A Study of the Donor–Acceptor Bond in Phosphine–Borane Complexes

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Abstract: An nmr study of 15 phosphine–boranes has been undertaken with a view to investigating the electronic nature of the P–B dative bond. A correlation between the ^{31}P–^{11}B coupling constant and the base strength of the phosphine toward BH_3 has been established on the basis of selected displacement reactions. The observed sequence of phosphine base strengths and scalar ^{31}P–^{11}B couplings is inconsistent with the borane hyperconjugative model *per se*, although this effect is not excluded. The results are best interpreted in terms of a combination of σ effects, dative π bonding from the phosphine substituents, and borane hyperconjugation. Similarly, the ^{11}B–^{1}H coupling constant data do not discriminate between the σ bonding and borane hyperconjugative models. Several ^{31}P, ^{11}B, and ^{1}H chemical shifts have also been measured, but these data do not provide definitive information concerning the nature of the P–B bond. It is noted, however, that the trend of coordination chemical shifts for the complexation of phosphines with the BH_3 moiety bears a marked resemblance to that observed for the complexation of phosphines with the isoelectronic oxygen atom.

There has been considerable discussion regarding the nature of the coordinate bond between phosphines and the borane group. In one hypothesis, hereinafter referred to as the "borane hyperconjugative model" the P→B dative σ bond is supplemented by a π-type interaction between the B–H σ-bonding electrons and the phosphorus 3d orbitals[2] (Figure 1). The borane hyperconjugative model was invoked initially[3] to explain the unexpectedly high thermal and oxidative stability of the phosphinoborine trimers and tetramers, $(R_2PBH_2)_{3,4}$. Subsequently, the model has been employed in rationalizing the existence of $COBH_3$ and PF_3BH_3 and the nonexistence of such species as $COBF_3$, PF_3BF_3, and NF_3BF_3.[4] "Base strength reversals" have also been interpreted from the standpoint of borane hyperconjugation; *e.g.*, toward BF_3 first-row donors such as amines and ethers exhibit greater Lewis basicity than second-row donors such as phosphines and sulfides; *viz.*, N > P, O > S, whereas toward the BH_3 group this order is inverted; *viz.*, P > N, S > O.[4,5]

The other P–B bonding hypothesis considers only σ bonding and relates the Lewis acid–base interaction energy (E) to the field strength of the Lewis acid (F), and the dipole moment (ρ) and polarizability (α) of the lone-pair electrons of the Lewis base.[6]

$$E = F[\rho + F\alpha/2] \tag{1}$$

The σ-bonding model has gained support from the fact that, contrary to the predictions of the hyperconjugative model, the base strength of PF_2H is greater than that of PF_3 toward the borane group.[6] Furthermore, base strength reversals have been observed with BCl_3 and $\overline{SCH_2CH_2S}BH$.[7] The former case is particularly noteworthy because of the impossibility of a B–H hyperconjugative interaction.

In the present work, nuclear spin coupling constant and chemical shift data have been secured for 15 phosphine–boranes. It was anticipated that the trends in these data might serve as additional experimental tests of the relative merits of the P–B bonding models. Particular emphasis has been placed on the ^{31}P–^{11}B coupling constant because this parameter is a property of the bond in question. Citations of previously published nmr data concerning these compounds are deferred until a later section.

Experimental Section

All operations involving the phosphines and phosphine–boranes were carried out under an inert atmosphere or by standard vacuum-line techniques. All solvents were dried and distilled prior to use.

Materials. Trimethyl phosphite, PH_3, and PF_3 were procured commercially and used without subsequent purification. The phosphines $C_6H_5PH_2$,[8] PHF_2,[9] $(CH_3)_2PH$,[10] $C_6H_5P(CH_3)_2$,[11] $(CH_3)_3P$,[12] $(CH_3)_2NPF_2$,[13] $[(CH_3)_2N]_2PF$,[13] $[(CH_3)_2N]_3P$,[14] CH_3OPF_2,[15] and $(CH_3O)_2PF$[16] were prepared and purified according to published methods. The compound CF_3PF_2 was made by the action of SbF_3 on CF_3PI_2 using a similar procedure to the one described[17] for the preparation of $(CF_3)_2PF$. Methylphosphine was prepared by the $LiAlH_4$ reduction of commercially available dimethyl methylphosphonate, following a very similar procedure to that described by Hatfield and Yoke[18] for the preparation of $C_2H_5PH_2$. The

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(2) Most discussions of π bonding have related to the use of the vacant 3d orbitals of, *e.g.*, P or S. However, derived valence-state ionization potential data indicate that for neutral atoms the 4p and 3d orbitals are very close in energy. Consequently, $2p\pi$–$4p\pi$ bonding may be as important as $2p\pi$–$3d\pi$ bonding. See L. C. Cusachs and J. R. Linn, *J. Chem. Phys.*, **46**, 2919 (1967).

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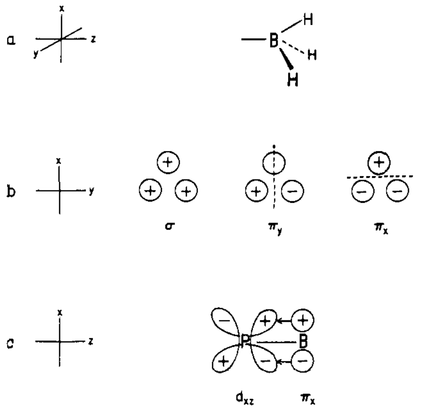

Figure 1. Borane hyperconjugative model: (a) orientation of the BH_3 group; (b) σ and pseudo-π orbitals of the BH_3 group; (c) a hyperconjugative interaction between one of the BH_3 pseudo-π orbitals and a vacant phosphorus 3d orbital.

crude CH_3PH_2 was purified by high-vacuum fractional condensation with U traps held at −100, −144, and −196°; the pure phosphine condenses in the −144° trap. Diborane was prepared by the action of $LiAlH_4$ on $(C_2H_5)_2O \cdot BF_3$.[19] Unless otherwise indicated, the phosphine–boranes were prepared by allowing mixtures of the appropriate phosphine with a slight excess of B_2H_6 to warm slowly from −196° in evacuated sealed tubes. Purification was effected by high-vacuum fractional condensation until the vapor tensions, ir and nmr spectra, etc., conformed to the literature specifications. The syntheses of $CF_3PF_2BH_3$[20] and PF_3BH_3[21] involved the reaction of B_2H_6 with an excess of the phosphine as described previously. The compounds $CH_3OPF_2BH_3$ and $(CH_3O)_2PFBH_3$ have not been reported hitherto.

$CH_3OPF_2BH_3$ was prepared by allowing a mixture of 2.0 mmol of CH_3OPF_2 and 1.1 mmol of B_2H_6 to warm overnight from −196° to ambient temperature in a sealed tube. High-vacuum fractionation of the volatiles through U traps held at −110 and −196° resulted in the condensation of 1.9 mmol of $CH_3OPF_2BH_3$ in the −110° trap. The vapor-phase ir spectrum of $CH_3OPF_2BH_3$ consisted of C–H strecthing modes at 2976 and 2856 cm^{-1}, B–H stretching at 2406 cm^{-1}, C–O and P–O stretching at 1207, 1102, and 1062 cm^{-1}, and P–F stretching at 924, 903 (sh), 895 (sh), and 842 cm^{-1}. The observed vapor-phase molecular weight was 114.5 *vs.* 113.8 calculated for $CH_3OPF_2BH_3$. The volatility data for $CH_3OPF_2BH_3$ are shown in Table I.

Table I. Volatility of $CH_3OPF_2BH_3$[a]

Temp, °C	P_{obsd}, mm	P_{calcd}, mm
5.45	75.70	76.86
9.95	94.40	94.29
16.40	124.35	124.98
20.90	151.65	151.03
24.65	177.10	176.07
28.75	208.50	207.31
32.75	240.55	242.10

[a] $\log P = 7.4694 - 1555.7/T$; $t_{760} = 65.87$; Trouton constant = 20.98 eu.

$(CH_3O)_2PFBH_3$ was prepared similarly in comparable yield from the reaction of 2.0 mmol of $(CH_3O)_2PF$ and 1.1 mmol of B_2H_6. The $(CH_3O)_2PFBH_3$ traps out at −55° and the vapor-phase ir spectrum consists of the anticipated features, namely C–H stretching at 2981 and 2881 cm^{-1}, B–H stretching at 2401 cm^{-1}, C–O and P–O stretching at 1205, 1107, and 1063 cm^{-1}, and P–F stretching at 840 cm^{-1}. The observed vapor-phase molecular weight was 123.7 *vs.* 125.8 calculated for $(CH_3O)_2PFBH_3$. The volatility data for $(CH_2O)_2PFBH_3$ are shown in Table II.

Table II. Volatiltiy of $(CH_3O)_2PFBH_3$[a]

Temp, °C	P_{obsd}, mm	P_{calcd}, mm
16.35	4.60	4.58
24.80	7.95	7.54
30.35	10.30	10.31
34.65	13.00	13.03
39.20	15.90	16.58
44.35	21.40	21.60
49.90	29.10	28.46
57.65	41.00	41.17
64.75	56.90	56.90

[a] $\log P = 8.3019 - 2212.2/T$; $t_{760} = 134.92$; Trouton constant = 24.79 eu.

Homogeneous Base Displacement Reactions. (i) **The Reaction of $(CH_3)_2NPF_2$ with $CH_3OPF_2BH_3$.** $CH_3OPF_2BH_3$ (1.92 mmol) and 3.33 mmol of $(CH_3)_2NPF_2$ were condensed in an evacuated tube at −196°. The tube was sealed and allowed to warm slowly −78°. After standing at −78° for 15 hr followed by 73 hr at 0° the tube was opened to the vacuum system and the volatiles were fractionally distilled using U traps at −50, −112, and −196°. On the basis of ir spectroscopic identification, the −196° trap was found to contain 1.92 mmol of CH_3OPF_2. The −50° trap contained 1.34 mmol of $(CH_3)_2NPF_2BH_3$ and the −112° trap contained the remainder of the $(CH_3)_2NPF_2BH_3$ and 1.41 mmol of $(CH_3)_2NPF_2$.

(ii) **The Reaction of $CH_3PH_2BH_3$ with $(CH_3O)_3P$ and the Reaction of PF_3BH_3 with CH_3PH_2.** The progress of these reactions was followed by ^{31}P nmr. The chemical shifts of the free and complexed phosphines are presented later (Table V). A mixture of 2.0 mmol of $CH_3PH_2BH_3$ and 1.26 mmol of $(CH_3O)_3P$ was sealed *in vacuo* in an nmr tube at −196°. The tube was allowed to warm gradually to 0° and was kept at this temperature for 40 hr. At the end of this period, the resonance at −140 ppm which corresponds to uncomplexed $(CH_3O)_3P$ was not detectable, and a resonance was observed at −118 ppm which is attributable to $(CH_3O)_3PBH_3$.

Similarly, a mixture of 1 mmol of PF_3BH_3 and 1 mmol of CH_3PH_2 was sealed in an evacuated nmr tube at −196°. After slowly warming to −40°, the tube was allowed to stand at this temperature for 46 hr. Integration of the ^{31}P resonances indicated that the equilibrium mixture contained 0.6 mmol each of $CH_3PH_2BH_3$ and PF_3 and 0.4 mmol each of PF_3BH_3 and CH_3PH_2.

Nmr Spectra. Most of the ambient-temperature ^1H spectra were recorded on a Varian Associates A-60 spectrometer. Low-temperature ^1H spectra and spectra where overlapping of resonances was observed at 60 MHz were run on a Varian Associates HA-100 spectrometer. Temperatures were calibrated against methanol spectra as described in the Varian Users Manual. The ^{11}B (32.1 MHz), ^{31}P (40.5 MHz), and ^{19}F (94.1 MHz) spectra were recorded on a Varian Associates HA-100 spectrometer; the chemical shifts are relative to sealed capillaries of $(CH_3O)_3B$, 85% H_3PO_4, and α,α,α-trifluorotoluene, respectively.

The sample of PH_3BH_3 was prepared *in situ* as described previously.[22] The sample of $[(CH_3)_2N]_3PBH_3$ was prepared by forming the adduct in a sealed 50-ml reaction bulb equipped with side arms leading to nmr tubes. After removing the excess B_2H_6 and resealing the reaction vessel, the solid complex was melted by the application of external heat and allowed to flow into the nmr tubes. The nmr tubes were sealed off at −196° and allowed to warm slowly to ambient temperature. The nmr spectra of PH_3BH_3 and $[(CH_3)_2N]_3PBH_3$ were run in the molten state. A similar procedure was employed in the preparation of the nonvolatile liquid adducts $(CH_3O)_3PBH_3$, $C_6H_5(CH_3)_2PBH_3$, and $(C_6H_5)_2PHBH_3$. The sample of $(CH_3)_3PBH_3$ was also prepared in a similar manner except that it was necessary to add C_6H_6 as solvent. The other borane adducts are volatile, and the samples were prepared by condensing the pure compounds in the nmr tube and sealing them off *in vacuo* at −196°.

Infrared Spectra. All ir spectra were measured on a Perkin-Elmer Model 337 grating spectrophotometer.

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Table III. ^{11}B–^{1}H Coupling Constant, ^{1}H Chemical Shift, ^{11}B Chemical Shift, and Miscellaneous Coupling Constant Data for Phosphine–Borane Complexes

Complex	$^{1}J_{^{11}B-^{1}H}$, Hz	$\tau(BH_3)^a$	$\delta(^{11}B)^b$	$J_{^{31}P-B-^{1}H}$, Hz	Miscellaneous $J_{^{31}P-X}$, Hz
$(CF_3)PF_2BH_3$	106	9.05	65.6	17	
PH_3BH_3	104	9.37	60.8^c	15.5	$J_{PH} = 372^c$
$C_6H_5PH_2BH_3$	101		59.8		
PF_3BH_3	107^c	9.18	66.6	18.5	$J_{PF} = 1406^c$
$(CH_3)PH_2BH_3$	100	9.45	58.8	16	$J_{PH} = 370$
PHF_2BH_3	103^c	9.22	60.4	18	$J_{PH} = 467,^c J_{PF} = 1151^c$
$(CH_3)_2PHBH_3$	96	9.48	56.2	16.6	$J_{PH} = 366$
$(C_6H_5)(CH_3)_2PBH_3$	97		55.5		
$(CH_3)_3PBH_3$	97.4	8.84	54.2	16	
$CH_3OPF_2BH_3$	102.4	9.40	64.5	20	$J_{POCH} = 11, J_{PF} = 1290$
$(CH_3)_2NPF_2BH_3$	100	9.38	61.4	20	$J_{PNCH} = 10.5, J_{PF} = 1166^d$
$[(CH_3)_2N]_2PFBH_3$	98^d	9.55	60.5	17	$J_{PNCH} = 9.8, J_{PF} = 1070$
$[(CH_3)_2N]_3PBH_3$	95^d	9.61	60.8	17	$J_{PNCH} = 9.5$
$(CH_3O)_2PFBH_3$	96.2	9.55	63.8	20	$J_{POCH} = 11, J_{PF} = 1206$
$(CH_3O)_3PBH_3$	97.2^e	9.70	63.8	19.5	$J_{POCH} = 11$

[a] Relative to internal $(CH_3)_4Si$. [b] Relative to external $B(OCH_3)_3$. [c] Reference 6. [d] Reference 13. [e] J. G. Verkade, R. W. King, and C. W. Hertsch, *Inorg. Chem.*, **3**, 884 (1964).

Table IV. ^{31}P–^{11}B Coupling Constant Data for Phosphine–Borane Complexes

Complex	$J_{^{31}P-^{11}B}$, Hz	
$(CF_3)PF_2BH_3$	18	
PH_3BH_3	27^a	
$C_6H_5PH_2BH_3$	35	
PF_3BH_3	39^a	
$(CH_3)PH_2BH_3$	43.5	Increasing coordinate bond strength ↓
PHF_2BH_3	49^a	
$(CH_3)_2PHBH_3$	58	
$(C_6H_5)(CH_3)_2PBH_3$	59	
$(CH_3)_3PBH_3$	59.8	
$CH_3OPF_2BH_3$	68.2	
$(CH_3)_2NPF_2BH_3$	79^b	
$[(CH_3)_2N]_2PFBH_3$	86^b	
$[(CH_3)_2N]_3PBH_3$	95	
$(CH_3O)_2PFBH_3$	96.2	
$(CH_3O)_3PBH_3$	97.2^c	

[a] Reference 6. [b] Reference 13. [c] Footnote *e*, Table III.

Results

All of the spectra of the phosphine–boranes considered here are first order, at ~23,500-G field strength, hence the coupling constant and chemical shift data were readily obtained from the recorded spectral traces. The spectra which are displayed in Figure 2 for the adduct $CH_3OPF_2BH_3$ are representative of the spectra which were obtained. The ^{11}B–^{1}H coupling constant and proton chemical shift data which are presented in Table III were obtained from the proton spectra of the $\geqslant P$–BH_3 moiety. Typically, these spectra consist of four equally intense resonances due to ^{11}B–^{1}H coupling, each component of which is further split into a doublet by ^{31}P–B–^{1}H coupling. In some cases, *e.g.*, $CH_3OPF_2BH_3$ (Figure 2a), other couplings such as ^{19}F–P–B–^{1}H are also evident. Unresolved ^{10}B–^{1}H coupling is sometimes evident in the base line (*e.g.*, Figure 2a).

The ^{31}P–^{11}B coupling constant data (Table IV) and ^{11}B chemical shift data (Table III) were obtained from the ^{11}B spectra. Most of these spectra (*e.g.*, Figure 2c) consist of a quartet due to ^{11}B–^{1}H coupling, each component being further split into a doublet by ^{31}P–^{11}B coupling. However, in the adducts $(CH_3O)_3PBH_3$, $[(CH_3)_2N]_3PBH_3$, and $(CH_3O)_2PFBH_3$ the ^{31}P–^{11}B and ^{11}B–^{1}H coupling constants are of the same magnitude, hence the ^{11}B spectrum simplifies to a quintet.

Generally the ^{31}P spectra were not very well resolved (*e.g.*, Figure 2d), hence these spectra were only used as a source of ^{31}P chemical shift data (Table V). The ^{31}P chemical shifts of the uncomplexed phosphines are also included in this table. Finally, a collage of miscellaneous coupling constants is also included in Table III.

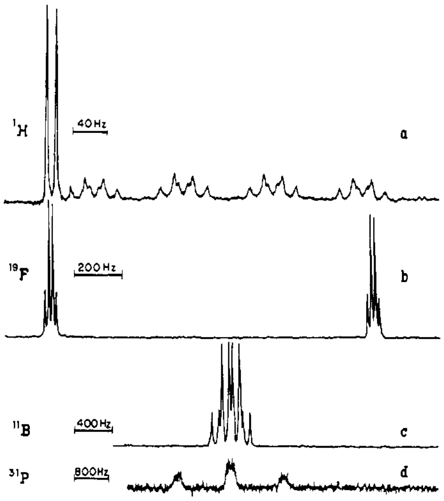

Figure 2. Nmr spectra of a neat liquid sample of $CH_3POF_2BH_3$: (a) 100-MHz ^{1}H spectrum; (b) 94.1-MHz ^{19}F spectrum; (c) 32.1-MHz ^{11}B spectrum; (d) 40.5-MHz ^{31}P spectrum.

Discussion

For convenience the coupling constant and chemical shift data are discussed separately.

Coupling Constants. (i) The ^{31}P–^{11}B Coupling Constant. The directly bonded ^{31}P–^{11}B coupling constant is of pivotal importance because it is a property of the donor–acceptor linkage in question. No relative sign data have been published for this scalar coupling; however, the following three arguments all indicate that it is positive. (1) The model of Jameson and Gutowsky[23] relates the sign of a directly bonded reduced coupling

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Table V. ^{31}P Chemical Shift Data for Phosphines and Phosphine–Borane Complexes

Complex	$\delta_{\text{free phosphine}}$[a]	δ_{complex}[a]	Coordination chemical shift[b]
PH_3BH_3	246[c]	113[c]	−133
$(CH_3)PH_2BH_3$	163.5[d]	68.5	−95
$(C_6H_5)PH_2BH_3$	123.5	49.3	−74.2
$(CH_3)_2PHBH_3$	98.5[d]	30.8	−67.7
$(CH_3)_3PBH_3$	62.8	1.8	−61
$(C_6H_5)(CH_3)_2PBH_3$	46	−49	−95
PF_3BH_3	−105[c]	−107[c]	−2
$CH_3OPF_2BH_3$	−111.8	−108.5	+3.3
$[(CH_3)_2N]_3PBH_3$	−122.5[e]	−102.5	+20
$(CH_3O)_2PFBH_3$	−131.6	−118.7	+12.9
$(CH_3O)_3PBH_3$	−140[f]	−118[f]	+22
$(CH_3)_2NPF_2BH_3$	−143[g]	−130[g]	+13
$[(CH_3)_2N]_2PFBH_3$	−153[g]	−134[g]	+19
$(CF_3)PF_2BH_3$	−158.1	−148.5	+9.6
PF_2HBH_3	−224[c]	−171[c]	+53

[a] Relative to external 85% H_3PO_4. [b] See F. Klanberg and E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 3296 (1968), for definition. [c] R. W. Rudolph, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1966. [d] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, **78**, 5715 (1956). [e] F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, **22**, 567 (1966). [f] Footnote *e*, Table III. [g] Reference 13.

constant,[24] K_{AB}, to the signs of the nuclear spin–electron spin contact contributions $\mathcal{A}_A$ and $\mathcal{A}_B$, each of which is expressed as a sum of two terms

$$\mathcal{A}_A = \mathcal{A}_A{}^S + \mathcal{A}_A{}^{\text{core pol}} \qquad (2)$$

$\mathcal{A}_A{}^S$ is the Fermi contact term which is necessarily positive; it relates to the bonding s electron density at the nucleus. On the other hand, $\mathcal{A}_A{}^{\text{core pol}}$ can take both positive and negative signs. For an s orbital, the core polarization term is positive, while for p, d, and f electrons, $\mathcal{A}_A{}^{\text{core pol}}$ is usually negative. This means that if atoms A and B both employ s electrons in their bonding then $\mathcal{A}_A{}^{\text{core pol}}$ and $\mathcal{A}_B{}^{\text{core pol}}$ will both be positive, thus resulting in a positive sign for K_{AB}. Since this is certainly the case in the phosphine–boranes (where the hybridization of both P and B is approximately sp^3), then K_{PB} and J_{PB} are predicted to be positive. (2) Using the theoretical approach described previously,[25] we calculate the contact contribution to J_{PB} in the model compound PH_3BH_3 to be +39.1 Hz. The calculated spin–dipolar and spin–orbital contributions are 0.71 and −0.04 Hz, respectively, and therefore much too small to offset the substantial positive contact contribution. (3) The model of Schaefer and Yaris[26] relates the sign of a directly bonded coupling constant to the electronegativity difference of the coupled atoms, being positive when this difference is less than 1.5 and negative when the difference exceeds 1.5. Since $x_P - x_B = 0.1$, the ^{31}P–^{11}B directly bonded coupling constant is predicted to be positive. In view of the foregoing arguments, it will be assumed that the sign of J_{PB} is positive in the remainder of the discussion.

The possibility of a correlation between J_{PB} and the Lewis basicity of a phosphine toward the borane unit has been discussed previously[27] in relation to the two series of bases PF_3, PF_2H, and PH_3 and $(CH_3)_3P$, $(CH_3)_2PH$, CH_3PH_2, and PH_3. In the present paper, more extensive ^{31}P–^{11}B coupling constant data have been obtained (Table V), and in addition it has been possible to demonstrate by means of displacement reactions that the correlation between J_{PB} and phosphine basicity extends to the 15 bases considered. This conclusion is based on the following criteria: (1) a pair of phosphines whose borane adduct J_{PB} values differed widely (reaction I) and (2) two pairs of phosphines whose borane adduct J_{PB} values were closely similar (reactions II and III)

$$(CH_3O)_3P + CH_3PH_2BH_3 \xrightarrow[0°]{40\text{ hr}} (CH_3O)_3PBH_3 + CH_3PH_2 \qquad \text{(I)}$$

$$(CH_3)_2NPF_2 + CH_3OPF_2BH_3 \xrightarrow[0°,\ 73\text{ hr}]{-78°,\ 15\text{ hr}} (CH_3)_2NPF_2BH_3 + CH_3OPF_2 \qquad \text{(II)}$$

$$CH_3PH_2 + PF_3BH_3 \xrightarrow{-78°,\ 46\text{ hr}} CH_3PH_2BH_3 + PF_3 \qquad \text{(III)}$$

Reactions I and II proceeded to completion in the directions indicated. Reaction III was ~60% complete in the direction indicated. It is recognized that in general it is inadvisable to make assessments of Lewis basicities on the basis of equilibrium constant data because of entropy effects;[28] however, when comparing the basicities of a series of structurally similar phosphines toward the same acceptor, the entropy changes accompanying coordination should be approximately constant. If this is assumed, then the orders of basicity toward the BH_3 group from the selected displacement reactions are $(CH_3O)_3P > CH_3PH_2$, $(CH_3)_2NPF_2 > CH_3OPF_2$, and $CH_3PH_2 > PF_3$. This is the same order as the J_{PB} values for the BH_3 adducts of these phosphines (Table IV), and together with Rudolph's observation[27] that the J_{PB} values for PF_2HBH_3, PF_3BH_3, and PH_3BH_3 are in the same order as the basicities of the parent phosphines, it is therefore concluded that the ^{31}P–^{11}B coupling constant of the borane adducts considered here may be taken as a measure of the basicity of the phosphine toward the BH_3 moiety.

The order of phosphine basicity indicated in Table IV is inconsistent with the borane hyperconjugative model for the following reasons. (1) On the basis of the CO stretching force constants in metal carbonyl complexes, Barlow, Nixon, and Webster[29] have established the following order of phosphine π-acceptor ability: $CF_3PF_2 > PF_3 > C_6H_5PF_2 > ROPF_2 > R_2NPF_2 > (R_2N)_2PF$. A somewhat similar order of π-acceptor ability, *viz.*, $PF_3 > (CH_3O)_3P > [(CH_3)_2N]_3P > (\text{alkyl})_3P$ emerged from one interpretation[30] of the

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[24] The reduced coupling constant, K_{AB}, is defined by the equation $K_{AB} = J_{AB}(2\pi/h\gamma_A\gamma_B)$, where γ_A and γ_B are the magnetogyric ratios of nuclei A and B, respectively. See J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

[25] A. H. Cowley and W. D. White, *J. Amer. Chem. Soc.*, **91**, 1913 (1969).

[26] J. Schaefer and R. Yaris, *Chem. Phys. Lett.*, **1**, 173 (1967).

[27] R. W. Rudolph, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1966.

[28] A case which illustrates this point concerns the compounds $(CH_3)_3NB(CH_3)_3$ and $(CH_3)_3PB(CH_3)_3$. The dissociation constants of these adducts at 100° are 0.472 and 0.128, respectively, suggesting that the phosphine is the stronger base. However, the enthalpies of formation of $(CH_3)_3NB(CH_3)_3$ and $(CH_3)_3PB(CH_3)_3$ are17.6 and 16.5 kcal/mol, respectively, indicating that the N→B bond is stronger than the P→B bond. See H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

[29] C. G. Barlow, J. F. Nixon, and M. Webster, *ibid.*, *A*, 2216 (1968).

[30] S. O. Grim, P. R. McAllister, and R. M. Singer, *Chem. Commun.*, 38 (1969). For an alternative explanation, however, see R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, **8**, 2115 (1969).

trend of ^{31}P–^{183}W coupling constants in tungsten–phosphine complexes. If borane hyperconjugation is important in the phosphine–boranes, the ^{31}P–^{11}B coupling constants should follow the above orders closely because, *e.g.*, the placement of electronegative groups on phosphorus should facilitate BH_3 hyperconjugation by contracting and lowering the energy of the phosphorus 3d orbitals.[2] In turn, an increase in π bonding should lead to a synergic increase in the P→B dative σ bond and therefore to an increase in J_{PB}. It is obvious, however, that there is no relationship between J_{PB} and the π-acceptor ability of the phosphine because PF_3BH_3 should exhibit the largest ^{31}P–^{11}B coupling constant of the phosphine–boranes considered, and, furthermore, the hyperconjugative model would not predict that the J_{PB} of $CF_3PF_2BH_3$ would be the smallest of the couplings considered here. (2) A second trend which is inconsistent with the hyperconjugative model is the sequence of basicities $(CH_3)_3P > (CH_3)_2PH > CH_3PH_2 > PH_3$ toward the BH_3 group, as inferred from the respective J_{PB} values. Significantly, this is the same order of basicity which Brown and coworkers[31] found for the reference acids $(CH_3)_3B$, BF_3, and H^+. Since there is no possibility of a π-type interaction with a proton, it is clear that hyperconjugative effects are unimportant in sequencing the Lewis basicities of PH_3 and the methylated phosphines. (3) The order of basicity of the fluorophosphines toward BH_3 is $PF_2H > PF_3 > PH_3$. As pointed out by Rudolph and Parry,[9] the basicity (and, therefore, J_{PB}) for PF_2H should interpolate those of PF_3 and PH_3 from the standpoint of the hyperconjugative model. Of course, the foregoing arguments do not *exclude* the possibility of some borane hyperconjugation. In fact, it is interesting to note that recent *ab intio* SCF–MO calculations[32] on PH_3BH_3 and PF_3BH_3 indicate that there is a small amount of this type of bonding. Rather, we infer that other interactions are more important in determining the observed order of phosphine base strengths and J_{PB} values.

It is equally obvious that purely σ bonding is also incapable of explaining all our data. If the isovalent hybridization hypothesis[33] is applicable to the second-row elements, then, *e.g.*, increasing the electronegativity of the phosphine substituents would divert P(3s) character into the P–B bond, thus *increasing* the contact contribution[34] to J_{PB}. On the other hand, the basicity of the phosphine would be expected to *decrease* when electronegative substituents are placed on phosphorus. This means that from the standpoint of σ effects alone, opposing trends should exist between phosphine basicities and J_{PB} values. This contradicts the observation of a correlation between these factors.

The other type of interaction which may be significant in certain of the phosphines considered here is a dative π bonding between the filled 2p orbitals of R_2N–, RO–, or F– groups and vacant P(3d) or P(4p) orbitals.[2] The importance of this type of interaction in aminophosphines has been suggested in a variety of structural,[35] stereochemical,[36] and basicity[37] observations which indicate or suggest that the nitrogen atom is planar and essentially nonbasic. Dative π bonding between oxygen and phosphorus may be inferred, *e.g.*, from the Lewis base behavior of the caged phosphite $P(OCH_2)_3P$;[38] here the basicity of the phosphite end of the molecule is greater than that of the phosphine end toward the acceptor BH_3. It therefore seems logical to ascribe the positioning of the six CH_3O– and $(CH_3)_2N$– substituted phosphines at the high end of the J_{PB} and phosphine basicity order (Table IV) to dative π bonding from N or O 2p orbitals into the appropriate vacant phosphorus orbitals of π symmetry. A similar argument presumably obtains in understanding the J_{PB} order $PF_3 > CF_3PF_2$, since dative π bonding is impossible for the CF_3 moiety. The decrease in J_{PB} and phosphine basicity upon successive replacement of CH_3O– and $(CH_3)_2N$– groups by fluorine is presumably a reflection of the increased importance of σ withdrawal compared to π donation.

(ii) **The ^{11}B–^{1}H Coupling Constant.** The relative sign of $J_{^{11}B-^{1}H}$ has not been related to $J_{^{13}C-^{1}H}$, which is universally taken to be positive; however, in BF_2H the ^{11}B–^{1}H and ^{11}B–^{19}F signs were found[39] to be opposite, hence it may be assumed that $J_{^{11}B-^{1}H}$ is absolute positive. The ^{11}B–^{1}H coupling data (Table III) do not discriminate between the borane hyperconjugative and σ-bonding hypothesis because the same trend is expected for either model. In Table VI the various phosphines are listed in descending order of π-acceptor strength as established by Nixon and collaborators[29] on the basis of the CO stretching force constants of the phosphine metal carbonyl compounds, the phosphine $(CH_3)_3P$ being an addendum to Nixon's list. Trialkylphosphines have been found to be less effective π acceptors than any of the other phosphines in Table VI by Grim and collaborators.[30] PH_3BH_3, J_{BH} = 104 Hz, has not been included in Table VI because the π-acceptor strength of PH_3 has not been compared with those of the other phosphines. However, it is interesting to note that in some transition metal complexes it appears that PH_3 behaves as a strong π-acceptor ligand.[40]

Table VI. ^{11}B–^{1}H Coupling Constants

Phosphine–borane	$J_{^{11}B-^{1}H}$, Hz	
$CF_3PF_2BH_3$	106	
PF_3BH_3	107	↑ Increasing π-acceptor strength of uncomplexed phosphine[a]
$C_6H_5PF_2BH_3$		
$CH_3OPF_2BH_3$	102.4	
$(CH_3)_2NPF_2BH_3$	100	
$[(CH_3)_2N]_2PFBH_3$	98	
$(CH_3)_3PBH_3$	97.4	

[a] See text and ref 29 and 30.

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(31) H. C. Brown, E. A. Fletcher, E. Lawton, and S. Sujishi, Abstracts, 121st National Meeting of the American Chemical Society, Buffalo, N. Y., March 1952, p 9N. For the proton affinity order $(CH_3)_3P > PH_3$, see D. H. McDaniel, N. B. Coffman, and J. M. Strong, *J. Amer. Chem. Soc.*, **92**, 6697 (1970).

(32) J. Demuynck and A. Veillard, *Chem. Commun.*, 873 (1970); I. H. Hillier, J. C. Marriof, V. R. Saunders, J. J. Ware, and D. R. Lloyd, *ibid.*, 1586 (1970).

(33) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(34) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(35) E. D. Morris, Jr., and C. E. Nordman, *Inorg. Chem.*, **8**, 1672 (1969).

(36) A. H. Cowley, M. J. D. Dewar, W. R. Jackson, and W. G. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970).

(37) See, for example, A. B. Burg and P. J. Slota, *ibid.*, **80**, 1107 (1958); T. Reetz and B. Katlafsky, *ibid.*, **82**, 5036 (1960); A. H. Cowley and R. P. Pinnell, *ibid.*, **87**, 4454 (1965); W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).

(38) J. G. Verkade, private communication.

(39) E. B. Whipple, T. H. Brown, T. C. Farrar, and T. D. Coyle, *J. Chem. Phys.*, **43**, 1841 (1965).

(40) F. Klanberg and E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 3296 (1968).

It is noted that increases in the π-acceptor strength of the phosphine are paralleled by increases in the scalar $^{11}B-^{1}H$ coupling. This could be interpreted as supportive of the borane hyperconjugative model, because interactions of the type depicted in Figure 1c might be expected to open the HBH angles slightly, thus increasing the 2s character in the boron bonding orbitals, which in turn would increase the $^{11}B-^{1}H$ coupling constant.

The last statement implies (1) that the diminution in J_{BH} by hyperconjugative delocalization of B–H bonding electrons is subordinate to the increase in J_{BH} due to increased B(2s) character in the B–H bonds and (2) that a smooth and monotonic relationship exists between $J_{^{11}B-^{1}H}$ and the per cent 2s character in the B–H bonds. Although such a relationship has not been established experimentally it is anticipated by analogy with the well known $^{13}C-^{1}H$ case.[41]

The $^{11}B-^{1}H$ results can, however, be interpreted without invoking a π component to the phosphorus–boron bond. It will be noted that, with the exception of PH_3BH_3, the trend of $^{11}B-^{1}H$ couplings depends upon the electronegativity of the phosphorus substituents in the sense that the placement of electronegative substituents on phosphorus leads to increases in $J_{^{11}B-^{1}H}$. This would be anticipated from the standpoint of the isovalent hybridization hypothesis,[33] *viz.*, in considering a structure XBH_3 increasing the electronegativity of the moiety X diverts more 2s character into the B–H bonds and thereby increases the contact contribution to $J_{^{11}B-^{1}H}$.

(iii) **Miscellaneous Coupling Constants.** The $^{31}P-^{1}H$ coupling constants of the complexed primary and secondary phosphines (Table III) are ~175–225 Hz larger[42] than those of the free phosphines. Comparable increases in the $^{31}P-^{1}H$ coupling constant have been observed[43] when phosphines coordinate with other Lewis acids. Such a trend is anticipated on the basis of the increase of the phosphorus bond angles upon coordination, resulting in a concomitant increase in the per cent 3s character in the phosphorus bonding orbitals.

The $^{31}P-^{19}F$ coupling constants of the fluorophosphines (Table III) show both increases and decreases upon coordination to the borane moiety. A similar situation has been noted[43] when fluorophosphines coordinate to transition metal derivatives; this may reflect the importance of noncontact contributions to the $^{31}P-^{19}F$ coupling constant.

Chemical Shifts. The chemical shifts of nuclei such as ^{31}P, ^{19}F, and ^{11}B may be conveniently discussed in terms of three conbributions,[44] *viz.*

$$\sigma = \sigma_d + \sigma_p + \sigma_o$$

The diamagnetic term, σ_d, depends on the electron distribution in the ground state of the molecule. The paramagnetic term, σ_p, derives from mixing ground and excited states under the influence of the magnetic field. It vanishes for electrons in s orbitals but can be appreciable when there is an asymmetric distribution of p and d electrons, and low-lying excited states are available. The term σ_o is the contribution from other atoms or groups in the molecule. This term is usually small because it has an inverse cube dependence on the interatomic distances.

^{31}P Chemical Shifts. If only the diamagnetic term is considered, one would expect that a good σ donor would exhibit a large negative coordination chemical shift[45] because of the transfer of charge that accompanies complex formation. Conversely, a good π acceptor would be expected to produce a small negative coordination chemical shift. It is evident (Table V) that no such trend is apparent in the case of coordination of phosphines with the borane unit. This may be taken to indicate that the coordination chemical shifts are dominated by changes in the paramagnetic term, σ_p. Previous studies, in fact, support this view. For instance, a theoretical study by Gutowsky and Larmann[46] showed that the paramagnetic contribution is dominant in tricoordinate compounds of the type PX_3 (X = H, CH_3, halogen). The paramagnetic contribution has also been found to be important in the coordination of phosphines with transition metal derivatives[43] and the coordination of PHF_2 with the borane unit.[27] Perhaps the best way of understanding the data in Table V is to point out the similarity in the trend of coordination chemical shifts for the borane unit and isoelectronic oxygen atom.[47] In both cases, the phosphines with the most positive chemical shifts have the largest negative coordination chemical shift and *vice versa.* The phosphines with negative (low field) ^{31}P chemical shifts are presumably those where the paramagnetic contribution is dominant. Since it is these phosphines which undergo the largest positive coordination chemical shifts, it would appear that the paramagnetic term is appreciable when the phosphine has electronegative substituents bearing at least one lone pair of electrons α to the phosphorus atom.

^{11}B Chemical Shifts. There has been relatively little attention paid to the theoretical interpretation of ^{11}B chemical shifts. However, since the paramagnetic term has been shown[48] to dominate in the boron trihalides, any attempt to relate the ^{11}B shifts to single factors such as electronegativities or phosphine donor strengths would be inappropriate.

^{1}H Chemical Shifts. The general trend of the proton chemical shifts of the borane group (Table III) is such that this resonance moves to higher field with increasing $J_{^{31}P-^{11}B}$. From the standpoint of the diamagnetic term, this would imply that the amount of charge which is transferred onto the BH_3 moiety is dependent upon the basicity of the phosphine. The obvious exception to this generalization is $(CH_3)_3PBH_3$. Since the nmr data for this compound were obtained in benzene solution (at infinite dilution), it is possible that this anomaly is associated with the magnetic anisotropy of the solvent.

Conclusions

The nmr data considered in this paper are not consistent with the borane hyperconjugative model *per se*, although this effect cannot be eliminated on the basis

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[41] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768 (1959).

[42] It has been established that $J_{^{31}P-^{1}H}$ is positive. See W. McFarlane, *Chem. Commun.*, 58 (1967).

[43] For a review, see J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, 2, 345 (1969).

[44] A. Saika and C. P. Slichter, *J. Chem. Phys.*, 22, 26 (1954); H. M. McConnell, *ibid.*, 27, 226 (1957); J. A. Pople, *Proc. Roy. Soc., Ser. A*, **239**, 541 (1957).

[45] Coordination chemical shift is defined as $\delta_{complexed} - \delta_{free\ phosphine}$

[46] H. S. Gutowsky and J. Larmann, *J. Amer. Chem. Soc.*, **87**, 3815 (1965).

[47] K. J. Packer, *J. Chem. Soc.*, 960 (1965).

[48] D. R. Armstrong and P. G. Perkins, *Chem. Commun.*, 377 (1965).

of the present evidence. Since the most sensitive test for CH_3 hyperconjugation comes from contact-shift studies,[49] we are currently attempting analogous experiments involving the BH_3 group.[50]

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(49) A. D. McLachlan, *Mol. Phys.*, 1, 233 (1958).

(50) Following the completion of this work, we learned that R. W. Rudolph and C. W. Schultz, *J. Amer. Chem. Soc.*, **93**, 6821 (1971), have determined that the sign of the ^{31}P–^{11}B directly bonded coupling constant is positive in $(CH_3)_3PBF_3$, $(CH_3)_2NPF_2BH_3$, $(CH_3)_3PBH_3$, and F_2PHBH_3. We thank Professor Rudolph for bringing his results to our attention prior to publication.

^{31}P–^{11}B Coupling Constant as a Qualitative Measure of Dative Bond Strength[1]

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Abstract: An empirical correlation between the magnitude of $^{1}J_{PB}$ and dative bond strength is evident for the BH_3 adducts of a series of smoothly varying phosphine ligands such as $F_{3-n}H_nP \rightarrow BH_3$, $Me_{3-n}H_nP \rightarrow BH_3$, $(Me_2N)_{3-n}F_nP \rightarrow BH_3$, and $F_2XP \rightarrow BH_3$ (X = F, Cl, Br). It is not known if the correlation can be quantified, and it does not appear to be general for cases where the ligands belong to different series. A similar correlation is not possible when the acid is smoothly varied and the ligand held constant in the series $Me_3P \rightarrow BX_3$ (X = F, Cl, Br, H). Relative sign determinations for $Me_3P \rightarrow BF_3$, $Me_3P \rightarrow BH_3$, $F_2HP \rightarrow BH_3$, and $(Me_2N)F_2P \rightarrow BH_3$ all indicate a positive sign for $^{1}J_{PB}$.

Scalar nuclear spin–spin coupling constants have been correlated to many aspects of molecular geometry and several molecular properties in both qualitative and semiquantitative manners.[2] For example, Bolles and Drago present evidence for a linear relation between $^{2}J_{^{119}Sn-CH_3}$ and the ΔH_f of trimethyltin chloride adducts.[3] However, to our knowledge, no correlations between $^{1}J_{D \rightarrow A}$ (D and A = donor and acceptor nuclei, respectively) and dative bond strength have been made. Since both of the nuclei which comprise the dative bond in phosphine–boranes are magnetically active, they represent one class of compounds where the effect of the bond strength on the coupling constant can be tested. Indeed, the subject correlation was first noted for the $H_3P \rightarrow BH_3$, $HF_2P \rightarrow BH_3$, $F_3P \rightarrow BH_3$ triad.[4] Now, with more extensive data and several $^{1}J_{PB}$ sign determinations, we wish to report other cases where the subject correlation is apparent and cases where it breaks down.

Results and Discussion

The $^{1}J_{PB}$ values for a number of adducts are ranked according to magnitude in Table I. The values which are listed embrace several series in which the P substituents are smoothly varied and the acid is BH_3; *i.e.*, $F_{3-n}H_nP \rightarrow BH_3$, $Me_{3-n}H_nP \rightarrow BH_3$, $(Me_2N)_{3-n}F_nP \rightarrow BH_3$, and $F_2XP \rightarrow BH_3$ (X = F, Cl, Br). Certain correlations hold among the latter, but a series where the acid is varied will be discussed first, *i.e.*, $Me_3P \rightarrow BX_3$ (X = F, Cl, Br, H).

Graham and Stone have shown that PMe_3 forms a stronger adduct with BH_3 than with BF_3[5] and Young, McAchran, and Shore indicate that $BCl_3 > BH_3 > BF_3$ is the order of stability with PMe_3.[6] Therefore, since the magnitude of $^{1}J_{PB}$ for the $Me_3P \rightarrow BX_3$ (X = F, Cl, Br, H) series would indicate that BH_3 is the weakest acid, it certainly is not a good measure of dative bond strength (Table I). Nevertheless, with $^{1}J_{PB}$ sign inversion as a function of the reference acid, the observed order of acid strength could conceivably be fit. The possibility was investigated. In the case of Me_3PBH_3 the sign of $^{1}J_{PB}$ was found to be the same as that of $^{1}J_{BH}$ by ^{1}H-{^{31}P} spin-tickling experiments. If the absolute sign of $^{1}J_{BH}$ is taken as positive,[7] then $^{1}J_{PB}$ is also. In the case of $Me_3P \rightarrow BF_3$, ^{19}F-{^{31}P} experiments showed that the signs of $^{1}J_{BF}$ and $^{1}J_{PB}$ were opposite, also yielding a positive $^{1}J_{PB}$ if a negative absolute sign for $^{1}J_{BF}$ is taken as usually accepted.[7,8]

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(1) For another article on this subject, see A. H. Cowley and M. C. Damasco, *J. Amer. Chem. Soc.*, 93, 6815 (1971). We wish to thank these authors for the opportunity to see their results prior to publication.

(2) (a) For example, see C. W. Schultz and R. W. Rudolph, *ibid.*, 93, 1898 (1971); (b) J. B. Lambert, *Accounts Chem. Res.*, 4, 87 (1971); (c) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 51, 2790 (1969); (d) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Elmsford, N. Y., 1966.

(3) T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, 88, 5730 (1966).

(4) R. W. Rudolph, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1966.

(5) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, 3, 164 (1956).

(6) D. E. Young, G. E. McAchran, and S. G. Shore, *J. Amer. Chem. Soc.*, 88, 4390 (1966).

(7) E. B. Whipple, T. H. Brown, T. C. Farrar, and T. D. Coyle, *J. Chem. Phys.*, 43, 1841 (1965).

(8) (a) S. A. Fieldhouse and I. R. Peat, *J. Phys. Chem.*, 73, 275 (1969). (b) In all other cases investigated, the sign of $^{1}J_{PB}$ was found to be positive relative to $^{1}J_{BH}$ as positive (signs are indicated in Table I where determined). It appears that all $^{1}J_{PB}$ values are positive.