In a separate experiment LiCl in THF was added to HBeCl. The ir spectrum of the resulting clear solution showed a very weak broad band at 1700 cm^{-1}. At the same concentration AlH_3 in THF shows a very intense band at 1739 cm^{-1}. One might, therefore, expect that a 1:1 mixture of $LiBeCl_2H$ and AlH_3 would give an ir spectrum with a broad band centered at approximately 1730 cm^{-1} as we indeed found for the reaction product of $LiAlH_4$ and $BeCl_2$ in THF. The predicted spectra of other possible products are not consistent with the observed spectrum of the reaction product of $LiAlH_4$ and $BeCl_2$ in 1:1 ratio in THF. The only difference between the reaction of $LiAlH_4$ and $BeCl_2$ in 1:1 ratio in ether and THF (eq 30 and 31) is the fact that in THF (eq 31) the AlH_3 formed does not react with HBeCl to form BeH_2 and H_2AlCl. This observation is not inconsistent with known reactivity differences of AlH_3 or other aluminum compounds in THF compared to ether.

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Registry No. $BeCl_2 \cdot 2THF$, 15663-55-5; $BeCl_2 \cdot 2Et_2O$, 14267-69-7; $LiAlH_4$, 16853-85-3; $BeCl_2$, 7787-47-5; $NaAlH_4$, 13770-96-2; HBeCl, 42016-55-7; AlH_3, 7784-21-6; BeH_2, 7787-52-2; $Li_2BeCl_2H_2$, 39405-85-1; $AlH_3 \cdot 0.25OEt_2$, 2835-71-1.

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Phosphine-Borane Derivatives. VI.[1] Hydrogen-1, Boron-11, Fluorine-19, and Phosphorus-31 Nuclear Magnetic Resonance Investigation of Some Alkyl- and Arylphosphine Adducts

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The ^1H and ^{11}B nmr parameters for the adduct series $R_nPH_{3-n} \cdot BX_3$ (R = Me, Ph; n = 0, 1, 2; X = H, F, Cl, Br, I) are reported. ^1H, ^{11}B, and ^{31}P nmr parameters are reported for the BX_nH_{3-n} (n = 0, 1, 2; X = Cl, Br, I) adducts of all R_nPH_{3-n} Lewis bases. ^{19}F nmr parameters are reported for all $R_nPH_{3-n} \cdot BF_3$ adducts except for PH_3BF_3. Chemical shift and coupling constant data are examined in the light of their utility as indicators of acid-base strength or complex stability. Internal consistency between the nmr parameters of the various nuclei is to be expected only where large changes in trend occur.

Introduction

Recent ^{11}B nmr investigations[2-5] of the properties of the phosphorus-boron bond have indicated that while coupling constant and chemical shift data can, within narrow limits, be correlated with bond strength, no unrestricted application can be made of these parameters as measures of compound stability or of relative orders of Lewis acidity and basicity. In our previous ^1H nmr study[1] of the phosphine-boron trihalide adducts attention was called to the apparent correlation between the value of the direct J_{PH} coupling constant and the Lewis acidity of the BX_3 species. We present here an extension of that investigation to the ^1H nmr parameters of boron trihalide adducts of dimethyl-, phenyl-, and diphenylphosphine. In addition ^{11}B chemical shifts and coupling constants have been obtained for all five series. ^{31}P data are presented for all systems sufficiently soluble to permit investigation. ^{19}F nmr determinations are reported where applicable. The various ^1H, ^{31}P, ^{11}B, and ^{19}F parameters are examined for their utility as predictive indicators and for their mutual internal consistency within a given adduct series.

Experimental Section

All adducts except for $PhPH_2 \cdot BI_3$ and $Ph_2PH \cdot BI_3$ were prepared by direct combination of reactants in standard nmr tubes (4-mm o.d.) on a vacuum line in a manner described previously.[1] The adducts $PH_3 \cdot BH_2X$ and $PH_3 \cdot BHX_2$ (X = Cl, Br) were prepared following the method of Drake and Simpson[6] while a procedure analogous to theirs was used to prepare the new adducts $PH_3 \cdot BH_2I$ and $PH_3 \cdot BHI_2$. The solvents employed, CD_3I (Stohler Isotope Chemicals, Montreal; 1% ^1H impurity) CH_3I, and CH_2Cl_2, were checked for spectroscopic purity prior to use.

^1H Nmr Spectra. CD_3I was used as solvent for all adducts except those of the $(CD_3)_2PH \cdot BX_3$ system where CH_2Cl_2 was found to be necessary for reasons previously given.[1] Spectra were recorded in sealed tubes over a carefully varied temperature range from −70 to +75° on a JEOL C60HL high-resolution spectrometer. Tetramethylsilane and solvent were distilled onto the adduct which was contained in an nmr tube attached to the vacuum line. The tube was then drawn off the line and sealed with a torch, with the contents held at −196°.

^{31}P Nmr Spectra. CH_3I was used as solvent for all adducts investigated. Spectra were recorded at 24.29 MHz in sealed tubes identical with those used in the ^1H nmr work. Temperatures were maintained between −10 and 0°. $POCl_3$ in small capillary tubes was used as external standard. The low solubility of the adducts severely reduced the intensity of the resonance peaks. Removal of the reference capillary when not needed by inverting the sample tube overcame this difficulty and allowed for a more precise measurement of coupling constants. Nevertheless, solubility limitations reduced the number of adducts studied to 11.

^{11}B Nmr Spectra. CH_3I was employed as solvent for all adduct systems. Spectra were recorded at 19.25 MHz with $BF_3 \cdot OEt_2$ serving as external reference. Temperatures were varied in *ca.* 10° intervals from −30° (where peak broadening became significant) to +25°. Manipulation of the reference capillary was identical with the ^{31}P procedure.

^{19}F Nmr Spectra. CH_2Cl_2 was employed as solvent for all BF_3 adducts. Spectra were recorded at 56.45 MHz using CCl_3F as internal standard. Temperatures were varied from −90 to +25° as the stability of the adduct warranted.

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Starting Materials. Phosphine (Matheson) was distilled through a trap at −126° and its ir spectrum corresponded to that of the pure material.[7] Methylphosphine[8] and dimethylphosphine[9] were each prepared by the deprotonation–methylation procedures described elsewhere. The published ir spectra of methylphosphine[10] and dimethylphosphine[11] as well as their nmr parameters[12] were used to confirm purity. $(CD_3)_2PH$ was prepared in an analogous manner, its nmr spectrum indicating a low degree of methyl proton impurity (*ca.* 4%). The nmr spectra of phenylphosphine[13] and diphenylphosphine[14] were used to check the purity of the commercially obtained materials (Research Organic/Inorganic Corp., Hillside, N. J.). Diborane, prepared after the method of Weiss and Shapiro,[15] was purified by trap to trap distillation and checked for purity by ir analysis.[16] The boron trihalides were purified as reported previously.[1]

Formation of the Adducts $PH_3 \cdot BX_3$ and $MePH_2 \cdot BX_3$ (X = H, F, Cl, Br, I). The single and mixed adducts of each of these series were prepared for the ^{11}B nmr study in the same manner as previously reported for the ^{1}H nmr investigation[1] except for the BI_3 adducts where a procedural modification was introduced. A benzene solution of purified BI_3 in appropriate molar quantity was introduced into the nmr tube under moisture-free conditions. After attachment to the vacuum line, the solution was frozen, the tube evacuated, and the gaseous reactant introduced. Upon warming and gentle agitation, the complex formed as a white, insoluble product. The contents were then brought to −78° where a small positive pressure of excess PH_3 or $MePH_2$ indicated completeness of reaction. The benzene was then removed and the adduct opened to the pump.

Formation of the Adducts $PhPH_2 \cdot BX_3$ and $Ph_2PH \cdot BX_3$ (X = H, F, Cl, Br). The low vapor pressure of both phenylphosphines made vacuum-line manipulation inefficient. Consequently, a measured quantity of either material (*ca.* 0.5 mmol) was transferred to the nmr tube under moisture-free conditions by means of a 1-μl syringe. Requisite volumes were calculated on the basis of the literature values for the densities of phenylphosphine[17] and diphenylphosphine.[18] Except in the preparation of the BF_3 adducts, a small quantity of benzene was added to the tube prior to attachment to the vacuum system. The solution was then frozen, the tube evacuated, and a measured excess of boron trihalide added. Upon warming and agitation, adduct formation was indicated by the presence of a cloudy, white suspension. (In the absence of benzene, reactions occasionally exhibited considerable localized heating with the formation of yellow or orange products. Benzene was omitted in the preparation of the $[BH_3]$ adducts where B_2H_6 and appropriate phosphine were allowed to react directly at 0°.) The benzene was distilled off and additional BX_3 was added to ensure completeness of reaction. After 1 hr the tube was evacuated and, except for the BF_3 and BH_3 systems, was opened to the pump for about 30 min. The appropriate solvent was then added.

Formation of $PhPH_2 \cdot BI_3$ and $Ph_2PH \cdot BI_3$. A measured quantity of the requisite phenylphosphine in slight excess was introduced to the nmr tube under moisture-free conditions. C_6H_6 was then added. This was followed by the addition of a benzene solution of purified BI_3 in approximately known molar quantity. The unmixed systems were then frozen, the tube evacuated, and the reaction allowed to occur at as low a temperature as possible. After removal of solvent, the adduct was opened to the pump overnight.

Results and Discussion

^{1}H Nmr Spectra. The ^{1}H nmr parameters for all five series of adducts are displayed in Table I. The general trend of chemical shifts within any of the five groups remains consistent with that found previously,[1] namely, that the shielding of the proton on phosphorus decreases as the apparent strength of the Lewis acid increases in accordance with the generally accepted order: $BF_3 < BCl_3 < BBr_3 < BI_3$.[19,20] (In this context, the chemical shift values would seem to indicate that $[BH_3]$ and BF_3 are of nearly equal acidity. Results from other investigations have shown variations in relative acidities.[21-23] The special properties of $[BH_3]$ as an acid have been noted elsewhere[24] and the results of our ^{11}B investigation would incline us to assign this species to a unique position outside the BX_3 series.) The drift of charge away from the phosphorus protons to an increasingly positive center suggests the possibility of a greater localization of charge on either the phosphorus atom or within the P→B bond.

An examination of the changes in chemical shift for the entire series of adducts upon methyl or phenyl substitution at phosphorus reveals no obvious general trend. For the Me_nPH_{3-n} adducts with any BX_3 (X = Cl, Br, I) there is greater deshielding of the phosphorus proton with increasing methyl substitution. The reverse is true for Me_nPH_{3-n} adducts of BF_3 or $[BH_3]$. When Ph_nPH_{3-n} is employed in adduct formation, there is a greater deshielding of the phosphorus proton with increasing phenyl substitution for *all* BX_3 species. The notable variance between δ values of $Me_nPH_{3-n} \cdot BX_3$ and $Ph_nPH_{3-n} \cdot BX_3$ (X = Cl, Br, I) may, in some measure, be attributable to the deshielding effects of ring currents induced in the phenyl group by the imposed magnetic field.[25,26] This effect, together with the opposing trends noted above in the case of methyl substitution, rules out the use of proton chemical shift values in any predictive capacity as indicators of relative base strength.

Similarly, a systematic variation of the Lewis base relative to any boron acid does not reveal any distinct trend in coupling constant values. However, variation of the Lewis acid relative to any donor species clearly exhibits a trend in J_{PH} which suggests that the degree of s character in the phosphorus orbitals bound to hydrogen increases with increasing acidity of the acceptor molecule.[1,27] (The spectrum of $PhPH_2 \cdot BF_3$ is not without ambiguity in this respect and may indicate only partial compound formation.) As a concomitant to the increase in s character in the P-H bonding orbitals, one must posit an increase in the p character of the phosphorus "lone pair" orbital as it becomes involved in adduct formation.

In summation then, on the basis of the ^{1}H nmr evidence reported here, it seems reasonable to assume that the magnitude of the downfield chemical shift of the phosphorus proton(s), as well as the value of the direct coupling constant, J_{PH}, is diagnostic of the relative acidities of various boron Lewis acids provided that the base (R_2PH, R = H, Me, Ph) is kept constant.

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Table I. Observed ^1H Nmr Parameters[a] for BH_3 and BX_3 (X = F, Cl, Br, I) for the Boron Trihalide Adducts of PH_3, $(Me\text{-}d_3)_nPH_{3-n}$, and Ph_nPH_{3-n} (n = 1,2)

	PH_3[b]		CD_3PH_2[b]		$(CD_3)_2PH$		$PhPH_2$		Ph_2PH	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}
BH_3	−4.31	372[c]	−4.58	375[d]	−4.78	369[e]	−5.65	375	−6.40	381
BF_3			−4.28	355	−4.80	384	−5.30	324(?)	−6.50	389
BCl_3	−5.92	426	−5.30	428	−5.20	420	−6.45	420	−6.80	422
BBr_3	−6.44	429	−5.60	430	−5.40	429	−6.80	430	−7.00	435
BI_3	−7.40	432	−6.20	434	−5.45	432	−7.45	434	−7.60	441

[a] Recorded at −70° in CD_3I, unless otherwise indicated. δ in ppm ± 0.05 ppm downfield from internal TMS; J_{PH} in Hz ± 2 Hz. [b] Reference 1. [c] R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, 5, 723 (1966). Recorded at 30°, neat. [d] J. Davis and J. E. Drake, *J. Chem. Soc. A*, 2959 (1970). Recorded at 35°, neat. [e] Reference 2: J_{PH} = 366 Hz; no δ_{PH}.

Table II. Observed ^{31}P Nmr Parameters[a] for the Adduct Series $R_nPH_{3-n}\cdot BH_3$ (R = H, Me, Ph)

	δ	J_{PH}		δ	J_{PH}
PH_3[b]	+238	182.2[f]	$Me_2PH\cdot BH_3$	+24	368[e]
$PH_3\cdot BH_3$	+106	372	$PhPH_2$[d]	+119	201[g]
$MePH_2$[b]	+168.5	186.4[f]	$PhPH_2\cdot BH_3$	+46	368
$MePH_2\cdot BH_3$	+66	388	Ph_2PH[e]	+41	239[g]
Me_2PH[c]	+103	191.6[f]	$Ph_2PH\cdot BH_3$	−3	390

[a] δ in ppm ± 2 ppm relative to external $POCl_3$. All R_nPH_{3-n} literature values adjusted to external reference $POCl_3$: $\delta_{POCl_3} = \delta_{H_3PO_4} + 4$ ppm. J_{PH} in Hz ± 10 Hz. All parameters recorded at −10° in CH_3I. [b] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, 78, 5715 (1956). [c] K. Moedritzer, L. Maier, and L. Groenweghe, *J. Chem. Eng. Data*, 7, 307 (1962). [d] E. Fluck and K. Issleib, *Chem. Ber.*, 98, 2674 (1965). [e] J. N. Shoolery, *Discuss. Faraday. Soc.*, 19, 215 (1955): J_{PH} = 350. [f] J_{PH} values obtained from ^1H nmr data.[12] [g] Reference 13.

Table III. Observed ^1H, ^{31}P, and ^{11}B Nmr Parameters[a] for the Adducts $PH_3\cdot BH_2X$ and $PH_3\cdot BHX_2$ (X = Cl, Br, I) and $Et_3P\cdot BH_2X$ and $Et_3P\cdot BHX_2$ (X = Cl, Br)[b]

	^1H		^{31}P		^{11}B		
	δ	J_{PH}	δ	J_{PH}	δ	J_{BH}	J_{PB}
$PH_3\cdot BH_3$[c]	−4.60	377	+105	372	+43	103	27
$Et_3P\cdot BH_3$			−11		+42	96	64
$PH_3\cdot BH_2Cl$[d]	−5.00	395	+104	388	+19	130	41
$PH_3\cdot BH_2Br$[d]	−5.30	396	+101	400	+26	130	55
$PH_3\cdot BH_2I$	−5.60	400	+99	400	+39	130	60
$Et_3P\cdot BH_2Cl$			−3		+20	115	85
$Et_3P\cdot BH_2Br$			−3		+25	111	94
$PH_3\cdot BHCl_2$[d]	−5.40	415	+99	416	+6	154	
$PH_3\cdot BHBr_2$[d]	−5.90	418	+97	424	+19	149	91
$PH_3\cdot BHI_2$	−6.30	418	+95	424	+54	154	91
$Et_3P\cdot BHCl_2$			+5		+6	131	131
$Et_3P\cdot BHBr_2$			+6		+16	<128	>128

[a] Under the conditions specified in Tables I, II, and IV. [b] As taken from ref 29 and 30 with ^{31}P chemical shifts adjusted to $POCl_3$ external reference according to the equation $\delta_{POCl_3} = \delta_{P_4O_6} - 109$ ppm. [c] ^{11}B nmr parameters obtained from R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, 89, 1621 (1967). [d] These ^1H nmr parameters differ only slightly from those obtained in CH_2Cl_2 solvent.[6]

^{31}P Nmr Spectra. ^{31}P nmr data have been secured on all $[BH_3]$ adducts (Table II) as well as on the $PH_3\cdot BH_2X$ and $PH_3\cdot BHX_2$ (X = Cl, Br, I) series (Table III). Data on the BX_3 adducts of any phosphine ligand could not be obtained because of solubility limitations. Of the three groups studied only the dihalide adducts were solids, but these remained sufficiently soluble to permit recording of their spectra. A comparison of the ^{31}P chemical shifts for the various free phosphines as given in Table II with those of the corresponding $[BH_3]$ adducts gives evidence of a pronounced deshielding of phosphorus upon adduct formation. The chemical shift difference, $\Delta\delta_{^{31}P} = \delta_{^{31}P\ \text{adduct}} - \delta_{^{31}P\ \text{ligand}}$, while large in each instance, is not constant as might have been expected on the assumption that $[BH_3]$ presents a similar positive field toward each ligand. Since changes in bond angles around phosphorus are known significantly to affect ^{31}P chemical shifts,[28] the largest $\Delta\delta_{^{31}P}$ value (PH_3 system) may reflect the greatest change in bond angles upon adduct formation.

The variation in $\delta_{^{31}P}$ as a function of halogen substitution at boron was also investigated and the results are displayed in Table III. The only comparable series previously reported is that of the triethylphosphine adducts $Et_3P\cdot BH_2X$ and $Et_3P\cdot BHX_2$ where X = Cl[29] and Br.[30] Again, with either base, a large change in shift value, $\Delta\delta_{^{31}P}$, takes place upon adduct formation. The long-range effects of halogen substitution at boron on the chemical shift show a relatively small downfield trend in the PH_3 series of adducts but a correspondingly small upfield trend in the Et_3P series. In view of the extensive, but largely unsuccessful, attempts to obtain a simple theoretical interpretation of ^{31}P chemical shifts,[31] an absence of consistency in such small changes is not surprising.

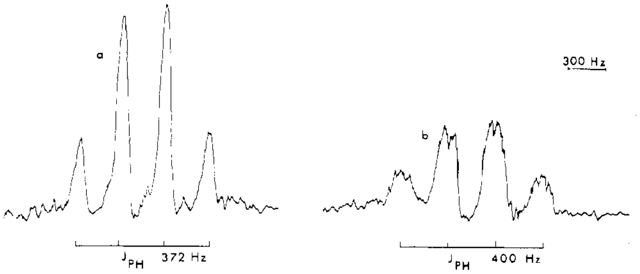

Figure 1. ^{31}P spectra of (a) PH_3BH_3 and (b) $PH_3\cdot BH_2I$ recorded in CH_3I at −10°; 300-ppm scale setting.

The ^{31}P spectrum of PH_3BH_3 given in Figure 1 exhibits the 1:3:3:1 quartet common to spectra of this series. [Because of reduced solubility of $PH_3\cdot BHI_2$ only the central members of the quartet were observed.] Generally, J_{PH} values were found to be in good agreement with those obtained from ^1H nmr studies. Boron-phosphorus coupling constants could not, however, be reliably assessed from ^{31}P spectra. This results from the broadness of its peaks and the unusually high instrument gains required to observe the spectra. The use of accumulation methods were found to be equally unsatisfactory. Broadness of peaks undoubtedly reflects the increase in J_{PB} (Table III) along the series of phosphine adducts of $[BH_3] \rightarrow BH_2X \rightarrow BHX_2$. (Compare $PH_3\cdot BH_3$ and $PH_3\cdot BH_2I$ spectra, Figure 1.)

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Table IV. Observed ^{11}B Nmr Parameters[a] for the Adduct Series $R_nPH_{3-n}\cdot BX_3$ (R = H, Me, Ph; X = H, F, Cl, Br, I)

	$[BH_3]$			BF_3		BCl_3		BBr_3		BI_3	
	δ	J_{BH}	J_{PB}	δ	J_{PB}	δ	J_{PB}	δ	J_{PB}	δ	J_{PB}
b	−57.0[c]			−10.8		−46.6		−39.1		+5.9	
PH_3	+43.4[d]	103	27			−1.5		+21.5	132	+91.0	122
$MePH_2$	+40.7[e]	108.8	43.5	−2.0		−1.5	151	+19.0	149	+80.0	130
Me_2PH	+38[e,f]	96	58	−1.5	43[i]	−3.0	163	+16.0	156	+73.0	134
Me_3P[g,h]	+39	95	62	−0.1	174	−2.0	166	+15.5	165		
$PhPH_2$	+41.4[e]	101	35	−3.5		−3.5	142	+17.0	139	+77.0	120
Ph_2PH	+44.0	100.8	38	−4.5		−2.5	161	+18.5	144	+78.5	127

[a] Recorded at −30° in CH_3I. δ in ppm ± 1 ppm relative to external $BF_3\cdot OEt_2$. $\delta_{^{11}B}$ literature values are adjusted to the external reference: $\delta_{BF_3\cdot OEt_2} = \delta_{B(OMe)_3} - 17.4$ ppm. J_{PB} in Hz ± 5 Hz. [b] $\delta_{^{11}B}$ values for the free boron acids taken from ref 32. [c] C. D. Good and D. M. Ritter, *J. Amer. Chem. Soc.*, 84, 1162 (1962). [d] R. W. Rudolph and R. W. Parry, *ibid.*, 89, 1621 (1967). [e] Reference 2. [f] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 81, 4496 (1959). [g] D. F. Gaines and R. Schaeffer, *ibid.*, 86, 1505 (1964). [h] Reference 4. [i] $J_{BF} = 55$ Hz; see Figure 3 and Table V.

^{11}B Nmr Spectra. The chemical shift values for all of the unmixed BX_3 adducts as well as for the free boron acids[32] are given in Table IV. As expected, the increased shielding of the boron atom upon adduct formation is reflected in the upfield trend of the chemical shifts of the adducts relative to those of the free BX_3 species. Within any given boron halide series this change is relatively constant which apparently supports the assumption made in the previous section that the boron acceptor species does indeed present a nearly constant positive field toward the various Lewis bases. Furthermore the mean shift difference, $\overline{\Delta\delta}_{^{11}B} = (\Sigma\delta_{^{11}B}(\text{adduct}) - \delta_{^{11}B}(BX_3))/n$, increases in a manner parallel to the accepted order of Lewis acidity: BF_3 ($\overline{\Delta\delta} = +7.6$) < BCl_3 ($\overline{\Delta\delta} = +44.3$) < BBr_3 ($\overline{\Delta\delta} = +56.9$) < BI_3 ($\overline{\Delta\delta} = +73.9$). As observed in a previous study[33] the chemical shift differences between the adducts and the planar compounds exhibits a qualitatively inverse relation to the amount of back-coordination in the planar species. The stabilities of the various adducts with respect to dissociation, as estimated on the basis of our temperature-dependent ^{1}H nmr study,[1] also parallel this order.

Inclusion of the $[BH_3]$ adducts in this series is not meaningful since the free adduct is not a planar $[BH_3]$ moiety and arguments based on differences in back-bonding are inappropriate. This is exemplified by the use of the calculated value for $\delta_{^{11}B}([BH_3])$[34] which gives an average $\Delta\delta$ value of 98.1 ppm. Assuming this value is reasonable, this is clearly not comparable with the BX_3 series. A direct relationship would imply the BH_3 adducts have much higher stability which is not the case because, aside from the very high dissociation pressure of $PH_3\cdot BF_3$,[35] that of phosphine-borane (20 cm at 0°)[36] is greater than that of $PH_3\cdot BCl_3$ (0.85 cm at 0°)[37] and $PH_3\cdot BBr_3$ (<1 mm at 25°)[37] and certainly greater than that of $PH_3\cdot BI_3$. If the value of −17.5 ppm (δ, B_2H_6)[38] is taken as a basis for calculating the mean shift difference, the discrepancy is reduced but not removed.

A general consistency between ^{11}B and ^{31}P shift parameters is evident in the sizable upfield trend of the former and the corresponding downfield trend of the latter (Table II) on formation of the P→B bond. It has been suggested that ^{11}B chemical shifts are not sensitive indicators of relative base strengths,[2,5] and in this regard a comparison of the corresponding compounds in the series $PH_3\cdot BHXY$ and $Et_3P\cdot BHXY$ (XY = HCl, HBr, Cl_2, Br_2)[29,30] shows nearly identical $\delta_{^{11}B}$ values, although the two bases in question are certainly different in strength. It is to be noted that despite the constant $\delta_{^{11}B}$, there are large differences in $\delta_{^{31}P}$. Thus a direct "internal consistency" cannot be expected between ^{31}P and ^{11}B chemical shifts for changes in substitution on phosphorus.

A recent ^{11}B nmr investigation has shown that the magnitude of J_{PB} empirically correlates with the dative bond strength of the $[BH_3]$ adducts of a series of smoothly varying phosphine bases.[3] Another study has indicated that for a given boron reference acid, $[BH_3]$, the magnitude of J_{PB} qualitatively correlates with the strength of a series of phosphine bases.[2] While an exception to this general relationship has been noted,[39] the ^{11}B coupling constant data obtained in our investigation (Table IV) are in general agreement with this observation in that increased basicity is more marked for methyl than for phenyl substitution. However, where relatively small changes are involved, the absolute order of base strength varies slightly when measured against different reference acids.

On the other hand, when the various Lewis acids are evaluated against any particular reference base in the adduct series $R_nPH_{3-n}\cdot BX_3$ (X = Cl, Br, I), J_{PB} is observed to *decrease* with increasing Lewis acidity (Table IV). The major contributions to the phosphorus-boron coupling constant are not clear. It is generally recognized, however, that when phosphine forms an adduct, the orbital involved in bond formation *decreases* in s character, since the other phosphorus orbitals are observed to *increase* in s character. (In CH_3PH_2, for example, the HPH angle is 93.4° and in its $[BH_3]$ adduct the HPH angle is 99.9°.[40]) For the acceptor species the situation is reversed upon adduct formation. As BX_3 moves from an sp^2 planar configuration to a near-tetrahedral sp^3 arrangement, the bonding orbital undergoes an *increase* in s character. Thus, even if the Fermi contact term is an important contributor to J_{PB},[3] these opposing trends limit the predictive utility of the coupling constant. Some insight into the significance of J_{PB} can be obtained if one considers two hypothetical extremes at which $J_{PB} = 0$: (a) no covalent interaction, $R_3P{:},BX_3$; (b) total electron transfer, R_3P^{2+}, $:BX_3^{2-}$. Between these extremes dative bond formation ($R_3P^{\delta+}{:}^{\delta-}BX_3$) leads to significant values of J_{PB} as a result of mutual sharing of electrons. It is quite unlikely that a perfect correspondence will be found between maximum

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Table V. Observed ^{19}F Nmr Parameters^a for the Adduct Series $R_nPH_{3-n}{\cdot}BF_3$ (R = H, Me, Ph)

Temp, °C	$PH_3{\cdot}BF_3$			$MePH_2{\cdot}BF_3$			$Me_2PH{\cdot}BF_3$			$PhPH_2{\cdot}BF_3$			$Ph_2PH{\cdot}BF_3$		
	δ	J_{PF}	J_{BF}	δ	J_{PF}	J_{BF}	δ	J_{PF}	J_{BF}	δ	J_{PF}	J_{BF}	δ	J_{PF}	J_{BF}
−90	+116^b	...	...	+121	300	49				+124	117	...	+125	175	...
−80	+118	...	...	+120	254	...	*b*			+124	...	...	+125	175	...
−70	*c*			+119	...		+135	275	54	+128			+125	150	...
−60				+119			+135	275	54	+128			+125	...	...
−50				+119			+135	275	54	+128			+130		
−40				+119			+135	275	54	+128			+130		
−30				+119			+135	275	54	+128			+130		
−20				+119			+135^d	275	49	+128			+130		

^{a} Recorded at various temperatures in CH_2Cl_2. δ in ppm ± 2 ppm relative to $CFCl_3$ as internal standard; J in Hz ± 10 Hz. ^{b} Solidification of sample. ^{c} Loss of signal. ^{d} Loss of J_{BF} at −10°; J_{PF} at 0°.

contribution to J_{PB} and maximum bond strength. We postulate that the former is reached before the latter. As a consequence, for the strong adducts in the series $R_nPH_{3-n}{\cdot}BX_3$ (X = Cl, Br, I; n = 0, 1, 2) J_{PB} decreases with increasing Lewis acidity. This decrease is paralleled by an increase in the magnitude of J_{PH} (Table I). This would be expected because the BX_3 species which can most effectively generate a positive field at boron[41,42] is the one most able to facilitate the rehybridization of the phosphine donor and hence bring about the largest increase in s character in the P-H bond. With the "weaker" $R_nPH_3{\cdot}BH_3$ adducts we postulate that neither the maximum J_{PH} nor the maximum donor-acceptor bond strength has yet been attained. Thus the weaker P-B bond is reflected in the lower value of J_{PB} *and* the lower value of J_{PH} as observed in the [BH_3] adducts.

For only two of the BF_3 adducts were we able to obtain values of J_{PB}. Assuming that BF_3 behaves as a BX_3 moiety rather than as [BH_3], the larger J_{PB} value of $Me_3P{\cdot}BF_3$ relative to $Me_3P{\cdot}BCl_3$ is consistent with a weaker dative bond. The large decrease in the value of J_{PB} in $Me_2PH{\cdot}BF_3$ is unlikely to be related solely to a decrease in P-B bond strength. Indeed, a comparison of its J_{PH} value with that of $Me_2PH{\cdot}BCl_3$ would support this argument. It is more probable that a kinetic factor is now dominating the process, namely, the apparent loss of coupling due to the rapid equilibrium in the general process $R_3P{:} + BX_3 \rightleftarrows R_3P{:}BX_3$.

A more dramatic example of this is found in the $PH_3{\cdot}BCl_3$ system. That the adduct is undoubtedly present is attested to by various parameters: dissociation pressure,[37] J_{PH} coupling constant relative to that of free phosphine, chemical shift data. The complete absence of J_{PB} points to a very rapid equilibrium even at −30°. The series of mixed hydride-halide boranes, $PH_3{\cdot}BH_2X$ and $PH_3{\cdot}BHX_2$, provide a group of compounds which reflect the convergence of rapid equilibria and relatively weak dative bonds (Table III; Figure 2). [Although each adduct was prepared separately, it was thought useful to prepare a totally mixed system for the boron chloride adducts of PH_3.] The better nmr indicator of relative acid strength in this series is therefore likely to be the J_{PH} parameter.

The absolute values of the direct coupling constant J_{BH} have been related to "π-acceptor strengths" of the uncomplexed phosphines[2] but we observe no trend (Table IV) in the $R_nPH_{3-n}{\cdot}BH_3$ series to support this concept and the changes are not very large. The coupling constant values are close to 100 Hz compared to 135 Hz reported for free diborane.[43] This supports the general concept that in its adducts [BH_3] at least approaches a tetrahedral configuration

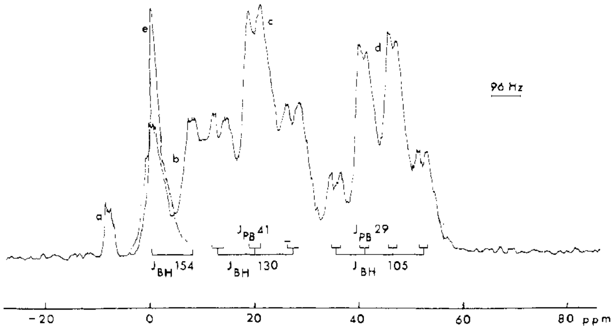

Figure 2. ^{11}B spectrum of the mixed system (a) $PH_3{\cdot}BCl_3$, (b) $PH_3{\cdot}BHCl_2$, (c) $PH_3{\cdot}BH_2Cl$, and (d) $PH_3{\cdot}BH_3$ recorded in CH_3I at −30°. Superimposed peak (e) is external reference $BF_3{\cdot}OEt_2$. A 900-ppm scale setting was used.

and hence has less s character than the terminal B-H bonds in B_2H_6 (HBH angle ≃121°).[44] In the series $PH_3{\cdot}BH_3$, $PH_3{\cdot}BH_2X$, and $PH_3{\cdot}BHX_2$ an increase in J_{BH} accompanies increasing halogen substitution but is relatively constant regardless of the nature of the halogen (Table III). This same trend is observed in $J_{^{13}CH}$ values of the isoelectronic systems SiH_3CH_3[45] and SiH_3CH_2X[46] [SiH_3CH_3, 122.5 Hz; SiH_3CH_2X, 146.8 Hz (Cl), 150.0 Hz (Br), 149.0 Hz (I)]. Hence, this behavior is not atypical for halogen substitution and is better rationalized on the basis of a concentration of p character in bonds attached to more electronegative groups[47] than in terms of a trend toward planarity.

^{19}F Nmr Spectra. The ^{19}F nmr parameters are displayed in Table V as a function of temperature. The greater solubility of the BF_3 complexes allowed the use of CH_2Cl_2 as a solvent and this permitted the recording of spectra at temperatures as low as −90°.

The trimethylamine adduct of BF_3 has a ^{19}F chemical shift of 164 ppm relative to $CFCl_3$,[48] reflecting increased shielding of the fluorine nucleus. This is in accord with expectation, since the formation of a strong adduct such as $Me_3N{\cdot}BF_3$ would distort BF_3 from planarity, reduce the degree of B-F π bonding, and thereby increase the shielding of fluorine.[48] The values of ^{19}F chemical shifts for the phosphine adducts indicate a lesser shielding of fluorine than in the amine adduct. This would be expected for a weaker acid-base interaction which still permits some B-F π bonding to be maintained.

Only the methylphosphine adducts exhibit boron-fluorine

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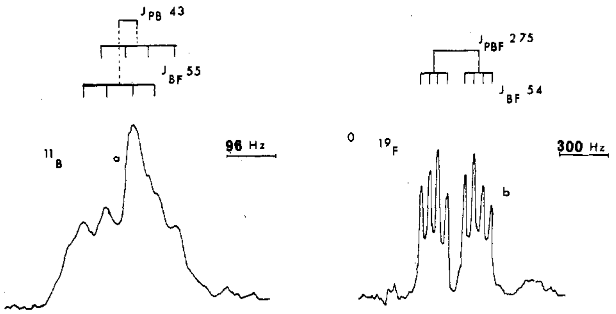

Figure 3. ^{11}B and ^{19}F spectra of $Me_2PH \cdot BF_3$ recorded at −30° in (a) CH_3I, with 900-ppm scale setting, and (b) CH_2Cl_2, with 300-ppm scale setting.

spin-spin splitting, yielding the 1:1:1:1 quartet. However, only in the dimethylphosphine complex is the hyperfine interaction maintained over an appreciable temperature range. The absolute value of 54 Hz for J_{BF} is comparable to that observed for the trimethylphosphine adduct.[5] A value of similar magnitude but of less precision was obtained from the ^{11}B nmr spectrum of $MePH_2 \cdot BF_3$ at −30° (Figure 3). The eventual collapse of the quartet at −10° is nearly coincidental with the collapse of the 1:1 doublet attributable to the indirect coupling J_{PBF} (Figure 4). [The somewhat unsymmetrical appearance of this doublet is unusual and difficult to explain.] The almost simultaneous loss of both couplings can be accounted for on the basis of the rapid-exchange mechanisms (P-B, B-F) within the system.

The retention of J_{BF} in the $Me_2PH \cdot BF_3$ spectrum over a considerable temperature range is unique to the adduct series investigated here. Its very early loss in the case of $MePH_2 \cdot BF_3$ and its total absence in the phenylphosphine spectra are best ascribed to nuclear quadrupole relaxation processes occurring at the boron nucleus as observed in other systems.[49-51] This would cause the fluorine nuclei to experience an averaged environment of the four descrete ^{11}B spin states, thereby giving rise to the unsplit J_{PBF} resonances. Apparently, in the dimethylphosphine adduct the electric field gradient around the boron nucleus is quite low. Thus the relaxation time is sufficiently lengthened to permit the interaction of each ^{11}B spin state with the fluorine nuclei even at relatively high temperatures. Hence, in this boron trifluoride adduct series, the loss of J_{BF} is ascribed to two different processes. In all adducts except that of dimethylphosphine, loss of boron-fluorine coupling is attributed to rapid relaxation processes induced by the interaction of the nuclear quadrupole with relatively high electric field gradients. But in the dimethylphosphine complex, the nearby simultaneous loss of J_{BF} and J_{PBF} clearly reflects a rapid-exchange process.

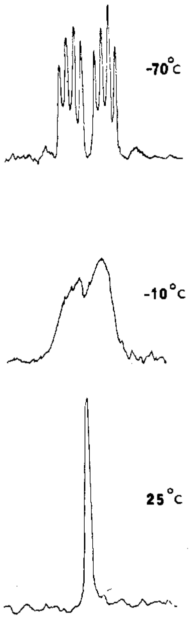

Figure 4. ^{19}F spectra of $Me_2PH \cdot BF_3$ recorded at various temperatures in CH_2Cl_2; 300-ppm scale setting.

The loss of J_{PBF} within the series as a function of temperature, while giving some indication of adduct stability with respect to exchange processes, does not reflect complete dissociation of the adducts because other nmr parameters such as J_{PH} and $\delta\, ^1H$ (Table I) are still those of the adduct rather than of a free base.

The chemical shift of BF_3 in methylene chloride at −90° has been given as +122.2 ppm relative to CCl_3F[49] although other values have been reported.[48,52] The chemical shift data for the PH_3-BF_3 system obtained in this study seem to indicate that the adduct $PH_3 \cdot BF_3$ does not form at the temperatures specified.

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Registry No. $BH_3 \cdot PhPH_2$, 6996-29-8; $BH_3 \cdot Ph_2PH$, 41593-58-2; $BF_3 \cdot (CD_3)_2PH$, 41593-59-3; $BF_3 \cdot PhPH_2$, 41593-60-6; $BF_3 \cdot Ph_2PH$, 41593-61-7; $BCl_3 \cdot (CD_3)_2PH$, 41593-62-8; $BCl_3 \cdot PhPH_2$, 41593-63-9; $BCl_3 \cdot Ph_2PH$, 41593-64-0; $BBr_3 \cdot (CD_3)_2PH$, 41593-65-1; $BBr_3 \cdot PhPH_2$, 41593-66-2; $BBr_3 \cdot Ph_2PH$, 3053-70-1; $BI_3 \cdot (CD_3)_2PH$, 41593-68-4; $BI_3 \cdot PhPH_2$, 41593-69-5; $BI_3 \cdot Ph_2PH$, 3053-71-2; $BH_3 \cdot PH_3$, 15120-00-0; $BH_3 \cdot MePH_2$, 14975-23-6; $BH_3 \cdot Me_2PH$, 4268-35-3; $BH_3 \cdot Et_3P$, 1838-12-6; $BH_2Cl \cdot PH_3$, 20214-19-1; $BH_2Br \cdot PH_3$, 16610-73-4; $BH_2I \cdot PH_3$, 41593-71-9; $BHCl_2 \cdot PH_3$, 20214-20-4; $BHBr_2 \cdot PH_3$, 20214-21-5; $BHI_2 \cdot PH_3$, 41593-72-0; $BCl_3 \cdot PH_3$, 13766-68-2; $BBr_3 \cdot PH_3$, 38822-66-1; $BI_3 \cdot PH_3$, 38822-60-5; $BF_3 \cdot MePH_2$, 41593-49-1; $BCl_3 \cdot MePH_2$, 41630-56-2; $BBr_3 \cdot MePH_2$, 41593-50-4; $BI_3 \cdot MePH_2$, 41593-51-5; $BF_3 \cdot Me_2PH$, 41593-52-6; $BCl_3 \cdot Me_2PH$, 41593-53-7; $BBr_3 \cdot Me_2PH$, 41593-54-8; $BI_3 \cdot Me_2PH$, 41593-55-9; $BF_3 \cdot PH_3$, 41593-56-0; $BH_3 \cdot (CD_3)_2PH$, 41593-57-1; ^{31}P, 7723-14-0; ^{11}B, 14798-13-1.

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