

A STUDY OF THE DONOR-ACCEPTOR BOND
IN
PHOSPHINE-BORANE COMPLEXES

by
Ms. Cristina Teresa Deasaco Padolina, B.S., M.S.

APPROVED BY SUPERVISORY COMMITTEE:

DISSERTATION

A. A. Bentley

Presented to the Faculty of School of

Michael T. S. Bruar

The University of

in Partial Fulfillment

L. Morgan

of the Requirements

Charles H. Wade

for the Degree of

DOCTOR OF PHILOSOPHY

The University of Texas at Austin

December, 1971

A STUDY OF THE DONOR-ACCEPTOR BOND
IN
PHOSPHINE-BORANE COMPLEXES

by

Ma. Cristina Casabar Damasco Padolina, B.S., M.S.

DISSERTATION

Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

The University of Texas at Austin

December, 1971

ACKNOWLEDGEMENTS

The author is indebted to Dr. Alan S. [unclear] for his supervision of this study. Not only his capabilities as a mentor are appreciated but also his fine qualities as a person. Gratitude is also extended to Drs. A. Keith Jameson and Cynthia S. Jameson for their encouragement and suggestions regarding this work. The helpful discussions with the members of our research group are also acknowledged. For his help in many ways, the author would like to thank his mother, Mrs. William C. [unclear].

to my Mother

and in memory of my Father

The author would like to thank the [unclear] Foundation and the [unclear] [unclear] Foundation for financial support.

Dr. William C. [unclear]
December 1971

ACKNOWLEDGEMENTS

The author is indebted to Dr. Alan H. Cowley for his supervision of this study. Not only his capabilities as a mentor are appreciated but also his fine qualities as a person. Gratitude is also extended to Drs. A. Keith Jameson and Cynthia J. Jameson for their encouragement and suggestions regarding this work. The helpful discussions with the members of our research group are also acknowledged. For his help in many ways, the author would like to thank her husband William G. Padolina. The author is grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support.

Ma. Cristina D. Padolina

November 1971

shifts have also been measured but these
provide A STUDY OF THE DONOR-ACCEPTOR BOND
of the P-B bond. The IN coordination chem
are interpreted PHOSPHINE-BORANE COMPLEXES

Publication No. ___

Ma. Cristina Casabar Damasco Padolina, Ph.D.
The University of Texas at Austin, 1971

Supervising Professor: Alan H. Cowley

borane moiety suggests that the amount of charge transferred to this unit is proportional to the basicity of the phosphine.
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 phosphines toward BH_3 has been established on the basis of selected base displacement reactions. The observed sequence of phosphine base strengths and J_{PB} 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 and dative π -bonding from the phosphine substituents. Similarly, the ^{11}B - ^1H coupling constant data do not discriminate between the sigma-bonding and borane hyperconjugative models. Several ^{31}P and ^{11}B chemical

shifts have also been measured but these data do not provide definitive information concerning the nature of the P-B bond. The ^{31}P coordination chemical shifts are interpreted in terms of changes in the paramagnetic and diamagnetic contributions. It is noted that the trends in the coordination chemical shifts for the complexation of phosphines with the borane unit is similar to that observed for the isoelectronic oxygen atom. The general trend of the ^1H chemical shifts of the borane moiety suggests that the amount of charge transferred to this unit is proportional to the basicity of the phosphine.

(a) The ^{31}P - ^{11}B Coupling Constant	24
(b) The ^{11}B - ^1H Coupling Constant	35
(c) Miscellaneous Coupling Constants	38
B. Chemical Shifts	39
(a) ^{31}P Chemical Shifts	39
(b) ^{11}B Chemical Shifts	40
(c) ^1H Chemical Shifts	40
V. SUMMARY	41
REFERENCES	42
VITA	43

LIST OF TABLES
TABLE OF CONTENTS

		PAGE
I.	INTRODUCTION	1
II.	EXPERIMENTAL	10
III.	A. Materials	10
	B. Homogeneous Base Displacement Reactions	12
	C. Spectroscopy Measurements	16
III.	RESULTS	18
IV.	DISCUSSION	24
	A. Coupling Constants	24
	(a) The ^{31}P - ^{11}B Coupling Constant	24
	(b) The ^{11}B - ^1H Coupling Constant	35
	(c) Miscellaneous Coupling Constants.	38
	B. Chemical Shifts	39
	(a) ^{31}P Chemical Shifts	40
	(b) ^{11}B Chemical Shifts	43
	(c) ^1H Chemical Shifts	44
V.	SUMMARY	45
	REFERENCES	47

VITA

LIST OF TABLES

TABLE		PAGE
I.	Volatility of $\text{CH}_3\text{OPF}_2\text{BH}_3$	13
II.	Volatility of $(\text{CH}_3\text{O})_2\text{PFBH}_3$	14
III.	^{11}B - ^1H Coupling Constant, ^1H Chemical Shift, ^{11}B Chemical Shift and Miscellaneous Coupling Constant Data for Phosphine-Borane Complexes	21
IV.	^{31}P - ^{11}B Coupling Constant Data for Phosphine-Borane Complexes	22
V.	^{31}P Chemical Shift Data for Phosphines and Phosphine-Borane Complexes	23
VI.	^{11}B - ^1H Coupling Constant	36

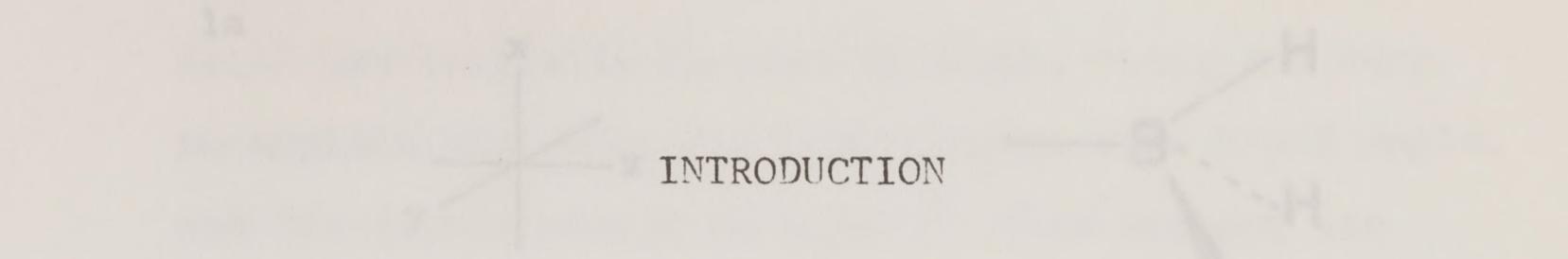
LIST OF FIGURES

FIGURE	INTRODUCTION	PAGE
1.	Borane hyperconjugative model	2
2.	(a) The nickel to carbon π bond in $\text{Ni}(\text{CO})_4$; (b) The boron to carbon π bond in H_3BCO	6
3.	Nmr spectra of a neat liquid sample of $\text{CH}_3\text{OPF}_2\text{BH}_3$	20

(11) The P-B dative sigma bond is supplemented by a π -type interaction between the B-B bonding electrons and the phosphorus $3d$ orbitals² as illustrated in Figure 1. The other model considers only sigma bonding and relates the Lewis acid-base interaction energy to the field strength of the Lewis acid and the dipole moment and polarizability of the lone pair of electrons of the Lewis base.

The delocalization of the B-B bonding electrons in the BH_2 group into low-lying empty orbitals of π symmetry of the Lewis base to which it is coordi-

²Recently calculated valence shell ionization potential data indicate that for neutral species the $3d$ and $4p$ orbitals are very close in energy. Consequently, $2p\pi-4p\pi$ bonding may be as important as $2p\pi-3d\pi$ bonding.



INTRODUCTION

Two bonding models have been proposed to explain the nature of the coordination bond in complexes between phosphorus Lewis bases and the Lewis acid borane, BH_3 : (i) the borane hyperconjugative model and (ii) the sigma bonding model. In the first hypothesis the P-B dative sigma bond is supplemented by a π -type interaction between the B-H bonding electrons and the phosphorus $3d$ orbitals* as illustrated in Figure 1. The other model considers only sigma bonding and relates the Lewis acid-base interaction energy to the field strength of the Lewis acid and the dipole moment and polarizability of the lone pair of electrons of the Lewis base.

The delocalization of the B-H bonding electrons in the BH_3 group into low-lying empty orbitals of π symmetry of the Lewis base to which it is coordi-

*Recently calculated valence shell ionization potential data indicate that for neutral species the $3d$ and $4p$ orbitals are very close in energy.¹ Consequently, $2p\pi-4p\pi$ bonding may be as important as $2p\pi-3d\pi$ bonding.

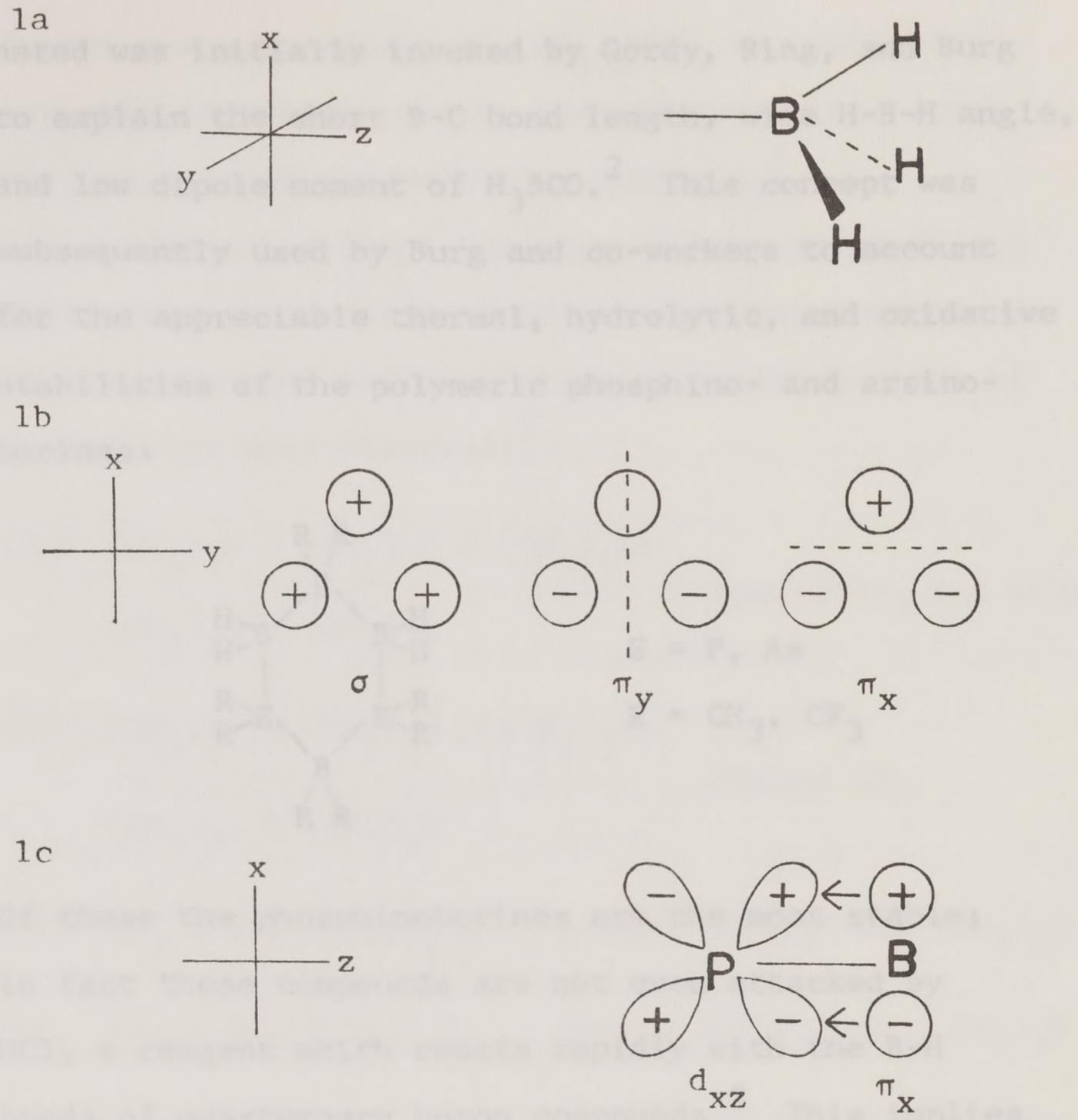
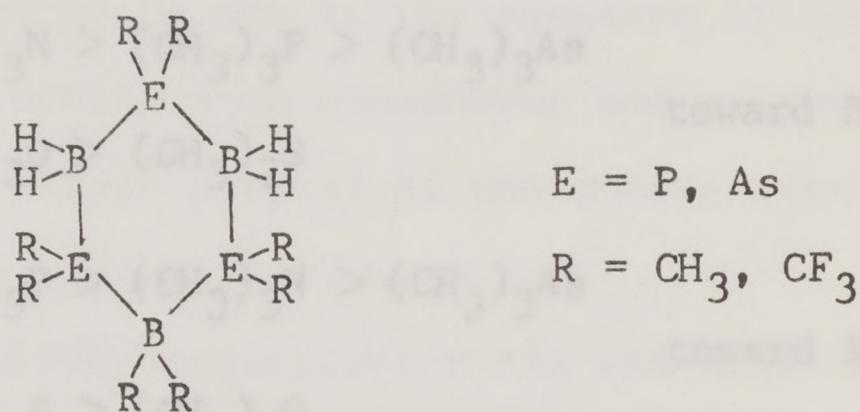


Figure 1.-Borane hyperconjugative model

(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.

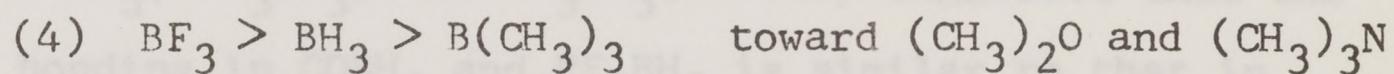
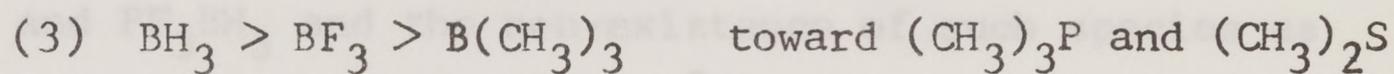
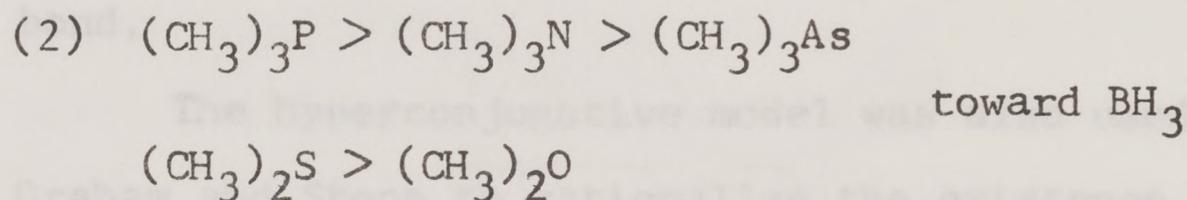
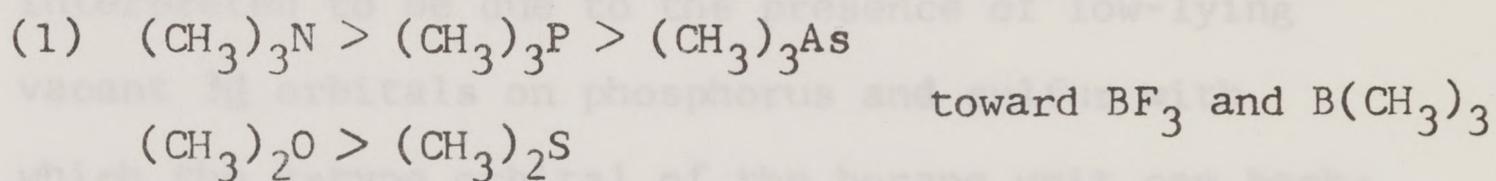
nated was initially invoked by Gordy, Ring, and Burg to explain the short B-C bond length, wide H-B-H angle, and low dipole moment of H_3BCO .² This concept was subsequently used by Burg and co-workers to account for the appreciable thermal, hydrolytic, and oxidative stabilities of the polymeric phosphino- and arsino-borines:



Of these the phosphinoborines are the most stable; in fact these compounds are not even attacked by HCl, a reagent which reacts rapidly with the B-H bonds of quaternary boron compounds.³ This implies that the borane hydrogen atoms in these polymers are not hydridic and thus suggests that charge has been transferred from the B-H bonding electrons to the phosphorus orbitals of π symmetry. Arsinoborine polymers are less stable and easier to hydrolyze than their phosphorus analogues presumably due to less effective overlap of the π -type orbital of the borane group with the 4d orbitals of arsenic.⁴

Furthermore, the dimer of $(\text{CH}_3)_2\text{NBH}_2$ is easily dissociable apparently due to lack of low-lying acceptor orbitals of π symmetry on nitrogen.³

Graham and Stone interpreted base strength and acid strength reversals from the standpoint of borane hyperconjugation and the following relative order of stabilities were observed:⁵



In terms of the classical coordinate bond the electron donating ability of Group VA and Group VIA bases decreases with increasing atomic size. The order of stabilities which are found in (1) illustrate this trend. However, toward the Lewis acid borane a reversal in base strength is observed as indicated in (2). This was attributed to the ability of the borane moiety to form a supplementary π bond when it coordinates with a Lewis base with suitable vacant π acceptor

orbitals, e.g. $(\text{CH}_3)_3\text{P}$ and $(\text{CH}_3)_2\text{S}$. If only electronegativity effects of the substituents on the Lewis acid are taken into consideration, BF_3 should be a better electron pair acceptor than BH_3 . The orders of stability in (3) and (4) show that this is indeed the case toward $(\text{CH}_3)_2\text{O}$ but toward the bases $(\text{CH}_3)_3\text{P}$ and $(\text{CH}_3)_2\text{S}$ the order is reversed. This was again interpreted to be due to the presence of low-lying vacant $3d$ orbitals on phosphorus and sulfur with which the π -type orbital of the borane unit can back-bond.

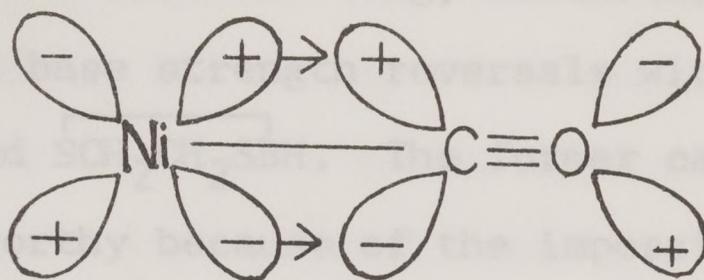
The hyperconjugative model was also used by Graham and Stone to rationalize the existence of COBH_3 and PF_3BH_3 and the non-existence of such species as COBF_3 , PF_3BF_3 , and NF_3BH_3 .⁵ They suggested that the bonding in COBH_3 and PF_3BH_3 is similar to that in $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{PF}_3)_4$ where the bonding is believed to be multiple in character. The analogy is illustrated in Figure 2.

The higher B-H stretching frequency in $(\text{CH}_3)_2\text{SBH}_3$ compared to $(\text{CH}_3)_2\text{OBH}_3$ and in $(\text{CH}_3)_3\text{PBH}_3$ compared to $(\text{CH}_3)_3\text{NBH}_3$ were also considered to offer support for the concept of back-bonding.⁶ The higher frequency was attributed to a smaller amount of charge transferred to boron when it is able to back-bond with

available orbitals on the Lewis base.

The sigma bonding model gained considerable support from the work of Young, McArdrae, and Shore,⁷

They observed that the ν_{C-O} frequency increases on the Lewis acids BCl_3 and SO_2 . This case is particularly noteworthy because the large increase in ν_{C-O} is not due to a hyperconjugative interaction. Furthermore, it was noted that the B-H stretching frequency is lower in $\overline{SO_2CH_2SBHP(CH_3)_3}$ than in $\overline{SO_2CH_2SBH(CH_3)_3}$. It was also pointed out that the $^{13}C-^{1}H$ coupling constant in the phosphine and in the sulfide and

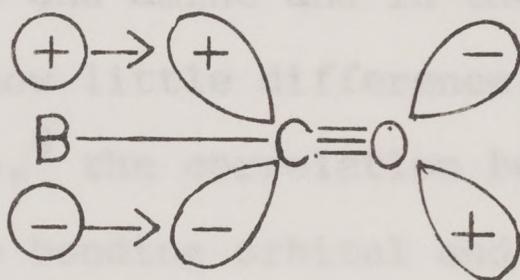


(a)

oxide adducts are different. If, as in $^{13}C-^{1}H$ coupling, the interaction between the $2p$ character in the sp^3 orbital and the magnitude of the coupling constant is important (e.g. the Fermi contact term is dominant) this would suggest that the hybridization of boron is the same in these com-

plexes. Figure 2.- (a) the nickel to carbon π bond

in $Ni(CO)_4$; (b) the boron to carbon π bond in H_3BCO .



(b)

plexes. Figure 2.- (a) the nickel to carbon π bond in $Ni(CO)_4$; (b) the boron to carbon π bond in H_3BCO .

Figure 2.- (a) the nickel to carbon π bond in $Ni(CO)_4$; (b) the boron to carbon π bond in H_3BCO .

placement of electronegative substituents on phosphorus should enhance back donation from the BH_3 moiety as a consequence of the lowering of the energy of and contracting the $P(3p)$ orbitals. Thus the order of basicity would be $PF_3 > PF_2H > PH_3$. However, on the basis of base competition reactions Rudolph and

suitable orbitals on the Lewis base.

The sigma bonding model gained considerable support from the work of Young, McAchran, and Shore,⁷ They observed base strength reversals with the Lewis acids BCl_3 and $\overline{\text{SCH}_2\text{CH}_2\text{SBH}}$. The former case is particularly noteworthy because of the impossibility of B-H hyperconjugative interaction. Furthermore, it was noted that the B-H stretching frequency is lower in $\overline{\text{SCH}_2\text{CH}_2\text{SBHP}(\text{CH}_3)_3}$ than in $\overline{\text{SCH}_2\text{CH}_2\text{SBHN}(\text{CH}_3)_3}$. It was also pointed out that the $^{11}\text{B}-^1\text{H}$ coupling constant in the phosphine and amine and in the sulfide and oxide adducts show little difference. If, as in $^{13}\text{C}-^1\text{H}$ couplings,⁸ the correlation between the $2s$ character in the bonding orbital and the magnitude of the coupling constant is valid (i.e. the Fermi contact term is dominant) this would suggest that the hybridization of boron is the same in these complexes.

On the basis of hyperconjugative effects, the placement of electronegative substituents on phosphorus should enhance back donation from the BH_3 moiety as a consequence of the lowering of the energy of and contracting the $\text{P}(3d)$ orbitals. Thus the order of basicity would be $\text{PF}_3 > \text{PF}_2\text{H} > \text{PH}_3$. However, on the basis of base competition reactions Rudolph and

Parry showed that the order is actually $\text{PF}_2\text{H} > \text{PF}_3 > \text{PH}_3$.⁹ To account for this observation they proposed a polarization model which relates the acid-base interaction energy (E) to the field strength of the Lewis acid (F), the dipole moment (ρ), and polarizability (α) of the lone pair of electrons of the Lewis base as indicated by equation (1).

$$E = F(\rho + F\alpha/2) \quad (1)$$

From the above-mentioned studies it is apparent that the nature of the phosphorus-boron bond in phosphine-boranes remains a subject of controversy. In the present work nuclear spin coupling constant and chemical shift data have been secured for several phosphine-boranes in an effort to provide additional understanding of the P-B linkage. Nuclear magnetic resonance spectroscopy is an excellent probe for the electronic structure of a molecule. Furthermore, both the ^{31}P and ^{11}B nuclei are suitable for nmr experiments and in many of the phosphine-boranes all the nuclei are nmr active. It was thus anticipated that the trends in these data might serve as additional experimental tests of the relative merits of the two P-B bonding models. Base displacement studies were also undertaken with the view of

correlating nmr data with the stability of the complexes.

EXPERIMENTAL

All reactions and operations involving the phosphine-boranes were carried out under inert atmosphere or in a standard high vacuum manifold. Vapor pressure measurements were made in an isopiestic tensimeter and molecular weights were determined with the same apparatus by the vapor tension method.

A. Materials

Triethylphosphite, PH_3 , and PF_3 were procured commercially and used without subsequent purification. The phosphines $\text{C}_6\text{H}_5\text{PH}_2$,¹⁰ PF_2 ,¹¹ $(\text{CH}_3)_2\text{PH}$,¹² $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$,¹³ $(\text{CH}_3)_3\text{P}$,¹⁴ $(\text{CH}_3)_2\text{NPF}_2$,¹⁵ $[(\text{CH}_3)_2\text{N}]_2\text{PF}$,¹⁵ $[(\text{CH}_3)_2\text{N}]_3\text{P}$,¹⁵ CH_3OPF_2 ,¹⁷ and $(\text{CH}_3)_3\text{PF}$ ¹⁸ were prepared and purified according to published methods. The compound CF_3PE_2 was made by the action of SBF_3 on CF_3PI_2 using a similar procedure to the one described for the preparation of $(\text{CF}_3)_2\text{PI}$.¹⁹ CF_3PI_2 phosphine was prepared by the PCl_5 reaction of commercially available diethyl phosphite. The preparation followed a very similar procedure to that described by Burrows and Cole¹⁹ for the preparation of

EXPERIMENTAL

All reactions and operations involving the phosphine-boranes were carried out under inert atmosphere or in a standard high vacuum manifold. Vapor pressure measurements were made in an immovable tensimeter and molecular weights were determined with the same apparatus by the vapor tension method.

A. Materials

Trimethylphosphite, PH_3 , and PF_3 were procured commercially and used without subsequent purification. The phosphines $\text{C}_6\text{H}_5\text{PH}_2$,¹⁰ PHF_2 ,¹¹ $(\text{CH}_3)_2\text{PH}$,¹² $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$,¹³ $(\text{CH}_3)_3\text{P}$,¹⁴ $(\text{CH}_3)_2\text{NPF}_2$,¹⁵ $[(\text{CH}_3)_2\text{N}]_2\text{PF}$,¹⁵ $[(\text{CH}_3)_2\text{N}]_3\text{P}$,¹⁶ CH_3OPF_2 ,¹⁷ and $(\text{CH}_3)_2\text{PF}$ ¹⁸ 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 for the preparation of $(\text{CF}_3)_2\text{PF}$.¹⁹ Methylphosphine was prepared by the LiAlH_4 reduction of commercially available dimethyl methylphosphonate following a very similar procedure to that described by Hatfield and Yoke²⁰ for the preparation of

$C_2H_5PH_2$. The crude CH_3PH_2 was purified by high vacuum fractional condensation with U-traps held at -100° , -144° , and -196° ; the pure phosphine condensed in the -144° trap. Diborane was prepared by the action of $LiAlH_4$ on $(C_2H_5)_2OBF_3$.²¹ Unless otherwise stated 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° to ambient temperature in evacuated sealed tubes. Purification was effected by high vacuum fractional condensation until the vapor tension, ir, and nmr spectra conformed to the literature specifications. The syntheses of $CF_3PF_2BH_3$ ²² and PF_3BH_3 ²³ 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.

$CH_3OPF_2BH_3$. A mixture of 2.0 mmoles CH_3OPF_2 and 1.1 mmoles B_2H_6 in a sealed tube was allowed to warm from -196° to ambient temperature overnight. High vacuum fractionation of the volatiles through U-traps held at -110° and -196° resulted in the condensation of 1.9 mmoles $CH_3OPF_2BH_3$ in the -110° trap. The vapor phase ir spectrum of the complex consisted of C-H stretching modes at 2976 and 2856 cm^{-1} ,

B-H stretching at 2406 cm^{-1} , C-O and P-O stretching at 1207 , 1102 , and 1206 cm^{-1} , and P-F stretching at 924 , 903 (shoulder), 895 (shoulder), and 842 cm^{-1} . The observed vapor phase molecular weight was 114.5 compared to a theoretical value of 113.8 . The volatility data for $\text{CH}_3\text{OPF}_2\text{BH}_3$ are shown in Table I.

$(\text{CH}_3\text{O})_2\text{PF}_2\text{BH}_3$. This complex was prepared similarly and in a comparable yield by the reaction of 2.0 mmoles $(\text{CH}_3\text{O})_2\text{PF}$ and 1.1 mmoles B_2H_6 . The adduct trapped out at -55° and the vapor phase ir spectrum consisted 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 molecular weight was 123.7 compared to the calculated value of 125.8 . The volatility data for $(\text{CH}_3\text{O})_2\text{PF}$ are shown in Table II.

B. Homogeneous Base Displacement Reactions

(a) The Reaction of $(\text{CH}_3)_2\text{NPF}_2$ With $\text{CH}_3\text{OPF}_2\text{BH}_3$. A mixture of 1.92 mmoles $\text{CH}_3\text{OPF}_2\text{BH}_3$ and 3.3 mmoles $(\text{CH}_3)_2\text{NPF}_2$ was condensed in an evacuated tube at -196° . The tube was sealed and allowed to warm slowly to -78° . After standing at -78° for 15 hrs followed by standing at 0° for 73 hrs the tube was opened

Table I

Volatility of $\text{CH}_3\text{OPF}_2\text{BH}_3$

Temp, °C	P(obsd), mm Hg	P(calcd), mm Hg
5.45	75.70	76.86
9.95	94.40	94.29
16.60	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

$$\log P_{\text{mm}} = 7.4694 - 1555.7/T$$

$$t_{760} = 65.67^\circ ; \text{ Trouton constant} = 24.75 \text{ eu}$$

$$\log P_{\text{mm}} = 8.3019 - 2212.2/T$$

$$t_{760} = 134.92^\circ ; \text{ Trouton constant} = 24.79 \text{ eu}$$

to the vacuum line. Table II Volatility of $(\text{CH}_3\text{O})_2\text{PFBH}_3$ and -196° .

Temp, $^\circ\text{C}$	P(obsd), mm Hg	P(calcd), mm Hg
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

Table V. A mixture of 2.0 moles $\text{CH}_3\text{PH}_2\text{BH}_3$ and 1.26 moles $(\text{CH}_3\text{O})_2\text{P}$ was sealed in vacuum in an evacuated tube at -196° . The tube was allowed to warm gradually

$$\log P_{\text{mm}} = 8.3019 - 2212.2/T$$

$$t_{760} = 134.92^\circ ; \text{ Trouton constant} = 24.79 \text{ eu}$$

to 0° and was kept at this temperature for 40 hrs. At the end of this period the resonance at -140 ppm, which corresponds to uncomplexed $(\text{CH}_3\text{O})_2\text{P}$, was not detectable, and a resonance was observed at -118 ppm which is attributable to $(\text{CH}_3\text{O})_2\text{PFBH}_3$.

Similarly a mixture of 1.0 mmole PF_3BH_3 and 1.0 mmole CH_3PH_2 was sealed in an evacuated nmr tube at -196° . After slowly warming the tube to -40° it was allowed to stand at this temperature for 46 hrs. Visual estimation of the relative intensities of the

to the vacuum line 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 mmoles CH_3OPF_2 . The -50° trap contained 1.34 mmoles of $(\text{CH}_3)_2\text{NPF}_2\text{BH}_3$ and the -112° trap contained the remainder of the $(\text{CH}_3)_2\text{NPF}_2\text{BH}_3$ and 1.41 mmoles $(\text{CH}_3)_2\text{NPF}_2$.

(b) The Reaction of $\text{CH}_3\text{PH}_2\text{BH}_3$ With $(\text{CH}_3\text{O})_3\text{P}$ and the Reaction of PF_3BH_3 With CH_3PH_2 . The progress of these reactions was followed by the ^{31}P nmr spectra of the mixtures. The chemical shifts of the free and complexed phosphines are presented later in Table V. A mixture of 2.0 mmoles $\text{CH}_3\text{PH}_2\text{BH}_3$ and 1.26 mmoles $(\text{CH}_3\text{O})_3\text{P}$ 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 hrs. At the end of this period the resonance at -140 ppm, which corresponds to uncomplexed $(\text{CH}_3\text{O})_3\text{P}$, was not detectable, and a resonance was observed at -118 ppm which is attributable to $(\text{CH}_3\text{O})_3\text{PBH}_3$.

Similarly a mixture of 1.0 mmole PF_3BH_3 and 1.0 mmole CH_3PH_2 was sealed in an evacuated nmr tube at -196° . After slowly warming the tube to -40° it was allowed to stand at this temperature for 46 hrs. Visual estimation of the relative intensities of the

^{31}P resonances indicated that the equilibrium mixture contained 0.6 mmole each of $\text{CH}_3\text{PH}_2\text{BH}_3$ and PF_3 , and 0.4 mmole each of PF_3BH_3 and CH_3PH_2 .

C. Spectroscopy Measurements

(a) Nmr Spectra. Most of the ambient temperature 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), ^{19}F (94.1 MHz) spectra were recorded on a Varian Associates HA-100 spectrometer; the chemical shifts are relative to sealed capillaries of $(\text{CH}_3\text{O})_3\text{B}$, 85% H_3PO_4 , and α,α,α -trifluorotoluene respectively.

The sample of PH_3BH_3 was prepared in situ as described previously.²⁴ The adduct of $[(\text{CH}_3)_2\text{N}]_3\text{PBH}_3$ was prepared 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 tubes were sealed at -196° and allowed to warm

slowly to ambient temperature. The nmr spectra of PH_3BH_3 and $[(\text{CH}_3)_2\text{N}]_3\text{PBH}_3$ were run in the molten state. A similar procedure was employed in the preparation of the non-volatile liquid adducts $(\text{CH}_3\text{O})_3\text{PBH}_3$, $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{PBH}_3$, and $(\text{C}_6\text{H}_5)_2\text{PHBH}_3$. The sample of $(\text{CH}_3)_3\text{PBH}_3$ was also prepared in a similar manner except that it was necessary to add benzene as solvent. The other borane adducts are volatile and the samples were prepared by condensing the pure compounds in the nmr tubes and sealing them in vacuo at -196° .

(b) Infrared Spectra. All ir spectra were measured on a Perkin-Elmer Model 337 grating spectrometer.

The spectra consist of four equally intense resonances due to the $^{11}\text{B}-^1\text{H}$ coupling, each component of which is further split into a doublet by $^{31}\text{P}-\text{B}-^1\text{H}$ coupling. In some cases, e.g. $(\text{CH}_3\text{O})_3\text{PBH}_3$ (Figure 3a) other couplings such as $^{19}\text{F}-\text{P}-\text{B}-^1\text{H}$ are also evident. Unresolved $^{10}\text{B}-^1\text{H}$ coupling is sometimes evident in the base line.

The $^{31}\text{P}-^{11}\text{B}$ coupling constant data (Table IV) and ^{11}B chemical shift data (Table III) were obtained from the ^{11}B spectra. Most of the spectra (e.g. Figure 3c) consist of a quartet due to $^{11}\text{B}-^1\text{H}$ coupling, each component being further split into a doublet by $^{31}\text{P}-^{11}\text{B}$ coupling. However, in the adducts

RESULTS

All of the spectra of the phosphine-boranes considered here are first order at 23,000 gauss field strength, hence the coupling constant and chemical shift data were readily obtained from the recorded spectral traces. Representative spectra are shown in Figure 3 for the adduct $\text{CH}_3\text{OPF}_2\text{BH}_3$. The $^{11}\text{B}-^1\text{H}$ coupling constant and chemical shift data which are presented in Table III were obtained from the proton spectra of the >P-BH_3 moiety. Typically, these spectra consist of four equally intense resonances due to the $^{11}\text{B}-^1\text{H}$ coupling, each component of which is further split into a doublet by $^{31}\text{P-B}-^1\text{H}$ coupling. In some cases, e.g. $\text{CH}_3\text{OPF}_2\text{BH}_3$ (Figure 3a) other couplings such as $^{19}\text{F-P-B}-^1\text{H}$ are also evident. Unresolved $^{10}\text{B}-^1\text{H}$ coupling is sometimes evident in the base line.

The $^{31}\text{P}-^{11}\text{B}$ coupling constant data (Table IV) and ^{11}B chemical shift data (Table III) were obtained from the ^{11}B spectra. Most of the spectra (e.g. Figure 3c) consist of a quartet due to $^{11}\text{B}-^1\text{H}$ coupling, each component being further split into a doublet by $^{31}\text{P}-^{11}\text{B}$ coupling. However, in the adducts

$(\text{CH}_3\text{O})_3\text{PBH}_3$, $[(\text{CH}_3)_2\text{N}]_3\text{PBH}_3$, and $(\text{CH}_3\text{O})_2\text{PFBH}_3$, the ^{31}P - ^{11}B and ^{11}B - ^1H 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 3d) hence these spectra were used only 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 3. -Nmr spectra of a neat liquid sample of $(\text{CH}_3\text{O})_3\text{PBH}_3$.

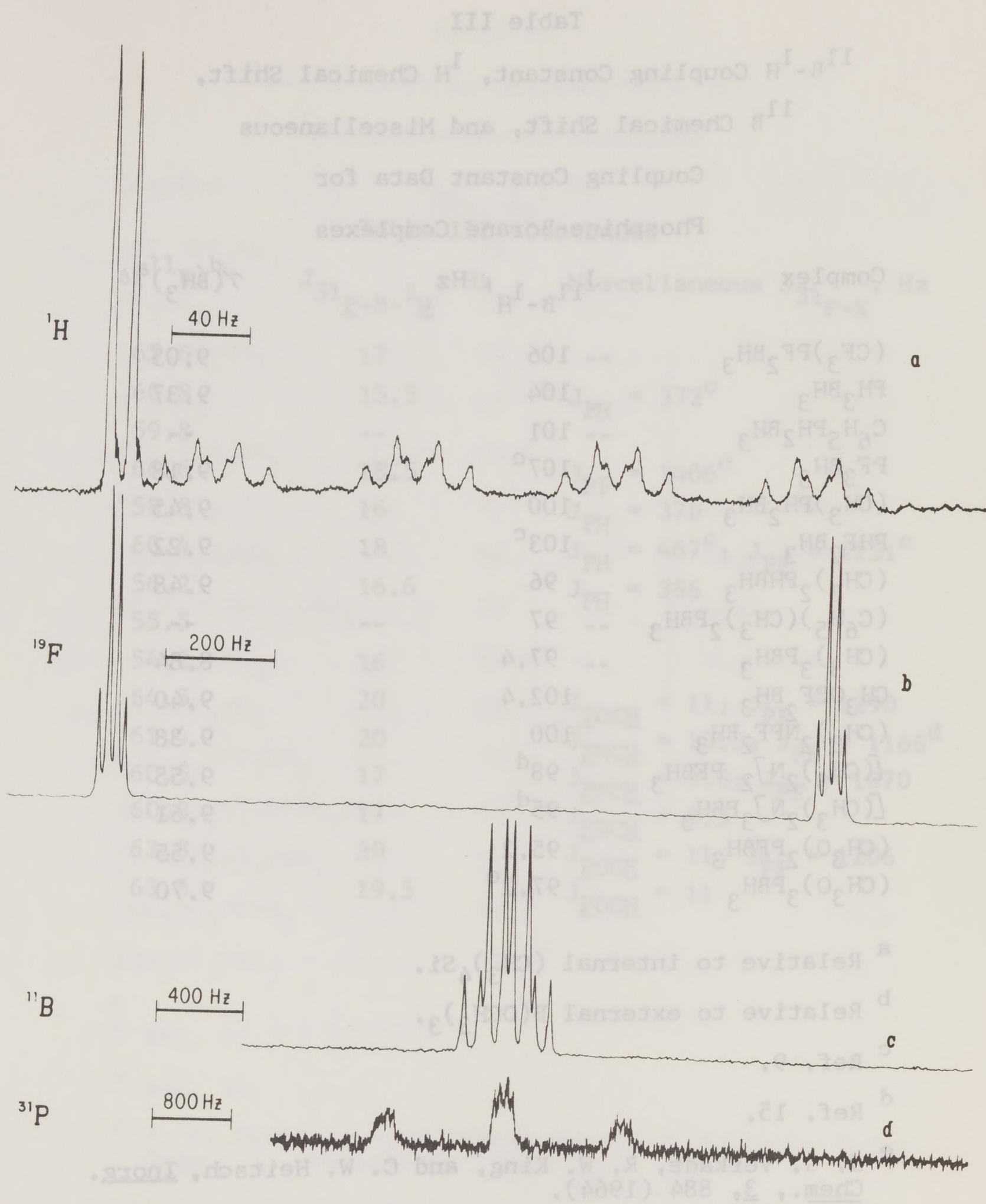


Figure 3.-Nmr spectra of a neat liquid sample of $\text{CH}_3\text{OPF}_2\text{BH}_3$

Table III

^{11}B - ^1H Coupling Constant, ^1H Chemical Shift,
 ^{11}B Chemical Shift, and Miscellaneous
 Coupling Constant Data for
 Phosphine-Borane Complexes

Complex	$J_{^{11}\text{B}-^1\text{H}}$, Hz	$\tau(\text{BH}_3)^a$
$(\text{CF}_3)\text{PF}_2\text{BH}_3$	106	9.05
PH_3BH_3	104	9.37
$\text{C}_6\text{H}_5\text{PH}_2\text{BH}_3$	101	--
PF_3BH_3	107 ^c	9.18
$(\text{CH}_3)\text{PH}_2\text{BH}_3$	100	9.45
PHF_2BH_3	103 ^c	9.22
$(\text{CH}_3)_2\text{PHBH}_3$	96	9.48
$(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{PBH}_3$	97	--
$(\text{CH}_3)_3\text{PBH}_3$	97.4	8.84
$\text{CH}_3\text{OPF}_2\text{BH}_3$	102.4	9.40
$(\text{CH}_3)_2\text{NPF}_2\text{BH}_3$	100	9.38
$[(\text{CH}_3)_2\text{N}]_2\text{PFBH}_3$	98 ^d	9.55
$[(\text{CH}_3)_2\text{N}]_3\text{PBH}_3$	95 ^d	9.61
$(\text{CH}_3\text{O})_2\text{PFBH}_3$	95.2	9.55
$(\text{CH}_3\text{O})_3\text{PBH}_3$	97.2 ^e	9.70

^a Relative to internal $(\text{CH}_3)_4\text{Si}$.

^b Relative to external $\text{B}(\text{OCH}_3)_3$.

^c Ref. 9.

^d Ref. 15.

^e J. G. Verkade, R. W. King, and C. W. Heitsch, Inorg. Chem., **3**, 884 (1964).

Figure 3.-Nmr spectra of a neat liquid sample of $\text{CH}_3\text{OPF}_2\text{BH}_3$

Table III--Continued

$\delta(^{11}\text{B})^b$	$J_{^{31}\text{P-B-}^1\text{H}}$, Hz	Miscellaneous $J_{^{31}\text{P-X}}$, Hz
65.6	17	--
60.8	15.5	$J_{\text{PH}} = 372^c$
59.8	--	--
66.6	18.5	$J_{\text{PF}} = 1406^c$
58.8	16	$J_{\text{PH}} = 370$
60.4	18	$J_{\text{PH}} = 467^c$; $J_{\text{PF}} = 1151^c$
56.2	16.6	$J_{\text{PH}} = 366$
55.5	--	--
54.2	16	--
64.5	20	$J_{\text{POCH}} = 11$; $J_{\text{PF}} = 1290$
61.4	20	$J_{\text{PNCH}} = 10.5$; $J_{\text{PF}} = 1166^d$
60.5	17	$J_{\text{PNCH}} = 9.8$; $J_{\text{PF}} = 1070$
60.8	17	$J_{\text{PNCH}} = 9.5$
63.8	20	$J_{\text{POCH}} = 11$; $J_{\text{PF}} = 1206$
63.8	19.5	$J_{\text{POCH}} = 11$

^a Ref. 9.

^b Ref. 15.

^c J. G. Verkade, R. W. King, and C. W. Miller, *J. Am. Chem. Soc.*, **86**, 884 (1964).

Table IV

 ^{31}P - ^{11}B Coupling Constant Data for
Phosphine-Borane Complexes

Complex	$J_{^{31}\text{P}-^{11}\text{B}}$, Hz	Coordination Chemical Shift ^a
$(\text{CF}_3)\text{PF}_2\text{BH}_3$	18	-133
PH_3BH_3	27 ^a	-95
$\text{C}_6\text{H}_5\text{PH}_2\text{BH}_3$	35	-74.2
PF_3BH_3	39 ^a	-67.7
$(\text{CH}_3)\text{PH}_2\text{BH}_3$	43.5	-61
PHF_2BH_3	49 ^a	-49
$(\text{CH}_3)_2\text{PHBH}_3$	58	-107 ^b
$(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{PBH}_3$	59	-108.5
$(\text{CH}_3)_3\text{PBH}_3$	59.8	-102.5
$\text{CH}_3\text{OPF}_2\text{BH}_3$	68.2	-118.7
$(\text{CH}_3)_2\text{NPF}_2\text{BH}_3$	79 ^b	-118 ^c
$[(\text{CH}_3)_2\text{N}]_2\text{PFBH}_3$	86 ^b	-130 ^c
$[(\text{CH}_3)_2\text{N}]_3\text{PBH}_3$	95	-130 ^c
$(\text{CH}_3\text{O})_2\text{PFBH}_3$	96.2	-132.5
$(\text{CH}_3\text{O})_3\text{PBH}_3$	97.2 ^c	-133

↑
 Increasing
 coordinate
 bond
 strength
 ↓

^a Ref. 9.

^b Ref. 15.

^c J. G. Verkade, R. W. King, and C. W. Heitsch, Inorg. Chem., **3**, 884 (1964).

^d F. Ramirez, O. P. Madou, and C. P. Searcy, J. Organomet. Chem., **22**, 367 (1964).

^e J. G. Verkade, R. W. King, and C. W. Heitsch, Inorg. Chem., **3**, 881 (1964).

^f Ref. 15.

Table V

³¹P Chemical Shift Data for Phosphines and
Phosphine-Borane Complexes

Complex	δ free phosphine	δ complex	Coordination Chemical Shift ^a
PH ₃ BH ₃	246 ^b	113 ^b	-133
(CH ₃)PH ₂ BH ₃	163.5 ^c	68.5	-95
(C ₆ H ₅)PH ₂ BH ₃	123.5	49.3	-74.2
(CH ₃) ₂ PHBH ₃	98.5 ^c	30.8	-67.7
(CH ₃) ₃ PBH ₃	62.8	1.8	-61
(C ₆ H ₅)(CH ₃) ₂ PBH ₃	46	-49	-95
PF ₃ BH ₃	-105 ^b	-107 ^b	-2
CH ₃ OPF ₂ BH ₃	-111.8	-108.5	+3.3
[(CH ₃) ₂ N] ₃ PBH ₃	-122.5 ^d	-102.5	+20
(CH ₃ O) ₂ PFBH ₃	-131.6	-118.7	+12.9
(CH ₃ O) ₃ PBH ₃	-140 ^e	-118 ^e	+22
(CH ₃) ₂ NPF ₂ BH ₃	-143 ^f	-130 ^f	+13
[(CH ₃) ₂ N] ₂ PFBH ₃	-153 ^f	-134 ^f	+19
(CF ₃)PF ₂ BH ₃	-158.1	-148.5	+9.6
PF ₂ HBH ₃	-224 ^b	-171 ^b	+53

^a See ref. 45 for definition

^b Ref. 30

^c J. R. van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, J. Amer. Chem. Soc., **78**, 5715 (1956).

^d F. Ramirez, O. P. Madau, and C. P. Smith, Tetrahedron, **22**, 567 (1966).

^e J. G. Verkade, R. W. King, and C. W. Heitsch, Inorg. Chem., **3**, 884 (1964).

^f Ref. 15.

the sign of K_{pq} is the same as that of J_{pq} since the magnetogyric ratios of both nuclei are positive.

DISCUSSION

The nuclear spin-electron spin interaction for each atom is For convenience the coupling constant and chemical shift data are discussed separately.

A. Coupling Constant

(a) 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. When this work was initiated no information was available regarding the relative sign of this coupling constant. However, the following three arguments all indicate that this is positive: (1) The model of Jameson and Gutowsky²⁵ relates the sign of a directly bonded reduced coupling constant, K_{AB} , to the signs of the nuclear spin-electron spin interactions a_A and a_B for the coupled atoms A and B. (The reduced coupling constant K_{AB} ²⁶ which is related to the observed coupling constant J_{AB} by the equation

$$K_{AB} = \frac{2\pi}{h\gamma_A\gamma_B} J_{AB} \tag{2}$$

is dependent only on the molecular electronic structure. In the case of the P-B coupling constant,

the sign of K_{PB} is the same as that of J_{PB} since the magnetogyric ratios of both nuclei are positive.)

The nuclear spin-electron spin interaction for each atom is expressed as a sum of two terms

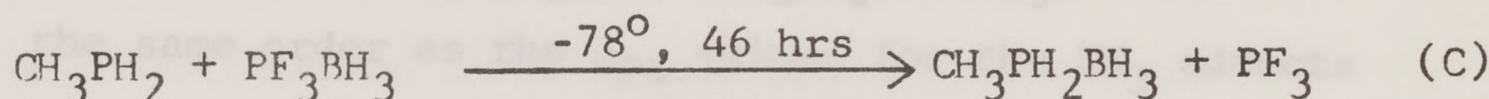
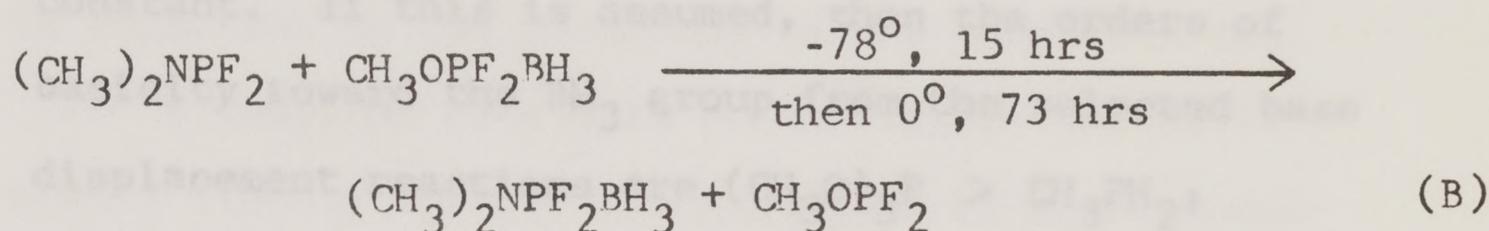
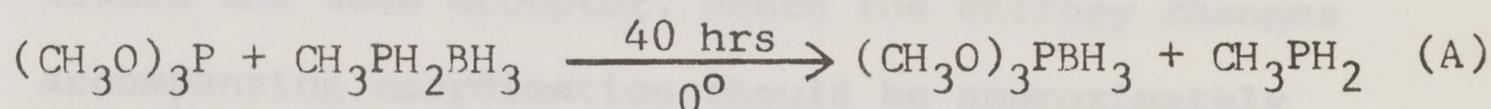
$$a_A = a_A^S + a_A(\text{core polarization}) \quad (3)$$

In this equation 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 $a_A(\text{core polarization})$ can take both positive and negative values. For an s orbital the core polarization term is positive, while for p , d , and f electrons $a_A(\text{core polarization})$ is usually negative. This means that if atoms A and B employ s electrons in the bond between them the $a_A(\text{core polarization})$ and $a_B(\text{core polarization})$ 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) the K_{PB} and J_{PB} are predicted to be positive. (ii) Using the theoretical approach described previously,²⁷ the contact contribution in the model compound PH_3BH_3 was calculated 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. (iii) The model of Schaefer and Yaris²⁸ 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 $^{31}\text{P}-^{11}\text{B}$ directly bonded coupling constant is predicted to be positive. Subsequently, Rudolph and Schultz²⁹ determined by spin tickling experiments that this coupling constant is in fact positive in the complexes $(\text{CH}_3)_3\text{PBF}_3$, $(\text{CH}_3)_2\text{NPF}_2\text{BH}_3$, $(\text{CH}_3)_3\text{PBH}_3$, and PF_2HBH_3 , thus supporting our original contention. In view of the foregoing arguments and experiments, the sign of J_{PB} will be taken to be 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 previously³⁰ in relation to the two series of bases PF_3 , PF_2H , and PH_3 and $(\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_2\text{PH}$, $(\text{CH}_3)\text{PH}_2$, and PH_3 . In the present work more extensive $^{31}\text{P}-^{11}\text{B}$ coupling constant data have been secured (Table IV) and in addition it has been possible to demonstrate by means of base displacement reactions that the correlation

between J_{PB} and phosphine basicity extends to the 15 bases considered. This conclusion is based on the results of the displacement reactions carried out with a pair of phosphines whose borane adduct J_{PB} values differed widely (Reaction A) and on two pairs of phosphines whose borane adduct J_{PB} values were closely similar (reactions B and C).



Reactions A and B proceed to completion in the directions indicated. Reaction C was approximately 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.³¹ A case which illustrates this point concerns the compounds $(\text{CH}_3)_3\text{NB}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{PB}(\text{CH}_3)_3$. The dissociation constants of these adducts at 100° are 0.472 and 0.182 respectively,

suggesting that the phosphine is the stronger base. However, the enthalpies of formation of $(\text{CH}_3)_3\text{NB}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{PB}(\text{CH}_3)_3$ are 17.6 and 16.5 kcal per mole respectively, thus indicating that in fact the N-B bond is stronger than the P-B bond. In this study however, the comparison is between the basicities of a series of structurally similar phosphines toward the same acceptor, hence 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 base displacement reactions are $(\text{CH}_3\text{O})_3\text{P} > \text{CH}_3\text{PH}_2$; $(\text{CH}_3)_2\text{NPF}_2 > \text{CH}_3\text{OPF}_2$; and $\text{CH}_3\text{PH}_2 > \text{PF}_3$. This is the same order as the J_{PB} values for the BH_3 adducts of these phosphines (Table IV). Together with Rudolph's observation³⁰ 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 phosphine, 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 the phosphine basicities indicated in Table IV is inconsistent with the borane hyperconjugative model for the following reasons: (i) On

the basis of the CO stretching force constants in metal carbonyl complexes, Barlow, Nixon, and Webster³² have established the following order of phosphine π acceptor ability: $\text{CF}_3\text{PF}_2 > \text{PF}_3 > \text{C}_6\text{H}_5\text{PF}_2 > \text{ROPF}_2 > \text{R}_2\text{NPF}_2$. A somewhat different order of π acceptor ability, *viz.* $\text{PF}_3 > (\text{CH}_3\text{O})_3\text{P} > [(\text{CH}_3)_2\text{N}]_3\text{P} > (\text{alkyl})_3\text{P}$ emerged from one interpretation of the trend of ^{31}P - ^{183}W coupling constants in tungsten-phosphine complexes.³³ If borane hyperconjugation is important in the phosphine-borane complexes the ^{31}P - ^{11}B coupling constants should follow the above orders closely because the placement of electronegative groups on phosphorus should facilitate BH_3 hyperconjugation by contracting and lowering the energy of the phosphorus $3d$ and $4p$ orbitals. In turn an increase in π bonding should lead to a synergic increase in the P-B dative 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. Furthermore, the hyperconjugative model would not predict that the J_{PB} of $\text{CF}_3\text{PF}_2\text{BH}_3$ would be the smallest of the couplings considered here. (ii) A second trend which

is inconsistent with the hyperconjugative model is the sequence of basicities $(\text{CH}_3)_3\text{P} > (\text{CH}_3)_2\text{PH} > \text{CH}_3\text{PH}_2 > \text{PH}_3$ toward the BH_3 group as inferred from the respective J_{PB} values. Significantly, this is the same order of basicity found by Brown and co-workers³⁴ found for reference acids $(\text{CH}_3)_3\text{B}$, BF_3 , and H^+ . Since there is no possibility of a π -type interaction with a proton, it is clear that the hyperconjugative effects are unimportant in sequencing the Lewis basicities of PH_3 and methylated phosphines. (iii) The order of basicity of the fluorophosphines toward BH_3 is $\text{PF}_2\text{H} > \text{PF}_3 > \text{PH}_3$. It has been pointed out by Rudolph and Parry¹¹ that the basicity (and ergo 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 ab initio SCF-MO calculations³⁵ 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 order of phosphine base strengths and J_{PB} values.

The effects of electronegative substituents

on the structure and physical properties of a molecule suggest that these substituents divert more s character toward the bonds which the central atom makes with other more electropositive groups.³⁶ Providing this so-called isovalent hybridization hypothesis is applicable to second-row elements, then increasing the electronegativity of the phosphine substituents should divert $P(3s)$ character into the P-B bond. The Fermi contact contribution to the coupling constant is a measure of the amount of s character of the bond between the two nuclei and this contribution is generally accepted to be dominant for directly bonded nuclei of the lighter atoms. Thus electronegative substituents should increase the P-B coupling constant. 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 sigma effects alone, opposing trends should exist between phosphine basicities and J_{PB} values. This contradicts the observation of a correlation between these two factors so that a pure sigma bonding model is also incapable of explaining all the data.

The other type of interaction which may be

significant in some 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. The importance of this type of interaction in aminophosphines has been suggested in a variety of structural, stereochemical, and basicity observations which indicate or suggest that the nitrogen atom is planar and essentially non-basic. For instance, the X-ray study³⁷ of $(CH_3)_2NPF_2$ which showed that the geometry around nitrogen is planar suggests that the lone pair of electrons on nitrogen is situated in a pure p orbital which has the ideal symmetry for back-bonding into the vacant $3d$ and $4p$ orbitals of phosphorus. Although the gas phase structure of the same molecule as obtained by electron diffraction showed a slight deviation of nitrogen from planarity, the P-N bond length is still considerably shorter than the normal single bond length which is still indicative of appreciable N-P π bonding in the gas phase. The P-N torsional barriers of several aminophosphines have also been ascribed to the partial double bond character of the P-N bond.³⁸ The decrease in basicity of nitrogen and the enhancement of the basicity of phosphorus in some aminophosphines has been attri-

buted also to P-N π bonding.³⁹ Similar evidence support the hypothesis of oxygen-phosphorus π bonding. A recent structure determination on CH_3OPF_2 indicates that the oxygen is sp^2 hybridized. The P-O-C bond angle is 123.5° . Furthermore, the P-O bond length of 1.569 \AA is quite short and is comparable to the length of the formal P-O double bond in $(\text{HO})_3\text{PO}$.⁴⁰ Dative π bonding may also be inferred from the Lewis base behavior of the caged phosphite $\text{P}(\text{OCH}_2)_3$ ⁴¹ since here the basicity of the phosphite end is greater than that of the phosphine end toward the acceptor BH_3 . Widely varying structural data⁴² for PF_3 have led to the differences in the interpretation of the nature of the P-F bond; however, ab initio SCF-MO calculations⁴³ on this molecule indicate significant F-P $p\pi-d\pi$ bonding.

The considerable evidence for dative π bonding from the nitrogen, oxygen, and fluorine $2p$ orbitals into the appropriate vacant phosphorus orbitals provide an understanding of the positioning of the six CH_3O - and $(\text{CH}_3)_2\text{N}$ - substituted phosphines at the high end of the J_{PB} and phosphine basicity order (Table IV). Apparently, this interaction enhances the electron donating ability of the phosphorus. A similar argument presumably obtains in

understanding the order of basicity of PF_3 and CF_3PF_2 toward BH_3 since dative π bonding is unlikely for the CF_3 moiety. However, this effect per se still does not explain all the aspects of the trends in the P-B coupling constants and adduct stabilities of the phosphine-boranes. For instance, if only this effect is significant PF_3 should be a strong Lewis base due to dative π bonding from fluorine to phosphorus. However, PF_3BH_3 has one of the weakest P-B bonds of the phosphine-boranes considered here.

To understand the observed trend it is necessary to invoke an interplay of the sigma effects and dative π bonding between phosphorus and its substituents. Thus the decrease in J_{PB} and phosphine basicity upon successive replacement of CH_3O - and $(\text{CH}_3)_2\text{N}$ - groups by fluorine is a reflection of the increased importance of sigma withdrawal, which diminishes basicity, compared to π donation which enhances basicity. Although fluorine is more electronegative than either the methoxyl or dimethylamino group, thus facilitating acceptor π bonding by lowering the energy of and contracting the phosphorus $3d$ and $4p$ orbitals, this same property of electronegativity is also responsible for the inductive withdrawal of electrons via the σ bonds. Apparently

the latter effect predominates in the case of fluorine. Thus PF_3 is understandably a weak base and CF_3PF_2 even weaker because the CF_3 group is electronegative and at the same time incapable of back-donating into the phosphorus π orbitals.

(b) The ^{11}B - ^1H Coupling Constant

The relative sign of the ^{11}B - ^1H coupling constant has not been related to that of the ^{13}C - ^1H coupling constant which is universally taken to be positive.⁸ However, in BF_2H the ^{11}B - ^1H and ^{11}B - ^{19}F signs were found⁴⁴ to be opposite, hence it may be assumed that the ^{11}B - ^1H coupling constant is absolute positive.

Borane hyperconjugative interactions might be expected to alter the electron density around boron and hence the ^{11}B - ^1H coupling constant in at least two ways: (i) the slight opening of the H-B-H angles should increase the percent $2s$ character in the bonding orbitals of boron; this in turn increases the ^{11}B - ^1H coupling constant and (ii) the diminution of J_{BH} by hyperconjugative delocalization of the B-H bonding electrons.

In Table VI the various phosphines are listed in descending order of π acceptor strength as established by Nixon and co-workers³² on the basis of the

Table VI
 $^{11}\text{B}-^1\text{H}$ Coupling Constant

Phosphine-Borane	$J_{^{11}\text{B}-^1\text{H}}$, Hz	
$\text{CF}_3\text{PF}_2\text{BH}_3$	106	 <p>Increasing π acceptor strength of uncomplexed phosphine^a</p>
PF_3BH_3	107	
$\text{C}_6\text{H}_5\text{PF}_2\text{BH}_3$	--	
$\text{CH}_3\text{OPF}_2\text{BH}_3$	102.4	
$(\text{CH}_3)_2\text{NPF}_2\text{BH}_3$	100	
$[(\text{CH}_3)_2\text{N}]_2\text{PFBH}_3$	98	
$(\text{CH}_3)_3\text{PBH}_3$	97.4	

^a See text and refs. 33 and 34.

CO stretching force constants of the phosphine-metal carbonyl complexes, the phosphine $(\text{CH}_3)_3\text{P}$ being an addendum to Nixon's list. Trialkyl phosphines have been found to be less effective π acceptors than any of the other phosphines in Table VI by Grim and collaborators.³³ The complex PH_3BH_3 ($J_{\text{BH}} = 104$ Hz) has not been included in Table VI because the π acceptor ability of phosphine 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.⁴⁵ It is noted that increases in the scalar $^{11}\text{B}-^1\text{H}$ coupling are paralleled by increases in the π acceptor strength of the phosphine. This could be interpreted as supportive of the borane hyperconjugative model with the implication that (i) 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 (ii) a smooth and monotonic relationship exists between J_{BH} and the percent $2s$ character in the B-H bonds; although such a relationship has not been established experimentally it is anticipated by analogy with the well-known $^{13}\text{C}-^1\text{H}$ case.⁸

The trend in the $^{11}\text{B}-^1\text{H}$ coupling constant, however, can be interpreted without invoking a π component in the phosphorus-boron bond arising from hyperconjugative interactions. It will be noted that with the exception of PH_3BH_3 the trend of $^{11}\text{B}-^1\text{H}$ couplings depends upon the electronegativity of the phosphorus substituents in the sense that placement of electronegative substituents on phosphorus leads to increases in J_{BH} . This could be anticipated from the standpoint of the isovalent hybridization hypothesis,³⁶ viz. in considering a structure XBH_3 , increasing the electronegativity of the X group diverts more $2s$ character into the B-H bonds and thereby increases the contact contribution to J_{BH} .

Thus the $^{11}\text{B}-^1\text{H}$ coupling constant data do not discriminate between the borane hyperconjugative model and sigma bonding hypothesis because the same trend is anticipated for either model. Dative π bonding from the lone pairs of the substituents on phosphorus due to vacant π acceptor orbitals on the latter is not anticipated to have a significant effect on the $^{11}\text{B}-^1\text{H}$ coupling constant because these substituents are quite remote.

(c) Miscellaneous Coupling Constants

The $^{31}\text{P}-^1\text{H}$ coupling constants of the complexed

primary and secondary phosphines (Table III) are about 175-225 Hz larger than those of the free phosphines.⁴⁶ Comparable increases in the ^{31}P - ^1H have been observed⁴⁷ 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 percent $3s$ 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 noted⁴⁷ when fluorophosphines coordinate to transition metal derivatives; this may reflect the importance of non-contact contributions to the ^{31}P - ^{19}F coupling constant.

B. Chemical Shifts

The chemical shifts of nuclei may be conveniently discussed in terms of three contributions,⁴⁸ viz.

$$\sigma = \sigma_d + \sigma_p + \sigma_o \quad (4)$$

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 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 distance.

(a) ^{31}P Chemical Shifts Apparently, the con-

The ^{31}P chemical shift data in Table V are listed in the order of decreasing (becoming more negative) chemical shift of the free phosphines.

A very notable feature of Table V is that the order of chemical shifts of the free phosphines remains essentially unchanged upon formation of the BH_3 adduct. This implies that the main contributors to the shielding of the ^{31}P nuclei in phosphine-boranes is the nature of its substituents which were originally present on the phosphine. Complex formation perturbs the shielding somewhat but not enough to rearrange the order of the chemical shifts. The general trend in the ^{31}P chemical shift data is such that the phosphines with electronegative substituents have more negative chemical shifts both in the free and complexed forms. This is to be expected if one

considers the diamagnetic contribution since electronegative substituents will deshield the ^{31}P nucleus. The same effect is expected in the paramagnetic contribution because of the greater deviation from symmetry which results from the substitution of electronegative groups on phosphorus. On the other hand, the effect of neighboring anisotropy is such that the shielding increases when the atoms bonded to phosphorus possess lone pairs. Apparently, the combination of diamagnetic and paramagnetic effects offsets the neighboring anisotropy contribution sufficiently to cause the observed order.

While the order of the coordination chemical shifts $\Delta\delta$ ($\Delta\delta$ is defined as $\delta_{\text{complex}} - \delta_{\text{free phosphine}}$) is not exactly the same as the order of the ^{31}P chemical shifts of the free and complexed phosphines, some order is preserved. Only four out of fourteen are out of place. Furthermore, it appears that δ is related to the algebraic value of the chemical shifts before and after adduct formation, *i. e.* downfield resonances are shifted upfield and the upfield resonances are shifted downfield upon formation of the complex. A reasonable explanation for this can be arrived at by considering the changes in the terms which comprise the total chemical shift upon complex

formation. The diamagnetic term gives a negative contribution to $\Delta\delta$ because of the increased deshielding which arises from the donation of the lone pair to the Lewis acid. Conversely the paramagnetic term has a positive contribution because the electron distribution around the ^{31}P nucleus becomes more symmetric owing to the change to an approximately sp^3 hybridized phosphorus upon complex formation. An interplay of these two contributions can account for the observations. For the case of the phosphines which are downfield from the reference, the predominant change appears to be in the paramagnetic term rather than in the diamagnetic term resulting in a change to more positive chemical shifts. Apparently, the change in the deshielding of the ^{31}P nucleus upon donation of its lone pair to the borane unit is not significant to offset this in these phosphines with electronegative substituents since in these cases the phosphorus nucleus is already deshielded. Another plausible explanation for the small contribution of the diamagnetic term is the presence of lone pairs on the atoms attached to phosphorus; removal of electron density from phosphorus upon adduct formation can be compensated for by the π donation of the lone pairs to the phosphorus $3d$ or $4p$

orbitals. In the case of the phosphines which have relatively electropositive substituents the change in the diamagnetic term is larger than the change in the paramagnetic term. In this case, deshielding by P-B bond formation is more effective.

The above arguments are admittedly over-simplified. However, they do provide a qualitative picture of the various contributions to the ^{31}P chemical shift and the changes which these contributions undergo upon complexation. It is also noteworthy that the above-mentioned trend in coordination chemical shifts for the complexation of phosphines with the borane unit is similar to that observed by Packer with the isoelectronic oxygen atom.⁴⁹ Packer pointed out that presumably the paramagnetic term is dominant when the phosphine has electronegative substituents bearing at least one lone pair of electrons which is α to the phosphorus atom.

(b) ^{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 shown⁵⁰ 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.

(c) ^1H Chemical Shifts

The general trend of the proton chemical shifts of the borane group (Table III) is such that this resonance is shifted to higher fields with increasing J_{PB} . 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 on the basicity of the phosphine. The obvious exception to this generalization is $(\text{CH}_3)_3\text{PBH}_3$. 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.

SUMMARY

Base displacement reactions carried out in conjunction with a study of the nmr parameters of several phosphine-borane complexes indicate that the directly bonded ^{31}P - ^{11}B coupling constant may be taken as a measure of the basicity of the phosphine toward the BH_3 moiety. It is inferred that the two most important interactions that determine the observed order of phosphine base strengths and J_{PB} values are the inductive effects of the substituents on the phosphorus and the dative π bonding between the lone pairs on the substituents of phosphorus and the vacant $\text{P}(3\text{d})$ or $\text{P}(4\text{p})$ orbitals. However, the possibility of borane hyperconjugation cannot be excluded. The ^{11}B - ^1H coupling data do not discriminate between the borane hyperconjugative and sigma bonding models. The ^{31}P chemical shifts of the free and complexed phosphines indicate (i) that the order of chemical shifts of the phosphines remain essentially unchanged upon formation of the BH_3 adducts thus implying that the main contributor to the shielding of the ^{31}P nuclei is the nature of its substituents such that the phosphines with electro-

negative substituents have more negative chemical shifts and (ii) that the change in chemical shift upon coordination of phosphines with electronegative substituents bearing at least one pair of electrons alpha to the phosphorus atom is dominated by changes in the paramagnetic contribution; the coordination chemical shift of phosphines with more electropositive substituents is dominated by changes in the diamagnetic term. A similarity is noted in the trend of the coordination chemical shift for the complexation of phosphines with the borane unit and with the isoelectronic oxygen atom. The general trend of the proton chemical shifts is such that this resonance is shifted to higher fields with increasing J_{PB} thus implying that the amount of charge transferred to the BH_3 moiety is proportional to the basicity of the phosphine.

10. S. Kuchan and H. Buchwald, *Chem. Ber.*, **91**, 2296 (1958).
11. R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965); R. W. Rudolph and R. W. Schiller, *J. Amer. Chem. Soc.*, **90**, 3581 (1968).
12. G. W. Parshall, *Inorg. Syn.*, **11**, 197 (1968).
13. F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).
14. F. G. Mann, A. F. Wells, and D. Parry, *J. Chem. Soc.*, 1621 (1967).

REFERENCES

1. L. C. Cusachs and J. R. Linn, J. Chem. Phys., 46, 2919 (1967).
2. W. Gordy, H. Ring, and A. B. Burg, Phys. Rev., 78, 512 (1950).
3. A. B. Burg and R. I. Wagner, J. Amer. Chem. Soc., 75, 3872 (1953).
4. F. G. A. Stone and A. B. Burg, J. Amer. Chem. Soc., 76, 386 (1954).
5. W. A. G. Graham and F. G. A. Stone, J. Inorg. Nucl. Chem., 3, 164 (1956).
6. T. D. Coyle and F. G. A. Stone, Prog. Boron Chem., 1, 83 (1964).
7. D. E. Young, G. E. McAchran, and S. G. Shore, J. Amer. Chem. Soc., 88, 4390 (1966).
8. J. N. Shoolery, J. Chem. Phys., 31, 1427 (1959); N. Muller and D. E. Pritchard, J. Chem. Phys., 31, 768 (1959); N. Muller and D. E. Pritchard, J. Chem. Phys., 31, 1471 (1959).
9. R. W. Rudolph and R. W. Parry, J. Amer. Chem. Soc., 89, 1621 (1967).
10. W. Kuchen and H. Buchwald, Chem. Ber., 91, 2296 (1958).
11. R. W. Rudolph and R. W. Parry, Inorg. Chem., 4, 1339 (1965); R. W. Rudolph and H. W. Schiller, J. Amer. Chem. Soc., 90, 3581 (1968).
12. G. W. Parshall, Inorg. Syn., 11, 157 (1968).
13. F. G. Mann and E. J. Chaplin, J. Chem. Soc., 527 (1937).
14. F. G. Mann, A. F. Wells, and D. Purdie, J. Chem.

30. Soc., 1828 (1937); F. G. Mann and A. F. Wells, ibid., 702 (1938).
15. M. A. Fleming, Ph. D. Dissertation, University of Michigan, Ann Arbor, Michigan, 1963.
16. A. B. Burg and P. J. Slota, J. Amer. Chem. Soc., 80, 1107 (1958).
17. D. R. Martin and P. J. Pizzolato, J. Amer. Chem. Soc., 72, 4584 (1950).
18. L. Z. Soborovskii and Yu G. Gololobov, Zh. Obshch. Khim., 34, 1141 (1964).
19. A. B. Burg and G. Brendel, J. Amer. Chem. Soc., 80, 3198 (1958).
20. W. E. Hatfield and J. T. Yoke, Inorg. Chem., 1, 470 (1962).
21. J. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, J. Amer. Chem. Soc., 74, 901 (1952).
22. R. W. Parry and T. C. Bissot, J. Amer. Chem. Soc., 78, 1524 (1956).
23. A. B. Burg and Y. C. Fu, J. Amer. Chem. Soc., 88, 1147 (1966).
24. R. W. Rudolph, R. W. Parry, and C. F. Farrar, Inorg. Chem., 5, 723 (1966).
25. C. J. Jameson and H. S. Gutowsky, J. Chem. Phys., 51, 2790 (1969).
26. J. A. Pople and D. P. Santry, Mol. Phys., 8, 1 (1964).
27. A. H. Cowley and W. D. White, J. Amer. Chem. Soc., 91, 1913 (1969).
28. J. Schaefer and R. Yaris, Chem. Phys. Lett., 1, 173 (1967).
29. R. W. Rudolph and C. W. Schultz, J. Amer. Chem. Soc., to be published.

30. R. W. Rudolph, Ph.D. Dissertation, University of Michigan, Ann Arbor, Michigan, 1966.
31. H. C. Brown, J. Chem. Soc., 1248 (1956).
32. C. G. Barlow, J. F. Nixon, and M. Webster, J. Chem. Soc., A, 2216 (1968).
33. S. O. Grim, P. R. McAllister, and R. M. Singer, Chem. Commun., 38 (1969).
34. H. C. Brown, E. A. Fletcher, E. Lawton, and S. Sujishi, Abstracts, 121st National Meeting of the American Chemical Society, Buffalo, New York, March 1952, p. 9N.
35. J. Demuynuck and A. Veillard, Chem. Commun., 873 (1970); I. H. Hillier, J. C. Marriot, V. R. Saunders, J. J. Ware, and D. R. Lloyd, ibid., 1586 (1970).
36. A. D. Walsh, Disc. Far. Soc., 2, 18 (1947); H. A Bent, Chem. Rev., 61, 275 (1961).
37. E. D. Morris, Jr., and C. E. Nordman, Inorg. Chem., 8, 1672 (1969).
38. A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, J. Amer. Chem. Soc., 92, 5206 (1970).
39. see for example, A. B. Burg and P. J. Slota, J. Amer. Chem. Soc., 80 1170 (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, 317 (1964).
40. R. Schwendeman, 26th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1971, F7.
41. J. B. Verkade, private communication.
42. Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys., 20, 164 (1952); O. L. Hersh, Ph. D. Dissertation, University of Michigan, Ann Arbor, Michigan, 1963; Y. Morino, K. Kuchitsu, and Y. Motitani, Inorg. Chem., 8, 867 (1969);

E. Hirota and Y. Morino, J. Mol. Spec., 33, 460 (1970).

- VITA
43. I. H. Hillier and V. R. Saunders, Chem. Commun., 316 (1970); A. Serafini, J. F. Labarre, A. Veillard, and G. Vinot, ibid., 996 (1971).
44. E. B. Whipple, T. H. Brown, T. C. Farrar, and T. D. Coyle, J. Chem. Phys., 43, 1841 (1965).
45. F. Klanberg and E. L. Muetterties, J. Amer. Chem. Soc., 90, 3296 (1968).
46. It has been established that $J_{31\text{P}-1\text{H}}$ is positive. See W. McFarlane, Chem. Commun., 58 (1967).
47. For a review see, J. F. Nixon and A. Pidcock, Ann. Rev. NMR Spectrosc., 2, 345 (1969).
48. A. Saika and C. P. Slichter, J. Chem. Phys., 22, 26 (1954); M.M. McConnell, ibid., 27, 226 (1957); J. A. Pople, Proc. Roy. Soc., A, 239, 541 (1957).
49. K. J. Packer, J. Chem. Soc., 960 (1965).
50. D. R. Armstrong and P. G. Perkins, Chem. Commun., 377 (1965).

doctoral degree in Chemistry.

She joined William S. Fadellus, also a Filipino, in the holy state of matrimony on August 21, 1971.

Permanent Address: 188 Chico St.,
 Quezon District,
 Quezon City, Philippines

The vita has been removed from the digitized version of this document.