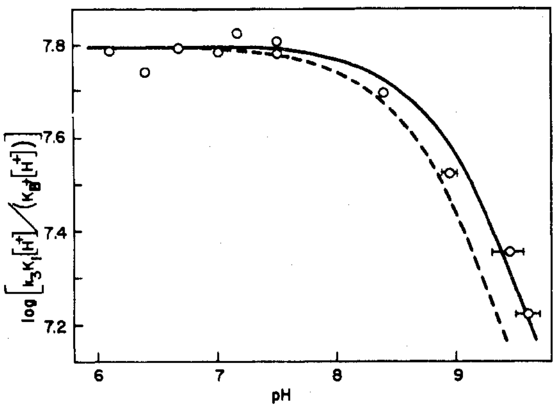

Figure 3. Comparison of experimental values of $k_B/[H^+]$ as a function of pH with the function $k_3K_1[H^+]/(K_B + [H^+])$ predicted by the proposed reaction mechanism: $k_3K_1 = 6.2 \times 10^7\ M^{-2}\ sec^{-1}$, $\mu = 0.50\ M$, $T = 25.0°$; dashed line, $K_B = 1.29 \times 10^{-9}$ from ref 13; continuous line, $K_B = 6.8 \times 10^{-10}$ from this work.

eters are numerically smaller than those found for the hydrogen ion catalyzed pathway.

N-Nitrosohydroxylamine-*N*-sulfonate and nitrohydroxamate, $^-ONNO_2^-$, may be viewed as *cis*-hyponitrite with an SO_3 group or oxygen atom added to one of the nitrogen atoms. Since decomposition of neither nitrohydroxamate nor *trans*-hyponitrite shows specific catalysis by borate buffers,[2] some specific interaction between the SO_3 group and $B(OH)_3$ would appear to be involved in the transition state for the decomposition of the sulfonate. An attractive possibility is coordination of the boron atom to one of the oxygen atoms of the SO_3 group as is found in $B(HSO_4)_4^-$ in concentrated sulfuric acid.[14] This coordination has the effect of reducing the electron density of the sulfur atom since one of its three oxygen atoms can no longer effectively donate electron density through p_π-d_π bonding. This facilitates breaking the N-S bond since the nitrogen atom already bears a positive formal charge of 1. Initial products from step 6 are then *cis*-$HONNO^-$ and $O_2SOB(OH)_3$. The latter hydrolyzes to sulfuric and boric acids while the *cis*-$HONNO^-$ decomposes as discussed earlier. Since $B(OH)_4^-$ is unable to undergo additional coordination, the catalytic activity of boric acid on the decomposition of $ON(SO_3^-)NO^-$ decreases at high pH.

The proposed mechanism requires that the isotopic experiment of Clusius and Schumacher[6] give equal amounts of ^{15}NNO and $N^{15}NO$ if carried out in the presence of boric acid. Unfortunately, the catalytic activity of boric acid was unknown to these authors and no such experiment was performed.

Solvated heavy-metal ions also catalyze the decomposition of $ON(SO_3^-)NO^-$ to form nitrous oxide and sulfate ion. Although their effect has not yet been the subject of a detailed study, we might anticipate that the activity of such metals arises from their coordination ability which would allow them to play a role similar to that which we have proposed for boric acid. The equal amounts of ^{15}NNO and $N^{15}NO$ found with cupric ions as a catalyst[6] are consistent with coordination at the SO_3 group and indirectly offer support for the boric acid model. However, metal ions have more than one potential coordination site and could also promote decomposition through the formation of a chelate complex utilizing both oxygen atoms of the *cis*-hyponitrite group in $ON(SO_3^-)NO^-$. Cleavage of the N-S bond then permits the two nitrogen atoms to become equivalent. With only one coordination site available boric acid cannot act in this way.

Registry No. $K_2N_2O_2SO_3$, 26241-10-1; $B(OH)_3$, 10043-35-3.

Acknowledgments. This work was supported by the National Science Foundation through a grant to Oberlin College. E. G. S. and G. A. D. were NSF undergraduate research participants.

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Spectra and Structure of Phosphorus-Boron Compounds.[1] II. A Vibrational and Nuclear Magnetic Resonance Spectral Investigation of Phosphine-Trichloroborane

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The infrared (45-3000 cm^{-1}) and Raman (50-2700 cm^{-1}) spectra of $H_3P\cdot BCl_3$ and $D_3P\cdot BCl_3$ in the solid state at −196° have been recorded. The spectra have been interpreted on the basis of C_{3v} molecular symmetry and 11 of the 12 fundamental vibrations have been assigned. The molecule was found to be completely dissociated at 0° which is in marked contrast to its previously reported stability. The high frequency of the P-H stretching mode is consistent with a shortening of this bond with coordination. A normal-coordinate calculation was carried out and the force constant of 1.96 mdyn/Å for the P-B stretch is compared to the similar quantity of several other phosphorus-borane molecules. Nuclear magnetic resonance and infrared studies of a solution of $H_3P\cdot BCl_3$ in benzene suggest that the adduct is in equilibrium with the free acid and base.

Introduction

There have been several recent microwave investigations of phosphorus-borane compounds and a wide range of P-B bond distances have been determined. For example, in trifluorophosphine-borane[4] and difluorophosphine-borane[5] the P-B bond distance was found to be 1.836 ± 0.012 and

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(1) Part I: J. R. Durig, Y. S. Li, L. A. Carreira, and J. D. Odom, *J. Amer. Chem. Soc.*, **95**, 2491 (1973).

(2) Taken from the thesis of S. Riethmiller.[3]

(3) To be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

1.832 ± 0.009 Å, respectively, whereas the distances for the same bond in trimethyl- and methylphosphine-borane[6] were found to be 1.901 ± 0.007 and 1.906 ± 0.006 Å, respectively. We have recently completed a microwave study of phosphine-borane and found a P-B distance of 1.937 ± 0.005 Å for this molecule.[1] Thus, the phosphorus-boron bond has been found to vary by 0.1 Å for this series of adducts. Since only the trimethyl- and methylphosphine-boranes are not extensively dissociated at room temperature, the commonly accepted correlation between bond length and stability does not appear to apply to these addition compounds.

In order to provide some additional P-B bond distances for this series of compounds, we investigated the microwave spectrum of phosphine-trichloroborane. This molecule was chosen since it was reported[7] to have a vapor pressure of 8.5 mm at 0° and to be only 90% dissociated at 31°. Also the reported dipole moment of 5.2 ± 0.1 D favored a microwave investigation of this molecule. Much to our surprise, we could find no evidence in the microwave spectrum for the phosphine-trichloroborane molecule at either 0 or −20°. Therefore we undertook a vibrational study in order to establish the relative stability of the addition compound and to check the previously reported infrared spectrum of the gaseous molecule. Nmr parameters of this molecule were also investigated. The results of this study are reported herein.

Experimental Section

With the exception of phosphine, all preparative work was carried out in a conventional high-vacuum system employing greaseless stopcocks.[8] Phosphine was prepared under a stream of nitrogen in a fume hood as described in the literature.[9] Phosphine-d_3 was prepared in a similar manner using D_2O and D_2SO_4. All phosphine species were purified by passing them through a −131° bath (n-C_5H_{12} slush) into a −196° bath. Purity was monitored by vapor pressure measurements[10] and infrared spectra.[11] Boron trichloride was obtained commerically (Matheson) and purified by trap-to-trap distillation until it had a vapor pressure of 476 mm at 0°.[8]

In a typical preparation of $H_3P\cdot BCl_3$, 5.0 mmol of PH_3 and 5.0 mmol of BCl_3 were condensed at −196° into an evacuated tube and isolated from the system by a greaseless stopcock. The tube was allowed to warm slowly to 0° and remained at that temperature for approximately 1 hr. At that time, the contents of the tube were pumped into the vacuum system and passed through a −45° bath into a −196° bath. The $H_3P\cdot BCl_3$ was retained in the −45° bath while traces of PH_3 and/or BCl_3 were retained in the −196° bath.

The ^1H nmr spectrum of a saturated solution of $H_3P\cdot BCl_3$ in C_6D_6 was obtained at ambient temperature on a Varian Associates A-60 spectrometer operating at 60 MHz. The spectrum consisted of a doublet with J_{PH} = 415 Hz and was 3.5 ppm deshielded from the protons in an external TMS reference.

The ^{11}B nmr spectra were obtained from the same sample under similar conditions on a Varian XL-100 spectrometer[12] operating at 32.1 MHz. Proton noise decoupling was accomplished using the Varian Gyrocode decoupler. The coupled spectrum consisted of a single line shielded by 17.0 ppm from the ^{11}B resonance of an external sample of $B(OCH_3)_3$. Under conditions of complete proton decoupling no change in line shape or line width was observed. An ^{11}B nmr spectrum of pure boron trichloride in C_6D_6 showed a chemical shift of 27.9 ppm deshielded with respect to the ^{11}B resonance of external $B(OMe)_3$.

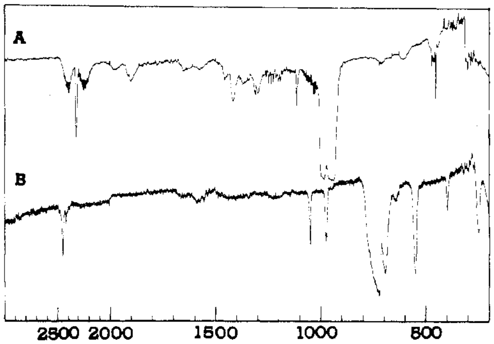

Figure 1. A. Infrared spectrum of $H_3P\cdot BCl_3$ in the gas phase at room temperature. Note, there is only evidence for "free" PH_3 and BCl_3. B. Infrared spectrum of solid $H_3P\cdot BCl_3$.

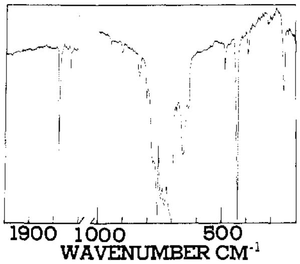

Figure 2. Infrared spectrum of solid $D_3P\cdot BCl_3$.

A Perkin-Elmer Model 621 infrared spectrophotometer purged with dry air was used for recording midinfrared spectra from 3000 to 200 cm⁻¹. The instruments were calibrated with standard gases[13] in the high-frequency region and atmospheric water vapor[14] in the lowest region. A low-temperature cell equipped with a CsI window was employed to record the spectra of the solid samples. Conventional vacuum deposition techniques were used to obtain the solid film on the CsI substrate. The CsI substrate was held at −190° during deposition and then the solid films were annealed until there was no change in the spectrum. Typical spectra are shown in Figures 1 and 2 and the observed frequencies are listed in Tables I and II.

Far-infrared spectra from 45 to 300 cm⁻¹ were recorded with a Beckman Model IR-11 spectrophotometer. The atmospheric water vapor was removed from the instrument housing by flushing with dry air. The instrument was calibrated by using atmospheric water vapor.[14] Single-beam energy checks were made periodically to ensure the energy transmission was at least 10-15% at all times. A low-temperature cell similar to that described earlier[15] was employed to record the spectra of solid samples. Modifications have been made to allow the circulation of liquid nitrogen through a hollow brass cold finger. A wedged silicon window was used for the solid film support plate. Deposition and annealing of the samples were similar to methods used for midinfrared studies. Typical spectra are shown in Figure 3.

The Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer[16] equipped with an argon ion laser source with a frequency of 5145 Å for excitation. Raman spectra of the solids were obtained using a cold cell similar to that employed for the far-infrared instruments, except that the sample holder consists of a solid brass plate an an angle of 75° from the normal. Deposition and annealing procedures were similar to those used for the mid-infrared studies. Typical spectra are shown in Figures 4 and 5.

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(12) This instrument was purchased with funds from the National Science Foundation through a Department Development Grant.

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(16) This instrument was purchased with funds from the National Science Foundation through Grant No. GP-28068.

Table I. Observed and Calculated Infrared and Raman Frequencies (cm^{-1}) of Solid (196°) Phosphine-Trichloroborane[a]

Ir	Raman	Calcd	Assignment and PED
2448 m	2450 s	2452	ν_7 PH_3 antisym str (100%)
2416 w	2416 vs	2430	ν_1 PH_3 sym str (100%)
	1118 w		$2\nu_{10} = 1106$
	1057 sh		
1052 m	1052 m	1046	ν_2 PH_3 sym def (100%)
977 m	977 m	967	ν_8 PH_3 antisym def (71%), PH_3 rock (27%)
725 s	730 w	721	ν_9 BCl_3 antisym str (50%), PH_3 def (35%), BCl_3 def (15%)
698 s	699 m	687	ν_3 PB str (60%), BCl_3 def (25%) BCl_3 str (15%)
553 s	559 m	553	ν_{10} PH_3 rock (45%), BCl_3 str (40%), BCl_3 def (15%)
397 m	401 m	400	ν_4 BCl_3 sym str (85%), PB str (15%)
255 m	255 m	255	ν_{11} BCl_3 anti sym def (90%), BCl_3 str (10%)
	240 m	243	ν_5 BCl_3 sym def (85%), PB str (15%)
174 w	179 w	154	ν_{12} BCl_3 rock (90%), BCl_3 def (10%)
153 m	154 vw		
	142 w		
	90 vw		Lattice modes
80 w			
	67 vw		
	57 w		

[a] Abbreviations used: v, very; s, strong; m, medium; w, weak; sh, shoulder; b, broad.

Table II. Observed and Calculated Infrared and Raman Frequencies (cm^{-1}) of Solid Phosphine-Trichloroborane-d_3[a]

Ir	Raman	Calcd	Assignment and PED
1784 m	1786 s	1767	ν_7 PD_3 antisym str (100%)
	1756 sh, w		
1740 w	1743 vs	1738	ν_1 PD_3 sym str (100%)
947 w			$\nu_9 + \nu_{11} = 975$
902 w			$\nu_2 + \nu_{12} = 932$
832 w			$\nu_4 + \nu_{10} = 838$
804 w			$\nu_8 + \nu_{12} = 792$
763 s	770 m	784	ν_2 PD_3 sym def (85%), BP str (15%)
708 s	710 w	721	ν_9 BCl_3 antisym str (60%) PD_3 def (30%), BCl_3 def (10%)
658 m	648 m	669	ν_3 PB str (65%), BCl_3 def (20%), BCl_3 str (15%)
636 m	634 m	644	ν_8 PD_3 antisym def (60%), BCl_3 str (30%), BCl_3 def (10%)
486 w			$2\nu_{11} = 508$
440 s	440 m	439	ν_{10} PD_3 rock (70%), BCl_3 str (30%)
395 m	397 m	399	ν_4 BCl_3 sym str (80%), PB str (20%)
253 m	250 m	254	ν_{11} BCl_3 antisym def (90%), BCl_3 str (10%)
	240 m	236	ν_5 BCl_3 sym def (85%), PB str (15%)
163 w	156 w	148	ν_{12} BCl_3 rock (95%), BCl_3 def (5%)
147 w	135 vw		
	90 vw		Lattice modes
78 vw			
67 vw, b			

[a] For abbreviations used see Table I.

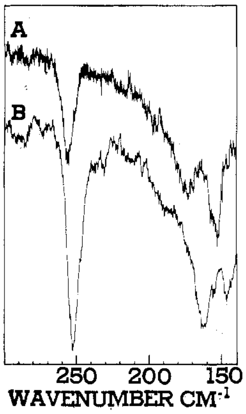

Figure 3. A. Far-infrared spectrum of solid $H_3P \cdot BCl_3$. B. Far-infrared spectrum of solid $D_3P \cdot BCl_3$.

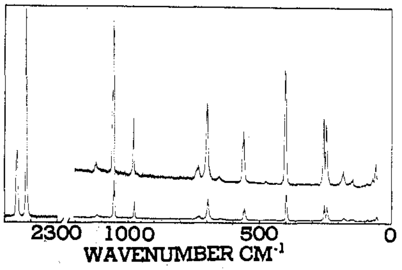

Figure 4. Raman spectrum of solid $H_3P \cdot BCl_3$.

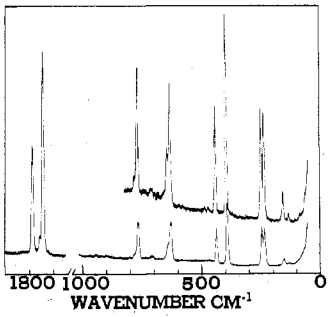

Figure 5. Raman spectrum of solid $D_3P \cdot BCl_3$.

Vibrational Assignment

Irrespective of whether the molecule phosphine-trichloroborane has the staggered or the eclipsed configuration, it must belong to the point group C_{3v}. There are 12 fundamental vibrations which span the representations: $5\ A_1 + A_2 + 6\ E$. Although vibrations of both A_1 and E symmetry are active in both the infrared and Raman techniques, frequently there will be normal modes which will not appear in one or the other spectrum. Thus, we have recorded both spectra over the entire 50-2700-cm^{-1} range. The internal rotation belongs to the A_2 symmetry species and is inactive for the "isolated" molecule. The normal vibrations associated with the H_3P moiety can be readily assigned on the basis of isotopic shifts and the frequencies reported for the "free" PH_3 molecule. The symmetric P-H stretching mode is observed at 2416 cm^{-1} in both spectra with the resulting Raman line being the most intense in the spectrum, whereas the corresponding infrared band is quite weak. The antisymmetric P-H stretch comes at 2450 cm^{-1} with the infrared band being much stronger than that of the symmetric motion, but the opposite is true in the Raman effect. These two modes shift to 1740 and 1784 cm^{-1}, respectively, with deuteration.

The PH_3 symmetric deformation is observed at 1052 cm^{-1} with the antisymmetric motion falling at 977 cm^{-1}. These two bands shift to 763 and 635 cm^{-1}, respectively, with deuteration; this shift is consistent with nearly "pure" hydrogen motion. The PH_3 rocking mode gives rise to a

Raman line of medium intensity at 559 cm^{-1} which shifts to 440 cm^{-1} with deuteration; the corresponding infrared band is quite strong. The P-B stretching mode is readily assigned to the Raman line of medium intensity at 699 cm^{-1} which has a strong infrared counterpart of 698 cm^{-1}. This mode is found at 653 cm^{-1} in the spectrum of the deuterium compound and the shift is slightly larger than one might expect for a pure P-B motion.

The remaining fundamentals are all associated with the BCl_3 moiety, except the torsion, and their assignment follows fairly straightforwardly from the frequencies previously determined for the uncomplexed molecule. The antisymmetric B-Cl stretch gives rise to a weak Raman line at 730 cm^{-1} with a strong infrared counterpart at 725 cm^{-1}. The small shift with deuteration indicates slight mixing with the P-H motions. The symmetric BCl_3 stretch falls at 401 cm^{-1}, whereas the BCl_3 antisymmetric and symmetric deformations are found at 255 and 240 cm^{-1}, respectively. None of these bands show significant shifts with deuteration. The skeletal rocking mode is split into two bands in both the infrared, 174 and 153 cm^{-1}, and Raman, 179 and 154 cm^{-1}, spectra. In addition, there is a rather poor correlation between the Raman and infrared frequencies. The frequency difference can be attributed to factor group splitting resulting from the lower site symmetry in the crystal. An investigation of the far-infrared spectrum of a saturated solution in benzene showed only one band at 152 cm^{-1} (see Figure 6) which is consistent with the splitting being attributed to the solid state. The shift with deuteration indicates considerable PH_3 motion.

The vibrational assignments are supported by the Teller-Redlich product rule calculation. For the normal vibrations of symmetry species A_1, the theoretical τ value is 1.98 and the observed value is 2.02. Similarly for the vibrations of species E, the observed τ value is 2.85 which compares quite well with the calculated value of 2.89. The τ value for the A_1 species is about 2% high but the uncertainty of ±2 cm^{-1} for the low-frequency bands can readily account for the discrepancy.

The phosphine torsional vibration, ν_6, is inactive in both the infrared and Raman spectra for the "free" molecule. In the solid state, however, the selection rules may be sufficiently relaxed to permit observation of this mode. In fact, this has been found to be true in a sufficient number of cases so that the observation of torsional modes in the solid has been found to be the rule rather than the exception for many molecules of C_{3v} symmetry.[17-19] However, a careful check of both the low-frequency Raman and infrared spectra showed no band with a shift factor near 1.4 and all of the observed bands that had not been assigned as intramolecular fundamentals could be assigned to lattice modes. Therefore, no information was obtained on the barrier to internal rotation of this molecule.

Normal-Coordinate Analysis

No calculations have been reported for the force constants or normal coordinates of H_3PBCl_3. Since we could not obtain a microwave spectrum of this material, we assumed the following parameters: P-H distance, 1.40 Å; P-B distance, 1.935 Å; B-Cl distance, 1.74 Å; HPH angle, 101°; ClBCl angle, 114°. The 20 internal coordinates which form a basis for the equations of motion were the same as those previously defined[20] for the CH_3GeI_3 molecule. Similarly, the same symmetry coordinates were defined and 11 valence force field constants were chosen, which included eight principal and three interaction constants. Schachtschneider's perturbation program[21] was used to adjust the constants for a best fit to the observed frequencies and to test the constants for significance. Because of the importance of the matrix J^tWJ in the least-squares equation, the determinant of the matrix was tested after each iteration for singularity by comparing the product of the diagonal elements[22] to the determinant and these two quantities were found to be of similar magnitude. The final constants which were found reproduced the observed frequencies to an average error of 6.0 cm^{-1} (1%). The final force field is given in Table III and the calculated frequencies are listed in Tables I and II. The potential energy distribution which is also given in Tables I and II shows appreciable mixing of the BCl_3 antisymmetric stretch and the PH_3 rock in the "light" molecule. There is also considerable mixing of the P-B stretch with the BCl_3 stretch and deformation. Most of the other vibrations appear to be "reasonably pure" motions.

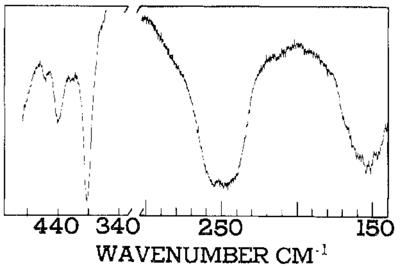

Figure 6. Far-infrared spectrum of a saturated C_6H_6 solution of $H_3P \cdot BCl_3$.

Table III. Internal Force Constants for $H_3P \cdot BCl_3$ and $D_3P \cdot BCl_3$

Force constant[a]	Group	Value,[b] mdyn/Å
K_Q	B-Cl str	2.20 ± 0.04
K_S	P-H str	3.43 ± 0.01
K_R	P-B str	1.96 ± 0.04
H_α	∠ClBCl bend	1.11 ± 0.04
H_β	∠ClBP bend	0.567 ± 0.034
H_γ	∠HPH bend	0.402 ± 0.005
H_δ	∠BPH bend	0.552 ± 0.010
F_{QQ}	B-Cl str, B-Cl str	0.605 ± 0.052
$F_{R\beta}$	P-B str, ∠ClBP bend	0.232 ± 0.034
$F_{Q\alpha}$	B-Cl str, ∠ClBCl bend	0.452 ± 0.027
$F_{\alpha\alpha}$	∠ClBCl bend, ∠ClBCl bend	0.209 ± 0.040

[a] Valence force field constants. [b] All bending coordinates weighted by 1 Å.

The force constants obtained in this study show some interesting trends. The P-H stretching force constant of 3.43 ± 0.01 mdyn/Å is slightly larger than the 3.32 mdyn/Å reported[23] for PH_3. This increase is consistent with the expected shortening of the P-H bond upon coordination. The B-Cl stretching force constant of 2.20 ± 0.04 mdyn/Å is appreciably lower than the 4.33-mdyn/Å value reported[24] for the corresponding force constant in BCl_3. It is

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(18) J. R. Durig, S. M. Craven, and J. Bragin, *J. Chem. Phys.*, 53, 38 (1970).

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Table IV. Comparison of Force Constants and Bond Distances of Some Phosphine-Boranes

Molecule	P-B dist, Å	P-B str freq, cm^{-1}	P-B force constant, mdyn/Å	Ref
$F_3P\cdot BH_3$	1.836	607	2.45	*a, b*
$(CH_3)_3P\cdot BH_3$	1.901	571	2.51	*c, d*
$H_3P\cdot BH_3$	1.937	563	2.04	*e, f*
$H_3P\cdot BCl_3$	(1.94)[g]	699	1.96	*h*

[a] Reference 4. [b] S. J. Meischen, Ph.D. Thesis, University of South Carolina, 1972. [c] Reference 6. [d] Part III: J. D. Odom, B. A. Hudgens, and J. R. Durig, to be submitted for publication. [e] Reference 1. [f] J. R. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.*, 11, 930 (1972). [g] Estimated value. [h] This work.

believed that this low force constant value reflects the unavailability with complex formation of the vacant orbital on boron. The change in the nature of the bonding is also shown by the large frequency shift to 725 cm^{-1} for the antisymmetric B-Cl stretch of the adduct from 954 cm^{-1} for the corresponding motion in BCl_3.[24]

The high frequency for the P-B stretching mode appears to be due in a large measure to the mixing with other motions. In Table IV are listed the P-B stretching frequencies, force constants, and bond lengths for a number of phosphorus-boron compounds. The P-B force constant value of 1.96 mdyn/Å is in the same range as that reported for the corresponding constant in $H_3P\cdot BH_3$. This low value in H_3PBCl_3 is consistent with the relative instability of this adduct in the gas phase.

In addition to the 11 force constants listed in Table III, the interaction constants $F_{Q\beta}$, F_{RQ}, $F_{R\alpha}$, and $F_{\alpha\beta}$ were also calculated but their values were all less than 0.02 mdyn/Å and the frequency fit was not appreciably improved. Therefore, these additional interaction constants were not retained in the final force field.

Discussion

The high frequency for the P-H stretching modes is consistent with the shortening of this bond with coordination. For example, we have found that the P-H bond has a distance of 1.398 Å in $H_3P\cdot BH_3$, which is more than 0.02 Å shorter than the P-H bond in PH_3. This shortening was accompanied by an increase of about 8° of the HPH angle. The frequency of 2450 cm^{-1} indicates that the P-H bond in $H_3P\cdot BCl_3$ is also near 1.40 Å.

We had no difficulty observing the infrared spectrum of the adduct in a saturated solution of benzene. Thus, the molecule appears to be quite stable at room temperature in this solution but all attempts to observe the spectrum of the adduct in the gas phase failed. The previously determined concentrations in the gas phase were obtained by measurements of the pressure from a known quantity of substance. However, we always observed a residue when the material was vaporized and we believe that such a residue could have led to the earlier erroneous results. The residue is probably a "higher" adduct of phosphine-trichloroborane or a polymeric material; it was not possible to characterize the residue by its vibrational spectrum.

Both infrared and nmr data indicate that in benzene solution an equilibrium exists between the adduct H_3PBCl_3 and the free Lewis acid and base and that rapid exchange is occurring. The infrared spectrum of H_3PBCl_3 in benzene is shown in Figure 6 and one can clearly see a distinct band at 440 cm^{-1} which corresponds to the A_2'' BCl_3 bending mode. This band results from the molecule which contains the ^{11}B isotope and the weak feature at 465 cm^{-1} results from the same motion for the $^{10}BCl_3$ molecule. These frequencies are identical with those observed for this motion in pure BCl_3 in benzene. Thus, the infrared data indicate that there must be some "free" BCl_3 present at room temperature even in solution.

The observation of boron-phosphorus coupling constants in acid-base adducts of this type is a common occurrence[25,26] and the absence of such a coupling in both the coupled and ^1H-decoupled spectra is consistent with a rapid exchange process. That the process is fast on an nmr time scale can be deduced from the fact that no resonance from free BCl_3 is observed (see Experimental Section for the chemical shift value of BCl_3 in C_6H_6). Thus, one is observing a ^{11}B chemical shift which is an average between that of free BCl_3 and the complexed species. The absence of a B-P coupling constant and a chemical shift value of +17.0 ppm from external $B(OMe)_3$ in $H_3P\cdot BCl_3$ can be contrasted to the results obtained for $H_3P\cdot BBr_3$. In this adduct the ^{11}B nmr exhibits a $J_{^{11}B-^{31}P}$ of 127 Hz and a chemical shift of +42.8 ppm from external $B(OMe)_3$.[27]

Registry No. $H_3P\cdot BCl_3$, 13766-68-2; $D_3P\cdot BCl_3$, 38656-85-8.

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