving successive displacements of bases, the following sequences of adduct stability were obtained: Me₃P·BCl₃ > Me₃As·BCl₃ > Me₃Sb·BCl₃; Me₃P·BBr₃ ≈ Me₃As·BBr₃ > Me₃Sb·BBr₃; Me₃P·BH₃ > Me₃As·BH₃; Me₃P·BF₃ > Me₃As·BF₃. These sequences are in accord with the order determined by gas-phase calorimetry².

All displacement reactions were performed at ambient temperature. The times required for quantitative displacement to occur varied widely. The displacement of BCl₃ from Me₃P·BCl₃ by BBr₃ was very slow, with a half-life of about 24 hr, whereas the displacement of BCl₃ from Me₃As·BCl₃

Table VII. Conductivity Data

Adduct	Λ , molar conductance, ^a ohm ⁻¹ cm ²
Me ₃ P·BBr ₃	1.84 × 10 ⁻³
Me ₃ As·BCl ₃	1.64 × 10 ⁻³
Me ₃ Sb·BBr ₃	1.56 × 10 ⁻³

^a Measured in CH₂Cl₂ at 25°.

Table VIII. Melting Point Data

Compd	Mp, °C	Comment
Me ₃ P·BF ₃	139	Decomp
Me ₃ P·BCl ₃ ^a	239	Sharp
Me ₃ P·BBr ₃	248	Decomp 180°
Me ₃ P·BMe ₃	91	Subl 50°
Me ₃ P·BH ₃ ^b	101	Sharp
Me ₃ As·BCl ₃	310	Decomp 190°
Me ₃ As·BBr ₃ ^c	242	Decomp 180°
Me ₃ As·BH ₃ ^b	72	Sharp
Me ₃ Sb·BCl ₃		Stable to 360°
Me ₃ Sb·BBr ₃ ^c	269	Decomp

^a G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 146 (1945). ^b See ref 20; see also A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, 75, 3872 (1953). ^c See ref 12.

by BBr₃ was quantitative after 48 hr. In contrast, the quantitative displacement of BMe₃ from Me₃P·BMe₃ by BF₃ required only 2 hr. No Me₃As was displaced from Me₃As·BBr₃ by Me₃P after 6 days, but Me₃As was displaced from Me₃As·BH₃ by Me₃P. The probable displacement mechanism involved the reaction of the very small amount of adduct in the gas phase with uncomplexed displacing reagent, rather than involving the heterogeneous reaction between solid adduct and gas-phase displacing reagent.

No metathesis reactions involving ligand exchange between the acid and base were observed during any of the displacement reactions during contact periods of 2 weeks. Methylation of the boron halides or halogenation of the bases would have been readily detected via gas-phase ir spectroscopy.

G. Melting Point Data. The melting points of the air-stable adducts given in Table VIII illustrate the danger of attempting to predict thermodynamic bond stabilities from only melting points. The correct general trend for Lewis base strengths of Me₃P > Me₃As > Me₃Sb was predicted by Holliday and Hewitt²⁰ in 1953 on the basis of the melting points of the respective borane adducts. The use of any other Lewis acids, such as those used in the present study, would have led to an entirely different order.

Summary and Conclusions

Of the 15 possible Lewis acid-Lewis base adducts which might arise by the reaction of the bases Me₃P, Me₃As, and

Me₃Sb with the boron acids BF₃, BCl₃, BBr₃, BH₃, and BMe₃, 11 combinations yielded one-to-one complexes, all of which were relatively air-stable except Me₃As·BF₃, due to its high dissociation vapor pressure. No reaction was observed between BMe₃ and either Me₃As or Me₃Sb, and Me₃Sb reacted anomalously with B₂H₆ and BF₃. The complexes exhibited "normal" adduct behavior; i.e., they were of only 1:1 stoichiometry, they exhibited no salt-like behavior, and no ligand exchange occurred. Proton NMR was an ineffectual probe of relative adduct stabilities, while vibrational spectroscopy and gas-phase displacement reactions yielded results which are in basic accord with our calorimetric determinations.²

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Registry No. Me₃P·BF₃, 420-21-3; Me₃P·BCl₃, 13292-83-6; Me₃P·BBr₃, 13292-85-8; Me₃P·BMe₃, 1558-34-5; Me₃P·BH₃, 1898-77-7; Me₃As·BF₃, 52827-78-8; Me₃As·BCl₃, 52827-80-2; Me₃As·BBr₃, 52827-82-4; Me₃As·BH₃, 2079-99-4; Me₃Sb·BCl₃, 52827-81-3; Me₃Sb·BBr₃, 52827-83-5; Me₃Sb, 594-10-5; BF₃, 7637-07-2; B₂H₆, 19287-45-7.

References and Notes

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