There are at least nine sharp low-frequency (32-111 cm^{-1}) Raman lines which can only be assigned to intermolecular fundamentals. Several of these lines have corresponding infrared bands and there appear to be several additional infrared bands between 80 and 140 cm^{-1}. The low-frequency Raman lines are probably librational modes, whereas the infrared bands probably arise from mainly translational motions. Further characterization of these bands is not possible without knowing the crystal structure. However, it should be pointed out that such a large number of intermolecular fundamentals implies more than two molecules per unit cell.

Discussion

It appears quite clear from our data that there are at least two isomers present in the gas and liquid phases. One of the forms is the planar conformation which is the conformer that remains in the solid state. The planar conformation is the one expected on the basis of earlier studies on BX_3 molecules. However, it should be pointed out that there may be nonbonded H- - -H repulsions of the terminal CH_2 groups from our model calculations on the planar form. By assuming B–C, C=C, and C–H bond lengths of 1.60, 1.347, and 1.081 Å, respectively, the nonbonded distances between the hydrogens of the CH_2 group and those of the adjacent CH group were found to be 2.00 Å which is somewhat less than twice the van der Waals radius of hydrogen (2.4 Å). Therefore, one might expect the presence of a second conformer in the fluid states which would have the vinyl groups tilted out of the plane to some degree. The symmetry of this second conformer cannot be confidently determined from the vibrational study.

The C_{3v} pyramidal forms (three) cannot unequivocably be ruled out and there is some evidence for their existence. The 9 A′ and 5 A″ modes for the planar C_{3h} form become 10 A_1 and 4 A_2 modes in the pyramidal C_{3v} conformations. The BC_3 out-of-plane A″ mode for the C_{3h} form becomes the tenth A_1 mode in the C_{3v} conformer. The other 4 A″ modes for the C_{3h} form become A_2 modes under C_{3v} symmetry. According to selection rules for this symmetry A_2 modes are both Raman and infrared inactive. This could account for the lack of the observation of the CH_2 twist and wag and CH out-of-plane motions for the other conformer which is present in the gas and liquid states. Although a pyramidal C_{3v} structure cannot be ruled out, it would seem likely that, if a planar form is present which has H- - -H nonbonded repulsions, the vinyl groups would repel each other out of the plane into a form (C_3) which is closer to planar but has minimized the H- - -H repulsion rather than into a pyramidal form which requires a change of boron hybridization (sp^2–sp^3) and which may have H- - -H nonbonded distances closer than those for the C_3 form.

The C_s conformer seems improbable on the basis of the BC stretching motions as well as the low-frequency vibrational data. This is particularly true for the Raman spectrum of the gas phase where no Q branches were observed for the skeletal bending modes but would be expected for a conformer of C_s or C_1 symmetry.

The possibility exists that some association between trivinylborane molecules may occur since both acidic and basic sites are located in the trivinylborane moiety. Such association could give rise to the broadening of the lines, but it should be more prevalent in the liquid state than in the gaseous state. Since such behavior was not observed between the two fluid states, this explanation does not appear to be very probable.

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Reaction of Methyldichlorophosphine with Some Simple Boron Compounds

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Boron trichloride, boron tribromide, and boron triiodide form 1:1 adducts with methyldichlorophosphine. Boron trifluoride does not react with methyldichlorophosphine, and diborane reacts with methyldichlorophosphine to give a mixture of products. Halogen exchange between methyldichlorophosphine and boron tribromide or boron triiodide is observed when phosphine–borane adducts derived from those compounds are formed.

Introduction

The formation of adducts between boron compounds and phosphines has been the subject of much recent work.[1-5] We have investigated the systems composed of boron trihalides or diborane and methyldichlorophosphine, in order to ascertain the basicity of this phosphine compared to that of trimethylphosphine or phosphorus trichloride. We also were interested in any similarity these systems might have to boronium compounds formed by the reactions of amines or phosphine oxides with boron trihalides.

Experimental Section

Materials. Boron trichloride and boron trifluoride were obtained from Matheson Coleman and Bell and were used without further purification. Boron tribromide and boron triiodide were obtained from RIC Chemicals and used as received. Diborane was prepared by standard procedures[6] on a vacuum line and was stored in an all-glass

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(1) See, for example, the excellent reviews by G. Urry and G. W. Parshall in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, pp 325 ff, 617 ff.

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vessel on the vacuum line. Methyldichlorophosphine was obtained from the Ethyl Corp. and was checked for purity by nmr spectroscopy.[7] All solvents were dried over calcium hydride or Linde Molecular Sieve 4A.

Manipulations. All air-sensitive or water-sensitive substances were handled and transferred in an atmosphere of dry nitrogen in a Vacuum Atmospheres Corp. inert-atmosphere box equipped with a Dri-Train Model HE-93B. Reactions were carried out in an all-glass vacuum line by transferring volatile reagents to a cooled reaction vessel, which was stirred magnetically by a Teflon-coated stir bar and external magnetic stirrer as the temperature was allowed to rise.

Product Characterization and Analyses. The phosphorus and boron analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn., carbon and hydrogen analyses were done by Peninsular ChemResearch, Gainesville, Fla., and halide analyses were done in this laboratory by the Volhard method. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. Nuclear magnetic resonance data were obtained using a Varian Associates A-60A spectrometer. The mass spectra of the compounds were determined with a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Sublimation pressures were measured in a glass manometer system with an operating range from 2 μ to 100 Torr. Details of construction are available on request.

Reaction of Boron Trichloride with Methyldichlorophosphine. A 14.47-g (124-mmol) sample of methyldichlorophosphine was weighed into a 50-ml round-bottom flask, to which 20 ml of dry $CHCl_3$ and a magnetic stir bar were added. A foam trap and adapter were attached, and the entire apparatus was removed from the drybox and attached to a vacuum line. The reaction mixture was frozen with liquid nitrogen and the pressure was reduced to 10^{-4} Torr. The vessel was then isolated from the vacuum line while a boron trichloride cylinder was attached and boron trichloride was transferred to a graduated trap cooled by liquid nitrogen. The boron trichloride in the trap was then allowed to melt, and 11 ml (120 mmol) was transferred to the reaction vessel. The reaction mixture was allowed to melt, was brought up to the temperature of a salt-ice slush, and then was stirred for 0.5 hr. A white solid was produced almost immediately. The reaction vessel was evacuated into a liquid nitrogen cooled trap (a considerable amount of product was lost in this operation because of the extreme ease with which the solid sublimes; the trap contained a great deal of white material) and was taken into the drybox; weight of residue 15.31 g (54.4% based on boron trichloride used). The product melts at 119–120° when heated rapidly but sublimes at a lower temperature when heated more slowly. A purified sample for analysis was obtained by sublimation at 10^{-3} Torr onto a Dry Ice cooled finger. *Anal.* Calcd for $BCl_3 \cdot PCl_2CH_3$: P, 13.23, B, 4.62; C, 5.13; H, 1.19; Cl, 75.75. Found: P, 12.99; B, 4.60; C, 4.98; H, 1.36; Cl, 75.73.

An attempt to carry out the reaction of boron trichloride with liquid methyldichlorophosphine in the absence of solvent at −25° resulted in the liberation of so much heat that the reaction was difficult to control on the vacuum line. Tensimetric titration[8] of the pure liquids with constant cooling clearly established a 1:1 stoichiometry for this reaction.

Reaction of Methyldichlorophosphine with Boron Tribromide. A 2.50-g portion of boron tribromide (10 mmol) was weighed into a vessel which was subsequently removed from the drybox and attached to the vacuum line. A 1.27-g (11-mol) portion of methyldichlorophosphine and 20 ml of dry chloroform were placed in a reaction vessel equipped with a stir bar, foam trap, and vacuum line adapter. This vessel was removed from the drybox and attached to the vacuum line. The contents of both containers were frozen with liquid nitrogen and evacuated. The boron tribromide was warmed to room temperature and allowed to enter the vacuum line and condense into the liquid nitrogen cooled reaction flask. The reaction vessel was isolated from the vacuum line, warmed to room temperature, and stirred for 0.5 hr, during which time a pink precipitate formed. The reaction vessel was protected from light by wrapping it in aluminum foil, since boron tribromide is known to decompose in light to form elemental bromine, a possible source of the pink coloration. The solvent was removed under high vacuum, yielding a cream-colored solid residue. The reaction flask was removed to the drybox, where the residue was weighed; yield 3.45 g (94.5% based on boron tribromide used). *Anal.* Calcd for $H_3CPCl_2 \cdot BBr_3$: C, 3.27; H, 0.82; B, 2.94; P, 8.43. Found: C, 3.00; H, 0.86; B, 2.81; P, 8.67. The ratio of total halogen found to the total halogen calculated was 0.977.

Reaction of Methyldichlorophosphine with Boron Triiodide. This reaction was performed in the same manner as the above, except benzene was used as solvent. A 3.93-g (10-mmol) sample of boron triiodide was mixed with 1.27 g (11 mmol) of methyldichlorophosphine. A 4.73-g amount of yellow, crystalline product was isolated (91.7% yield based on boron triiodide). A portion of the crude product was sublimed by heating under high vacuum. This substance exhibited no melting point, but only a deepening in color, up to 320°, at which temperature the solid sublimed, seemingly unchanged, in the sealed capillary. *Anal.* Calcd for $BI_3 \cdot PCH_3Cl_2$: B, 2.13; P, 6.09; C, 2.36; H, 0.59. Found: B, 2.19; P, 6.04; C, 2.06; H, 0.29. The ratio of total halogen found to the total halogen calculated was 0.948.

Reaction of Boron Trifluoride with Methyldichlorophosphine. In two experiments, one involving boron trifluoride etherate at room temperature and the other boron trifluoride in methylene chloride at −78°, we found no evidence that boron trifluoride forms a stable adduct with methyldichlorophosphine. Methyldichlorophosphine was recovered and characterized by its nmr spectrum, in amounts essentially equal to the amounts used in the reactions.

Reaction of Diborane with Methyldichlorophosphine. Diborane was prepared by adding slowly 1.89 g (50 mmol) of sodium borohydride to 50 ml of degassed 85% phosphoric acid on a vacuum line and was purified as described by Norman and Jolly.[6] A 2.3-g sample of methyldichlorophosphine (20 mmol) was weighed into a 100-ml round-bottom flask to which 20 ml of dry methylene chloride and a magnetic stir bar were added. The flask containing methyldichlorophosphine was cooled by liquid nitrogen and evacuated. Diborane was then condensed into this flask at −198° and the uncondensable gas was pumped out. The liquid nitrogen bath was then replaced by a Dry Ice–acetone bath (−78°) and the contents allowed to stand for 5 hr. The pressure at this temperature was 190 Torr but dropped to 50 Torr when the Dry Ice–acetone bath was removed. The sudden drop of pressure may suggest that methyldichlorophosphine and diborane react slowly at −78° but react more rapidly at higher temperatures. After the reaction flask reached room temperature it was allowed to stand for 6 hr more. About 50% of the methylene chloride was transferred out and the reaction flask was taken into the drybox. The proton nmr spectrum of the product (Table I) indicated that the reaction product was $(CH_3)PCl_2 \cdot BH_3$. The rest of the methylene chloride was removed under high vacuum and the absence of methylene chloride was confirmed by observing the proton nmr spectrum of the product in benzene. The final product was a colorless liquid weighing 2.499 g. The yield was 95.5% based on the methyldichlorophosphine taken and calculated for $Cl_2(CH_3)P \cdot BH_3$. The infrared spectrum of the product had a strong absorption at 2400–2460 cm^{-1} which was attributed to B–H stretching. The rest of the infrared data are recorded in Table II. *Anal.* Calcd for $BH_3PCH_3Cl_2$: C, 9.18; H, 4.63; Cl, 54.25. Found: C, 8.66; H, 4.00; Cl, 52.52, 53.15. The proton nmr spectrum of the product recorded after storing for 5 days gave a multiplet for methyl protons.

Results and Discussion

It is evident from the observations made during the course of this study that methyldichlorophosphine acts as a base toward certain of the boron compounds chosen here. As has been found in other investigations[9] and borne out here by its lack of reactivity toward methyldichlorophosphine, boron trifluoride is the weakest of the Lewis acids that we studied with respect to this particular base. Methyldichlorophosphine seems to be a good base, stronger than phosphorus trichloride,[10] which may be rationalized on the basis of there being one fewer chlorine atom present in methyldichlorophosphine. An enhancement of base strength in either phosphorus trichloride or methyldichlorophosphine by a p → d π bond between chlorine and phosphorus seems unlikely, since such 3p → 3d π bonds now appear to have relatively little importance.[11]

We have investigated the base strength of trimethylphos-

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Table I. Proton Nuclear Magnetic Resonance Spectra of Adducts of Methyldichlorophosphine

Boron compd	Multiplicity and shift	Coupling constant
$\mathrm{BCl_3}$ (sublimed)	Doublet, 154 Hz[a]	$J_{\mathrm{P-C-H}} = 3.0$ Hz
$\mathrm{BBr_3}$ (sublimed)[b]	Doublet, 162 Hz[a]	$J_{\mathrm{P-C-H}} = 6.8$ Hz
	Doublet, 169 Hz[a]	$J_{\mathrm{P-C-H}} = 6.0$ Hz
	Doublet, 177 Hz[a]	$J_{\mathrm{P-C-H}} = 4.8$ Hz
$\mathrm{BI_3}$ (crude)	Doublet, of quartets, 175 Hz[a]	$J_{\mathrm{P-C-H}} = 7.8$ Hz
		$J_{\mathrm{B-P-C-H}} = 1.4$ Hz
$\mathrm{B_2H_6}$ (sublimed)	Unresolved Doublet, 177 Hz[a]	$J_{\mathrm{P-C-H}} = 8$ Hz
$\mathrm{B_2H_6}$ (crude)	Doublet ($\mathrm{CH_3}$ protons), 83.5 Hz[c]	$J_{\mathrm{P-C-H}} = 4.5$ Hz
		$J_{\mathrm{P-B-H}} = 0.75$ Hz
	Quartet ($\mathrm{BH_3}$ protons), 145 Hz[c]	$J_{\mathrm{B-H}} = 104$ Hz

[a] Downfield from internal tetramethylsilane. [b] Three products obtained. [c] Measured in $\mathrm{CH_2Cl_2}$; shift reported as hertz upfield from the $^{13}\mathrm{C}$ side band at 230.5 Hz downfield from internal tetramethylsilane.

phine relative to that of methyldichlorophosphine by allowing trimethylphosphine to react with $\mathrm{PCH_3Cl_2\cdot BCl_3}$ in a mole ratio of 1:1. The nmr spectrum of the solid product of this reaction matched that of $\mathrm{P(CH_3)_3\cdot BCl_3}$ prepared according to the procedure of Sirtl and Adler.[12] There was also nmr evidence that trimethyldichlorophosphorane and pentamethylcyclopentaphosphine are present in the products of the displacement reaction, as would be expected from the known reactions[13] of halophosphines with trialkylphosphines. Here, some of the methyldichlorophosphine released by displacement is presumed to react with some of the trimethylphosphine present in accord with ref 13.

Table II. Infrared Spectra of Boron–Phosphorus Adducts

Compd	Spectral lines and intensities,[a] $\mathrm{cm^{-1}}$
$\mathrm{PCH_3Cl_2\cdot BCl_3}$	3500–3000 vs, vb, 1460 vs, b, 1392 m, 1285 w, b, 1192 m, 1150 w, 1095 w, 1020 w, b, 985 m, 855 s, 740 vs, b, 575 s, 545 m, sh, 510 s, 475 m, sh
$\mathrm{PCH_3Cl_2\cdot BBr_3}$[b]	3500–3000 vs, vb, 1450 vs, vb, 1305 m, 1020 w, 880 m, 730 s, 630 m, 575 m, 540 m, 500 w, 465 m
$\mathrm{PCH_3Cl_2\cdot BI_3}$[b]	3500–3000 vs, vb, 1390 m, 1275 m, 1190 w, 892 s, 885 sh, 873 vs, 855 sh, 805 w, 745 m, 675 m, 560 vs, 520 m, 485 vs, 395 s, 370 m, 335 m, 325 m
$\mathrm{PCH_3Cl_2\cdot BH_3}$[b]	3020 m, 2930 m, 2460–2400 s, 1415 s, 1370–1360 vw, 1305 m, 1265 w, 1110 vw, 1070 m, 990 s, 950 s, 890 w, 810 vw, 740 vw, 710–630 vs, 500 m, 450 vw, 390 vw, 280 s

[a] Key: s, strong; m, medium; w, weak; sh, shoulder; v, very; b, broad. [b] Mixture of products; see text.

The nuclear magnetic resonance spectra and the infrared spectra of the compounds formed in this research are shown in Tables I and II. There is evidence in the spectra of the products of the reaction between methyldichlorophosphine and boron tribromide or boron triiodide that halogen exchange has taken place, as has been found[10,14] in other work involving boron–phosphorus adducts wherein both phosphorus–halogen and boron–halogen bonds are present. The infrared absorptions found between 710 and 750 $\mathrm{cm^{-1}}$ in these adducts are close enough to the B–Cl stretching frequency assigned by Taylor[15] at 755 $\mathrm{cm^{-1}}$ in trimethylamine–trichloroborane to be assigned to that bond in this instance. The infrared absorptions for P–Br and P–I bonds are generally found between 495 and 320 $\mathrm{cm^{-1}}$ and between 350 and 290 $\mathrm{cm^{-1}}$,[16] respectively. The appearance of a peak at 465 $\mathrm{cm^{-1}}$ in the infrared spectrum of what should be $\mathrm{CH_3PCl_2\cdot BBr_3}$ and the peaks at 335 and 325 $\mathrm{cm^{-1}}$ in the infrared spectrum of what should be $\mathrm{CH_3PCl_2\cdot BI_3}$, therefore, is very likely the result of phosphorus–halogen bonds produced by halogen exchange between the boron and phosphorus atoms. The exchange of halogens is clearly noticeable when the mass spectra of these bromo and iodo adducts are examined. Table III shows the major peaks in the mass spectra of the compounds. Since there is a possibility that the halogen exchange occurs only in the mass spectrometer's electron beam, we undertook to isolate the "exchanged" phosphines by a displacement reaction as follows. A fivefold excess of freshly distilled γ-picoline was added to these solids, and methylene chloride was added as solvent. The methylene chloride was checked for methyldichlorophosphine by nuclear magnetic resonance spectroscopy and none was found (by comparison with the known chemical shifts and coupling constants of methyldichlorophosphine and by the addition of pure methyldichlorophosphine and production thereby of new peaks). Rather, new peaks were observed, which could only, by their shifts and coupling constants, be assigned to phosphines. The methylene chloride was, along with all volatile material, stripped into a vessel on the vacuum line and then evaporated. The residue from these evaporations showed mass spectral peaks for methyldibromophosphine or methyldiiodophosphine, as the solid boronium compounds that are also products of this displacement reaction showed the mass fragments $\mathrm{B(\gamma\text{-}pic)_2Cl^+}$ and $\mathrm{B(\gamma\text{-}pic)Cl_2^+}$. Using standard references[17] for values of bond strengths, we find that the enthalpy changes from halogen exchange are favorable, as shown for the illustrative reactions

$$\mathrm{PCH_3Cl_2\cdot BBr_3 = PCH_3ClBr\cdot BBr_2Cl} \qquad \Delta H = -4\ \mathrm{kcal}$$

$$\mathrm{PCH_3Cl_2\cdot BBr_3 = PCH_3Br_2\cdot BCl_2Br} \qquad \Delta H = -8\ \mathrm{kcal}$$

$$\mathrm{2PCH_3Cl_2\cdot BBr_3 = PCH_3Br_2\cdot BCl_3 + PCH_3Br_2\cdot BBr_2Cl} \qquad \Delta H = -16\ \mathrm{kcal}$$

$$\mathrm{2PCH_3Cl_2\cdot BBr_3 = PCH_3BrCl\cdot BCl_3 + PCH_3Br_2\cdot BBr_3} \qquad \Delta H = -12\ \mathrm{kcal}$$

$$\mathrm{2PCH_3Cl_2\cdot BBr_3 = PCH_3BrCl\cdot BCl_2Br + PCH_3Br_2\cdot BClBr_2} \qquad \Delta H = -12\ \mathrm{kcal}$$

We do not mean to say that the favorable enthalpy changes imply rapid halide exchange but only that since the entropies of reactants and products should be similar, the negative enthalpy values shown should favor formation of the products shown. All our attempts to isolate the mixed compounds by differential sublimation and differences in solubility failed, however.

There is also evidence that rapid exchange of phosphine as ligand occurs in the case of $\mathrm{PCH_3Cl_2\cdot BCl_3}$ in solution, as shown by the nuclear magnetic resonance spectra which we have obtained and which are shown in Table IV. The addition of successively larger amounts of methyldichlorophosphine to a solution of pure $\mathrm{PCH_3Cl_2\cdot BCl_3}$ in methylene

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Table III. Mass Spectra of Compounds

m/e	Intens[a]	Fragments[b]
		Reactants: $\mathrm{BBr_3}$, $\mathrm{PCH_3Cl_2}$
115	12	$^{10}\mathrm{B}^{35}\mathrm{Cl}_3$
116	19	$^{11}\mathrm{B}^{35}\mathrm{Cl}_3$, $\mathrm{PCH_3}{}^{35}\mathrm{Cl}_2$
117	10	$^{10}\mathrm{B}^{35}\mathrm{Cl}_2{}^{37}\mathrm{Cl}$
118	19	$^{11}\mathrm{B}^{35}\mathrm{Cl}_2{}^{37}\mathrm{Cl}$, $\mathrm{PCH_3}{}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$
119	6	$^{10}\mathrm{B}^{35}\mathrm{Cl}^{37}\mathrm{Cl}_2$
120	18	$^{11}\mathrm{B}^{35}\mathrm{Cl}^{37}\mathrm{Cl}_2$, $\mathrm{PCH_3}{}^{37}\mathrm{Cl}_2$
121	0	$^{10}\mathrm{B}^{37}\mathrm{Cl}_3$
122	1	$^{11}\mathrm{B}^{37}\mathrm{Cl}_3$
159	1	$^{10}\mathrm{B}^{79}\mathrm{Br}^{35}\mathrm{Cl}_2$
160	19	$^{11}\mathrm{B}^{79}\mathrm{Br}^{35}\mathrm{Cl}_2$, $\mathrm{PCH_3}{}^{35}\mathrm{Cl}^{79}\mathrm{Br}$
161	3	$^{10}\mathrm{B}^{79}\mathrm{Br}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$, $^{10}\mathrm{B}^{81}\mathrm{Br}^{35}\mathrm{Cl}_2$
162	30	$\mathrm{PCH_3}{}^{37}\mathrm{Cl}^{79}\mathrm{Br}$, $^{11}\mathrm{B}^{79}\mathrm{Br}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$, $^{11}\mathrm{B}^{81}\mathrm{Br}^{35}\mathrm{Cl}_2$, $\mathrm{PCH_3}{}^{35}\mathrm{Cl}^{81}\mathrm{Br}$
163	4	$^{10}\mathrm{B}^{79}\mathrm{Br}^{37}\mathrm{Cl}_2$, $^{10}\mathrm{B}^{81}\mathrm{Br}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$
164	10	$^{11}\mathrm{B}^{79}\mathrm{Br}^{37}\mathrm{Cl}_2$, $^{11}\mathrm{B}^{81}\mathrm{Br}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$, $\mathrm{PCH_3}{}^{37}\mathrm{Cl}^{81}\mathrm{Br}$
165	1	$^{10}\mathrm{B}^{81}\mathrm{Br}^{37}\mathrm{Cl}_2$
166	2	$^{11}\mathrm{B}^{81}\mathrm{Br}^{37}\mathrm{Cl}_2$
203	1	$^{10}\mathrm{B}^{79}\mathrm{Br}_2{}^{35}\mathrm{Cl}$
204	82	$^{11}\mathrm{B}^{79}\mathrm{Br}_2{}^{35}\mathrm{Cl}$, $\mathrm{PCH_3}{}^{79}\mathrm{Br}_2$
205	2	$^{10}\mathrm{B}^{79}\mathrm{Br}_2{}^{37}\mathrm{Cl}$, $^{10}\mathrm{B}^{79}\mathrm{Br}^{81}\mathrm{Br}^{35}\mathrm{Cl}$
206	100	$^{11}\mathrm{B}^{79}\mathrm{Br}_2{}^{37}\mathrm{Cl}$, $^{11}\mathrm{B}^{79}\mathrm{Br}^{81}\mathrm{Br}^{35}\mathrm{Cl}$, $\mathrm{PCH_3}{}^{79}\mathrm{Br}^{81}\mathrm{Br}$
207	3	$^{10}\mathrm{B}^{79}\mathrm{Br}^{81}\mathrm{Br}^{37}\mathrm{Cl}$, $^{10}\mathrm{B}^{81}\mathrm{Br}_2{}^{35}\mathrm{Cl}$
208	52	$^{11}\mathrm{B}^{79}\mathrm{Br}^{81}\mathrm{Br}^{37}\mathrm{Cl}$, $^{11}\mathrm{B}^{81}\mathrm{Br}_2{}^{35}\mathrm{Cl}$, $\mathrm{PCH_3}{}^{81}\mathrm{Br}_2$
209	1	$^{10}\mathrm{B}^{81}\mathrm{Br}_2{}^{37}\mathrm{Cl}$
210	0	$^{11}\mathrm{B}^{81}\mathrm{Br}_2{}^{37}\mathrm{Cl}$
		Reactants: $\mathrm{BI_3}$, $\mathrm{PCH_3Cl_2}$
207	1	$\mathrm{I}^{10}\mathrm{B}^{35}\mathrm{Cl}_2$
208	16	$\mathrm{I}^{11}\mathrm{B}^{35}\mathrm{Cl}_2$, $\mathrm{PCH_3I}^{35}\mathrm{Cl}$
209	1	$\mathrm{I}^{10}\mathrm{B}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$
210	6	$\mathrm{I}^{11}\mathrm{B}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$, $\mathrm{PCH_3I}^{37}\mathrm{Cl}$
211	1	$\mathrm{I}^{10}\mathrm{B}^{37}\mathrm{Cl}_2$
212	1	$\mathrm{I}^{11}\mathrm{B}^{37}\mathrm{Cl}_2$
299	1	$\mathrm{I}_2{}^{10}\mathrm{B}^{35}\mathrm{Cl}$
300	100	$\mathrm{I}_2{}^{11}\mathrm{B}^{35}\mathrm{Cl}$, $\mathrm{PCH_3I_2}$
301	2	$\mathrm{I}_2{}^{10}\mathrm{B}^{37}\mathrm{Cl}$
302	1	$\mathrm{I}_2{}^{11}\mathrm{B}^{37}\mathrm{Cl}$

[a] The relative intensities within $\mathrm{BBr_3}$ listings are comparable as a group and have no bearing on the intensities in the $\mathrm{BI_3}$ compounds. [b] Isotopes of P, C, H, and I are not considered.

Table IV. Nuclear Magnetic Resonance Spectra of Boron Trichloride–Methyldichlorophosphine Mixtures

Nature of species	τ, ppm	J_{PCH}, Hz
$\mathrm{PCH_3Cl_2{\cdot}BCl_3}$ sublimed	2.58	3.0
$\mathrm{PCH_3Cl_2{\cdot}BCl_3}$, sublimed + crude	2.58	3.8
$\mathrm{PCH_3Cl_2{\cdot}BCl_3}$, crude	2.59	4.8
$\mathrm{PCH_3Cl_2{\cdot}BCl_3}$, sublimed with $\mathrm{PCH_3Cl_2}$ added	2.36	10.2
$\mathrm{PCH_3Cl_2}$	2.24	17.0

chloride produces no peaks for unreacted methyldichlorophosphine and no peaks indicative of formation of phosphinoboronium ions such as $(\mathrm{CH_3PCl_2})_2\mathrm{BCl_2}^+$. We observe only a doublet, intermediate in both position and $J_{\mathrm{P-C-H}}$ between the doublet observed for pure $\mathrm{PCH_3Cl_2{\cdot}BCl_3}$ and the doublet found for pure methyldichlorophosphine. This strongly indicates rapid exchange. It is interesting to note that we have found no nmr, analytical, or tensimetric evidence that additional methyldichlorophosphine reacts with the 1:1 boron trichloride adduct to form ionic boronium compounds, as has been found in studies involving adducts of phenylphosphonic dichloride with boron trichloride or as have been synthesized using nitrogen-containing bases as ligands.[18-20] This may well result from the fact that oxygen atom is the coordinating species as in Gutmann's work and is less hindered in its approach to the boron atom (attached as it is to one other group only) than is phosphorus in our endeavors. It would be much more difficult sterically to place two phosphine-type phosphorus atoms on a single boron than two oxygen atoms from the phosphonic species. The lack of ionic nature is also evidenced in the extreme volatility of some of the species we have isolated.

The sublimation pressures of pure $\mathrm{PCH_3Cl_2{\cdot}BCl_3}$ were measured in the temperature range 17–61° and found to fit the equation $\ln P(\mathrm{mm}) = (-6420/T) + 23.8$. We found no evidence in this temperature range for dissociation of the adduct in the vapor phase.

There is evidence that pyrolysis plays a significant role in the behavior of these compounds. The nmr spectra of the freshly formed compounds were, in some cases, substantially different from those of the sublimed or even, in the case of the borane compound, aged substance. The unsublimed boron triiodide adduct displays a doublet of quartets in methylene chloride, which corresponds to $J_{\mathrm{P-CH}} = 7.8$ Hz and $J_{\mathrm{B-P-CH}} = 1.4$ Hz; the sublimed compound is difficultly soluble in the same solvent and shows only a broad doublet. Upon storing the $\mathrm{BH_3}$ complex, decomposition occurs as shown by the radical changes observed in the nmr spectrum of the compound and by the fact that the analysis changes markedly when the compound is allowed to stand. Similar instability of this nature has been observed[21] in the reaction of dimethylaminodichlorophosphine with diborane.

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Registry No. $\mathrm{PCH_3Cl_2}$, 676-83-5; $\mathrm{BCl_3}$, 10294-34-5; $\mathrm{PCH_3Cl_2{\cdot}BCl_3}$, 42583-15-3; $\mathrm{BBr_3}$, 10294-33-4; $\mathrm{PCH_3Cl_2{\cdot}BBr_3}$, 42583-16-4; $\mathrm{BI_3}$, 13517-10-7; $\mathrm{PCH_3Cl_2{\cdot}BI_3}$, 42583-17-5; $\mathrm{B_2H_6}$, 19287-45-7; $\mathrm{PCH_3Cl_2{\cdot}BH_3}$, 42583-18-6.

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