Boron Bis(trifluoromethyl)phosphinites¹

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Abstract: The prototype boron phosphinites $(CH_3)_2BOP(CF_3)_2$ (bp estd 70°), $CH_3B[OP(CF_3)_2]_2$ (bp estd 131°), and $B[OP(CF_3)_2]_3$ (mp -21°; bp estd 168°) were made by cleaving $(CF_3)_2POP(CF_3)_2$ with $(CH_3)_2BCI$, CH_3BCl_2 , or BCl₃. Their stability against dissociation to $(CF_3)_2POP(CF_3)_2$ and B-O-B compounds decreases in the order of listing, much as expected in view of the stability order of the conjectured products $(CH_3)_2BOB(CH_3)_2$, $(CH_3BO)_3$, and B_2O_3 . None of the three compounds showed any tendency toward an Arbuzov-like rearrangement to form P-B bonds. Their infrared and nmr spectra are fully reported, and in liquid dimethyl ether the ¹¹B results show complex bonding of boron, increasing in strength as CH_3 in $(CH_3)_3B$ is replaced by one, two, or three $OP(CF_3)_2$ groups.

The class of phosphinite esters $ROP(CF_3)_2$ recently was augmented by the synthesis of a new series in which R is any of a number of groups bonding through silicon,² and now is expanded further to include the new boron phosphinites $(CH_3)_2BOP(CF_3)_2$, $CH_3B[OP(CF_3)_2]_2$, and $B[OP(CF_3)_2]_3$, again with no observable tendency to convert to phosphine oxide types in the Arbuzov manner. The syntheses were performed most expeditiously by using B-Cl compounds to cleave the diphosphoxane $(CF_3)_2$ - $POP(CF_3)_2$.³ The processes could be observed by nmr spectroscopy, and the reactants and products were managed in a nearly quantitative manner by means of a Stock-type high-vacuum manifold.

Of special interest is the electron-acceptor character of boron in these phosphinites. In B(OCH₃)₃, the $O_{2p} \rightarrow B_{2p}$ π bonding suppresses the tendency of bases to draw boron out of its planar configuration, and in $(CH_3)_3B$ the methyl-group steric effect also is important; hence only fairly strong bases can bond to boron in these compounds. In our boron phosphinites, however, the strongly electronegative CF₃ groups not only strongly aid σ -electron withdrawal from boron, but also support the effective use of P_{3d} to draw electrons away from $O_{2p} \rightarrow B_{2p} \pi$ bonding. Accordingly, even such a weak base as dimethyl ether can form complexes, with $(CH_3)_2O \rightarrow B$ bond strength increasing as CH_3 on B is replaced by $OP(CF_3)_2$ groups. However, boron here still is not such a strong electron acceptor as to form a mechanistically effective bond to the virtually nonbasic lone-pair electrons of the $P(CF_3)_2$ group. Accordingly, the mechanism required for an Arbuzov-like rearrangement seems not to be available; the decomposition of $B[OP(CF_3)_2]_3$ occurs in other ways.

These boron phosphinites would be expected to dissociate to form $(CF_3)_2POP(CF_3)_2$ and the respective B-O-B bonded products $(CH_3)_2BOB(CH_3)_2$, $(CH_3BO)_3$, or B_2O_3 . Such processes would not lack feasible mechanisms, for it is very difficult to eliminate minute traces of hydrolysis products, including spectroscopic traces of $(CF_3)_2$ POH, which would be an effective catalyst for the formation of $(CF_3)_2$ POP $(CF_3)_2$. In the actual tests of thermal stability (all at 100°), there was no detectable formation of $(CF_3)_2$ POP $(CF_3)_2$ from $(CH_3)_2$ BOP $(CF_3)_2$, whereas $CH_3B[OP(CF_3)_2]_2$ formed an amount of $(CF_3)_2$ -POP $(CF_3)_2$ representing approximately 4% destruction in the suggested manner. Far less stable was B[OP- $(CF_3)_2]_3$, which was 97% destroyed at 100° (and indeed proved to be unstable even at 50°), with extensive formation of $(CF_3)_2$ POP $(CF_3)_2$.

The stability of $(CH_3)_2BOP(CF_3)_2$ against conversion to $(CF_3)_2POP(CF_3)_2$ and $(CH_3)_2BOB(CH_3)_2$ may be related to the previously stated rule that the reaction of ROR with QOQ to make 2ROQ becomes irreversible if R and Q are very different in regard to π -acceptor bonding power.² The same rule would account for the fairly high resistance of $CH_3B[OP(CF_3)_2]_2$ against dissociation to $(CF_3)_2POP(CF_3)_2$ and $(CH_3BO)_3$, but the π stabilization of the (BO)₃ ring would help to account for the observed minor conversion. In the case of $B[OP(CF_3)_2]_3$, however, the extensive formation of $(CF_3)_2POP(CF_3)_2$ would have to be attributed primarily to the high stability of the other main product, B_2O_3 .

It is suggested that $B[OP(CF_3)_2]_3$ would be an interesting ligand for the formation of tridentate complexes of transition metals. Especially the etherate would offer the possibility of a cluster of three six-atom rings sharing boron and metal atoms at the three-way junction points, but with the ether removed, there would be a possibility of drawing boron inward by dative-bond employment of electrons in the d_{z²} orbital of the metal.

Preparation of Special Reactants. The diphosphoxane $(CF_3)_2POP(CF_3)_2$ was made cleanly from Ag_2CO_3 and $(CF_3)_2PCI$. The method offered two advantages over the earlier $(CF_3)_2PI$ process:³ the easier purification of $(CF_3)_2PCI$ and the absence of attack upon vacuum-line mercury.

For virtually pure $(CH_3)_2BCl$, a mixture with slightly more than $2(CH_3)_3B$ per BCl₃ was heated in a closed container (12 hr at 200°), and the excess $(CH_3)_3B$ was easily removed from the product by high-vacuum fractional condensation.⁴ For nearly pure CH₃BCl₂ we employed a mixture containing slightly more than 2BCl₃ per

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⁽²⁾ A. B. Burg and J. S. Basi, J. Am. Chem. Soc., 90, 3361 (1968).

⁽³⁾ J. E. Griffiths and A. B. Burg, ibid., 84, 3442 (1962).

⁽⁴⁾ This method for obtaining $(CH_3)_2BCl$ free of CH_3BCl_2 was suggested by Dr. R. E. Williams of Space-General Corp. His kindness in supplying a sample of this product at one stage of our work is duly appreciated.

Table I. Volatility of Liquid $(CH_3)_2BOP(CF_3)_2$ (Log $P = 7.8170 + 1.75 \log T - 0.008T - 2273/T$) ($t_{760} = 69.6^{\circ}$; Trouton constant = 21.15 eu)

Temp, °C	-32.60	-21.45	-15.75	0.00	10.55	23.6
P_{obsd} , mm	4.04	9.48	14.15	37.43	67.35	128.8
P_{calcd}, mm	4.08	9.48	13.99	37.50	67.29	128.8

Table II. Volatility of Liquid $CH_3B[OP(CF_3)_2]_2$ (Log $P = 6.7520 + 1.75 \log T - 0.0055T - 2510/T$) ($t_{760} = 131.1^\circ$; Trouton constant = 21.70 eu)

Temp, °C	0.00	7.90	15.20	19.90	35.2	42.0
P_{obsd} , mm	2.11	3.64	5.85	7.76	18.5	26.8
P_{calcd}, mm	2.11	3.64	5.84	7.80	18.7	26.7

 $(CH_3)_3B$, with a trace of diborane for catalysis. After 12 hr at 400° (doubtless unnecessarily drastic conditions) the mixture was subjected to high-vacuum fractional condensation to remove the excess BCl₃. Both of the methylboron chloride products were better than 99% pure, according to their proton and boron nmr spectra.

The Dimethylboron Phosphinite. The nearly quantitative process (with millimole stoichiometry)

$$\begin{array}{rcl} (CH_3)_2BCl + (CF_3)_2POP(CF_3)_2 \rightarrow \\ 1.37 & 1.25 \\ & (CH_3)_2BOP(CF_3)_2 + (CF_3)_2PCl \\ & 1.20 & < 1.32 \end{array}$$

occurred during 5 days in a sealed tube at 50°. There was no residual diphosphoxane. The excess $(CH_3)_2BCl$ was not readily separable from the product $(CF_3)_2PCl$, and so was included in the "<1.32" fraction. The slight deficiency of the pertinent product is ascribed to incomplete recovery after the removal of all traces of $(CF_3)_2PCl$ by means of the high-vacuum microcolumn at -78° . The purity of the final product was indicated by its clean nmr spectra and by the appropriately correlated vapor-tension results shown in Table I.

The formula was confirmed by the vapor-phase molecular weight (found, 226.7; calcd, 225.9) and by a basic hydrolysis experiment in which a 0.371-mmole sample (by weight) gave 0.73 mmole of HCF₃ (calcd, 0.74).

For a test of thermal stability, a 0.072-mmole sample of $(CH_3)_2BOP(CF_3)_2$ was heated for 6 days in a sealed 2-ml tube at 100°. The recovery of $(CH_3)_2BOP(CF_3)_2$ now amounted to 0.060 mmole. The loss could be attributed almost entirely to a tiny trace of moisture, forming approximately 0.01 mmole of $(CF_3)_2POH$. This hydrolysis product was easily identifiable by its strong infrared bands at 3600 and 857 cm⁻¹, but the strong 924-cm⁻¹ band for $(CF_3)_2POP(CF_3)_2$ was either absent or not quite surely recognizable when the various fractions were investigated. No more than a 1% yield of it could have been formed, and even that could be related to the hydrolytic formation of $(CF_3)_2POH$.

The Methylboron Diphosphinite. The somewhat less accurately quantitative process (again with millimole stoichiometry)

$$\begin{array}{c} CH_{3}BCl_{2} + 2(CF_{3})_{2}POP(CF_{3})_{2} \rightarrow \\ 1.20 & 2.43 \\ CH_{3}B[OP(CF_{3})_{2}]_{2} + 2(CF_{3})_{2}PCl \\ 1.01 & 2.37 \end{array}$$

occurred during 8 days in a sealed tube at 50°. The reactants were completely consumed, and the virtually quantitative yield of the expected $(CF_3)_2PCl$ indicated the formula of the main product, even though the high-vacuum column fractionation (a 12-hr process with the reflux at -46°) did not afford a quite complete recovery of the pure product. Its composition was confirmed by a basic hydrolysis whereby 0.221 mmole of the substance yielded 0.86 mmole of HCF₃ (calcd, 0.88). Its molecular weight (in the vapor phase at 49°, 18 mm) was 394 (calcd, 395.8). If the slightly low result were due to an impurity, its presence was too slight to affect the normal correlation of the vapor-tension values shown in Table II.

For the thermal-stability test, a 0.1338-mmole sample was heated in a 1.5-ml sealed tube for 48 hr at 100°. There was no product volatile enough to pass a high-vacuum trap at -78° . The yield of $(CF_3)_2POP(CF_3)_2$, determined from the known intensity of its 924-cm⁻¹ infrared band, was 0.005 mmole, and with it came about 0.002 mmole of $(CF_3)_2POH$. The expected $(CH_3BO)_3$ could not have been isolated well enough for direct identification, nor recognized in the mixture by an infrared spectrum lacking adequate intensity or distinctiveness. The recovery of $CH_3B[OP(CF_3)_2]_2$ (measured as a vapor at 50° and 16 mm pressure) was 0.1267 mmole, or 94.7%, consistent with the observed yields of $(CF_3)_2POP(CF_3)_2$ and $(CF_3)_2POH$.

The Boron Triphosphinite. The synthesis of B[OP- $(CF_3)_2]_3$ was achieved by the use of either BCl₃ or $B(OCH_3)_3$ to cleave $(CF_3)_2POP(CF_3)_2$, at first giving no more than 15% yields of the desired triphosphinite. The difficulty seemed to be that either the final product or the intermediates $Cl_2BOP(CF_3)_2$ and $ClB[OP(CF_3)_2]_2$ or $(CH_3O)_2BOP(CF_3)_2$ and $CH_3OB[OP(CF_3)_2]_2$ (all too unstable for convenient isolation, but clearly indicated by the boron nmr spectra) were decomposing irreversibly long before the desired reaction could be completed. In the best experiment, 0.562 mmole of $(CF_3)_2POP(CF_3)_2$ and 0.174 mmole of BCl₃ were heated in a sealed nmr tube, first for 63 hr at 50°. The ¹¹B nmr spectrum now showed 3% BCl₃, 26% of presumed Cl₂BOP(CF₃)₂ (12.3 ppm upfield from BCl₃), 53% of presumed ClB[OP- $(CF_3)_2]_2$ (22.0 ppm upfield from BCl₃), and 18% of $B[OP(CF_3)_2]_3$ (30.3 ppm upfield from BCl_3). After 123 hr more at 50-57°, the respective proportions were 0, 17, 51, and 32%. These percentages, of course, omit the nonboron parts of the mixture, such as $(CF_3)_2PCI$.

After a further 48 hr at 57° and 10 days at 24° , the tube was opened to the vacuum line, into which it delivered 0.474 mmole of $(CF_3)_2PCI(90.6\%)$ of theory), 0.161 mmole of excess $(CF_3)_2POP(CF_3)_2$, and a fraction only slightly more volatile than pure B[OP(CF_3)_2]_3. The yield of this was 45.7 mg, or 60\% if it were virtually pure; however, final purification required 2–3 days at 25°, allowing the impurities (and perhaps some of the product) to decompose. The decomposition produced a colorless film and volatiles which could be removed by passage through a high-vacuum trap at -30° , and purification was complete when further standing formed no more of these products. The yield now was 49%, and purity was demonstrated by clean boron and fluorine nmr spectra.

It is an open question, whether the nonvolatile film (seen in the above process) contained $B_{-}P_{-}O$ patterns resulting from Arbuzov-like rearrangements. Such a film would not be seen in the nmr spectra, but it is interesting

that its aqueous solution showed far less of either strong acid or boric acid than would have been expected from the hydrolysis and air oxidation of a B— $OP(CF_3)_2$ polymeric film. One explanation might be the resistance of a B—P=O pattern to hydrolysis.

When quite pure, however, $B[OP(CF_3)_2]_3$ seems fairly resistant to any kind of decomposition at room temperature; for example, a sample was allowed to repose as a liquid upon the window of a closed infrared cell for 2 days at 24° and then distilled back into the high-vacuum system. The window now was clean, showing no infrared absorption even in the very sensitive C-F stretching region; obviously no film had formed.

The pure B[OP(CF₃)₂]₃ melted sharply at -21° . The vapor-tension measurements (0.27 mm at 0°, 0.53 mm at 7.7°, 0.70 mm at 11.0°, 0.92 mm at 14.6°, 1.26 mm at 18.6°, and 1.63 mm at 22.0°) are reproduced within 0.01 mm by the equation log $P = 9.960 + 1.75 \log T - 0.009T - 3369/T$, which gives the normal boiling point as 168 ± 10° and the Trouton constant as 21.3 eu.

The formula of the triphosphinite was confirmed by the basic hydrolysis of an 89.0-mg sample, yielding 0.936 mmole of HCF₃ (calcd, 0.943). The vapor-phase molecular weight determination (at 48° and 3.86 mm) gave 570 ± 4 (calcd, 565.8). However, an attempt at mass-spectrographic confirmation (with the Varian M66 instrument) failed for lack of appearance of the parent molecule ion. A strong record for $(CF_3)_2POP(CF_3)_2$ indicated dissociation as the reason.

Pure B[OP(CF₃)₂]₃, although conveniently stable at 25°, could not be kept long at 50° without some decomposition. A 49.8-mg sample, left in a 10-ml sealed tube for 48 hr at 100°, was 97% decomposed, forming 0.04 mmole of CO, 0.02 mmole of a mixture of BF₃, COF₂, and PF₃, 0.02 mmole of CF₃PF₂, 0.05 mmole of (CF₃)₂PF, and 0.03 mmole of (CF₃)₂POP(CF₃)₂. All of these except CO were identified and roughly estimated by the intensities of their most characteristic infrared bands. It is assumed that some CF₃ groups were destroyed to make P–F products and COF₂, and that CO came from this by the reducing action of some of the phosphines.

The nonvolatile glassy residue was titrated by standard base, showing 0.092 mmole of strong acid and 0.055 mmole of $B(OH)_3$. However, it is not certain that all of the possible impure B_2O_3 was dissolved.

Nuclear Magnetic Resonance Spectra. The chemical shifts (δ , ppm) and coupling constants (J, cps) for all magnetic nuclei in the three boron phosphinites are shown in Table III. All chemical shifts downfield from the standard are reported as negative. The Varian A-60 instrument was used for protons, with the usual tetra-methylsilane reference. For the others, the Varian HA-100 instrument was employed, with trimethyl borate, phosphoric acid, and chlorotrifluoromethane as substitution references.

All of the boron peaks were broad singlets, with all couplings to H, P, and F wholly blurred out; the half-height widths were three to five times that of the $B(OCH_3)_3$ signal. The phosphorus spectra were sharp $(1 + 1)^6$ septets (not appreciably disturbed by the boron quadrupole) with the outer peaks just visible above the noise level. The fluorine doublets were very sharp, whereas the single proton peaks were too broad for resolution of the expected quartets.

The Dimethyl Ether Complexes. The formation of

Table III. Nmr Spectra of Boron Phosphinites

		¹¹ B	³¹ P	¹⁹ F	¹ H
$(CH_3)_2BOP(CF_3)_2$	δ	-42.0	-31.2	67.0	-0.17
	J	• • •	87	88	•••
$CH_3B[OP(CF_3)_2]_2$	δ	-15.3	- 81.3	67.5	-0.31
	J	• • •	89.5	90.4	• • •
$B[OP(CF_3)_2]_3$	δ	1.1	-36.3	66.8	• • •
	J	•••	91.5	91.4	•••

 $(CH_3)_2O$ complexes of all three boron phosphinites in liquid dimethyl ether at 35° was demonstrated by ¹¹B δ values 15–23 ppm upfield from those for the "neat" samples.

When such complexes are incompletely formed, there can be a very rapid exchange at the base-boron bond. In that case, the ¹¹B nmr spectrum will show a single peak with δ representing an average of free and complexbonded boron. Accordingly, as the temperature is raised or lowered, δ varies with the changing equilibrium constant. An example relevant to the present study is the following series of δ values for ¹¹B in an approximately 5% solution of (CH₃)₃B in liquid dimethyl ether, measured upfield from "neat" (CH₃)₃B in an internal capillary tube.

<i>t</i> , °C.	35	0	- 20	- 40	- 60	- 70	- 80
δ, ppm	1.87	2.04	6.6	14.6	26.3	37.8	49.3

It is apparent that the etherate was only slightly present at the 35° probe temperature (ether pressure, ca. 8 atm), but the extreme movement of δ to higher field at lower temperatures could only mean a very substantial increase of involvement of the ether with the boron. However, we would not attempt to employ these rough data for actual determinations of the equilibrium constants, especially in the absence of any clear decision that the complex involves tetrahedral boron rather than a weak approach by $2(CH_3)_2O$ on two sides of the boron plane.

In contrast to $(CH_3)_3B$, liquid dimethyl ether solutions of $B(OCH_3)_3$ showed no change of δ for ¹¹B in the range 35 to -80° . In this case, the $O_{2p} \rightarrow B_{2p} \pi$ interaction wholly prevents effective attachment of the ether.

For the formally analogous $B[OP(CF_3)_2]_3$, however, the dimethyl ether solution showed δ 14.7 ppm farther upfield than the "neat" sample, and this shift did not change more than the experimental error (0.3 ppm) in the range 35 to -80° . This indication of complete complex formation was confirmed by a direct experiment in which 0.0307 mmole of $B[OP(CF_3)_2]_3$ and 0.0368 mmole of $(CH_3)_2O$ were condensed together in a U tube closed off by mercury float-valves and warmed to -78° . Now a high-vacuum fractional condensation through a trap at -78° yielded 0.006 mmole of free (CH₃)₂O, so that the condensate in the -78° U tube contained (CH₃)₂O and $B[OP(CF_3)_2]_3$ in a 1.003 to 1 ratio. This means that the complex was completely formed as the vapor mixture entered the -78° trap, even though the same sample, wholly evaporated in a closed bulb at 74°, showed a gas volume equivalent to 0.0611 mmole, representing complete dissociation. The infrared spectrum confirmed the complete dissociation of the complex in the vapor phase at 30°: the 1355-cm⁻¹ band, assigned to asymmetric B–O stretching in the BO₃ plane of $B[OP(CF_3)_2]_3$, showed its normal intensity, and there were no new bands.

Table IV. Infrared Spectra of Boron Phosphinites

$(CH_3)_2BOP(CF_3)_2$	$CH_3B[OP(CF_3)_2]_2$	$B[OP(CF_3)_2]_3$
3006 (1.1)	3018 (0.3)	
2941 (0.5)	2927 (0.14)	
1319 (14)	1357 (15)	1495 (2.9)
1266 sh (8?)	1320 (20)	1400 (45)
1248 (20)	1291 (67)	1355 (190)
•••	1253 (17)	1296 (3.6)
	•••	1274 (3.7)
1206 (48)	1212 (90)	1217 (189)
1176 (51)	1177 (120)	1181 (265)
1158 (15)	•••	
1146 (16)	1146 (40)	1147 (95)
1117 (26)	1124 (60)	1132 (148)
961 (4.2)	965 (2.0)	••• `
940 sh (1.5)	941 sh (2.2)	
	923 (6,3)	• • • •
830 (0,4)	890 sh (2.3)	837 (55)
808 (1.6)	787 (11)	751 sh (1.4)
748 (0.25)	746 (0.9)	747 (1,6)
674 (1.6)	667 (1.3)	679 (1.6)
		653 (3.7)
563 (1,6)	568 (3.2)	574 (11)
545 sh (0,5)	545 (1.3)	548 (4.3)
•••	494 (4,3)	492 (23)
464 (6)	460 (8,3)	457 (18)
•••	440 sh (1,4)	433 (7.4)
	410 (0,2)	•••
359 (0.7)	388 (2.9)	•••

The compound $CH_3B[OP(CF_3)_2]_2$, also in liquid dimethyl ether, showed δ for ¹¹B 23.0 ppm upfield of the "neat" sample, with no variation in the range 35 to -80° . Again it appears that the ether complex was completely formed even at 35°. It would be expected to be somewhat less stable than the etherate of $B[OP(CF_3)_2]_3$, but our only evidence of this difference is that it seems easier to remove the ether by high-vacuum fractional condensation.

Definitely less stable is the etherate of $(CH_3)_2BOP-(CF_3)_2$, which showed the following $(CH_3)_2O$ solution values of δ , measured upfield from "neat" $(CH_3)_2BOP-(CF_3)_2$.

t, °C	35	0	- 30	- 60
δ, ppm	20.5	25.8	36.3	40.9

In sum, then, it appears that the stability order of these dimethyl ether complexes is $B(OCH_3)_3 < (CH_3)_3B < (CH_3)_2BOP(CF_3)_2 < CH_3B[OP(CF_3)_2]_2 < B[OP-(CF_3)_2]_3$, in accord with reasonable predictions.

Infrared Spectra. The frequencies of band peaks for the B-O-P compounds in the vapor phase were recorded accurately to 1 cm^{-1} (calibrated) by the Beckman IR7 instrument with NaCl or CsI optics. For accurate comparison of intensities, cells with two path lengths (*e.g.*, 11.7 and 113 mm) were employed. The relative intensities were defined by $k = (100/PL) \log I_0/I$, for pressure *P* and path *L*, both in centimeters. The *I* values (per cent transmission) were taken literally even for shoulders residing on stronger bands. The *k* values appear in parentheses after the frequencies in Table IV.

The assignments of frequencies are obvious in some regions but very uncertain in others. The methyl compounds show the expected C-H stretching modes in the 3000-cm⁻¹ region, but the methyl-group deformations are not clearly apparent and may be very weak on account of the relatively high polarity at other bonds in the same molecule. The B-O stretching modes (1266, 1248; 1320, 1291; 1400, 1355) are identified by intensity ratios corresponding to the boron isotopes, with the frequency difference increasing with the number of $OP(CF_3)_2$ groups. Indeed, the 1355- and 1400-cm⁻¹ peaks for B[OP(CF₃)₂]₃ are much like the 953- and 995-cm⁻¹ peaks for BCl₃,⁵ representing an asymmetric stretching motion in which boron has the greatest amplitude. However, other nearby strong bands (1319; 1357, 1253; 1495, 1296, 1274) are not so easy to identify; some of these could be due to Fermi resonance.

The 1100–1220-cm⁻¹ range is normal for the very intense C-F stretching modes, and surely 837 cm⁻¹ represents P–O stretching, but for the CH₃–B compounds the 780–970-cm⁻¹ range undoubtedly includes also CH₃ wagging and rocking. The CF₃ deformation modes are normal, in the 540–75- and 740–60-cm⁻¹ range; and P–CF₃ stretching appears strongly in the 400–500-cm⁻¹ range but here may be accompanied by other modes.

The very similar 674-, 667- (not CO_2 !), and 679-cm⁻¹ peaks might represent either P-O stretching or B-O bending, but more probably would be a complex rhythm involving both. The 359- and 388-cm⁻¹ peaks, not matched in the triphosphinite spectrum, probably represent CH₃ torsions, the relatively high frequency of which would be ascribed to an interaction of C-H electrons with the out-of-plane B_{2p} orbital.

Not shown in Table IV (but clearly seen) were peaks which we attribute to overtones and combinations. For the dimethylboron phosphinite, these were 2649 (0.10), 2280 (0.24), 2256 (0.26), 1991 (0.08), 1922 (0.17), 1896 (0.10), 1863 (0.04), 1767 (0.14), 1633 (0.21), and 1615 (0.14); for the diphosphinite, 2580 (0.11), 2541 (0.12), 2505 (0.05), 2464 (0.07), 2452 (0.09), 2399 (0.10), 2284 (0.42), 2038 (0.22), 1957 (0.35), 1923 (0.33), 1897 (0.20), 1843 (0.11), 1752 (0.19), 1691 (0.14), 1636 (0.11), and 1575 (0.27); and for the triphosphinite, 2282 (1.0), 2267 (1.0), 1908 (0.6), 1676 (0.7), 1570 (0.5), and doubtless weaker peaks not easily seen at 2 mm pressure.

(5) A. B. Burg and J. S. Sandhu, J. Am. Chem. Soc., 89, 1627 (1967).