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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(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.

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^{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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Table I. $^{1}J_{PB}$ Values[a]

Adduct	$^{1}J_{PB}$	Ref
$Me_3P \rightarrow BF_3$	+174[m]	*b*
$Me_3P \rightarrow BCl_3$	166[m]	*c*
$Me_3P \rightarrow BBr_3$	165[m]	*c*
$(MeO)_3P \rightarrow BH_3$	97.2	*d*
$(Me_2N)_2FP \rightarrow BH_3$	86[n]	*e*
$(Me_2N)F_2P \rightarrow BH_3$	+79[n]	*e*
$Me_3P \rightarrow BH_3$	+64[m,o]	*b*
$(CH_2I)F_2P \rightarrow BH_3$	59	*f*
$F_2POPF_2 \rightarrow BH_3$	55.8	*g*
$HMe_2P \rightarrow BH_3$	54[o]	*h*
$F_2PCH_2PF_2 \cdot 2BH_3$	51	*f*
$HF_2P \rightarrow BH_3$	+49[p]	*i*
$H_2MeP \rightarrow BH_3$	43[o]	*h*
$F_3P \rightarrow BH_3$	39[n,p,q]	*i*
$H_2PPF_2 \rightarrow BH_3$	36	*j*
$F_2PSPF_2 \rightarrow BH_3$	32	*f*
$H_3P \rightarrow BH_3$	27[o,p]	*i*
$ClF_2P \rightarrow BH_3$	27[q]	*k*
$BrF_2P \rightarrow BH_3$	19[q]	*k*
$(CF_3)_2PPF_2 \rightarrow BH_3$	14	*j*
$F_2PPF_2 \rightarrow BH_3$	13	*l*

[a] The values are given in hertz. The signs which were determined in this study precede the corresponding value. [b] C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965). [c] D. E. Young, G. E. McAchron, and S. G. Shore, *J. Amer. Chem. Soc.*, **88**, 4390 (1966). [d] J. G. Verkade, R. W. King, and C. W. Heitsch, *Inorg. Chem.*, **3**, 884 (1964). [e] M. A. Fleming, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1963. [f] G. N. Bokerman, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1968. [g] L. F. Centofanti and R. W. Parry, *Inorg. Chem.*, **7**, 1005 (1968). [h] K. D. W. Morse, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1966. [i] R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, **89**, 1621 (1967). [j] H. W. Schiller and R. W. Rudolph, *Inorg. Chem.*, **10**, 2500 (1971). [k] R. T. Paine, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1970. [l] H. L. Hodges and R. W. Rudolph, unpublished results. [m] The $Me_3P \rightarrow BX_3$ (X = F, Cl, Br, H) series. [n] The $(Me_2N)_{3-n}F_nP \rightarrow BH_3$ series. [o] The $Me_{3-n}H_nP \rightarrow BH_3$ series. [p] The $F_{3-n}H_nP \rightarrow BH_3$ series. [q] The $F_2XP \rightarrow BH_3$ (X = F, Cl, Br) series.

Therefore, sign inversion does occur.

Considerable data are available where the acid is BH_3 and the phosphine ligand varies (Table I and ref 1). Here it is evident that $^{1}J_{PB}$ qualitatively mirrors the dative bond strength for a series of ligands where the P substituents are smoothly varied. Thus $^{1}J_{PB}$ decreases regularly as the number of methyl groups decreases in the series $Me_{3-n}H_nP \rightarrow BH_3$ in concert with the decrease in basicity of the phosphines.[9] The correspondence between $^{1}J_{PB}$ and relative dative bond strength is particularly evident in the triad $H_3P \rightarrow BH_3$, $F_2HP \rightarrow BH_3$, $F_3P \rightarrow BH_3$, where the stability of $F_2HP \rightarrow BH_3$ does not interpolate those of $H_3P \rightarrow BH_3$ and $F_3P \rightarrow BH_3$.[10] The dative bond decreases in stability as the electronegativity of X decreases in the $F_2XP \rightarrow BH_3$ [X = F, Cl, Br] series.[11] Again, the latter trend is mirrored by the P–B coupling (Table I).

Although quite different P–B couplings, such as those observed for $Me_3P \rightarrow BH_3$ and $F_3P \rightarrow BH_3$, undoubtedly reflect correct relative bond strengths, a comparison of $^{1}J_{PB}$ values of similar magnitude but in different series may not do so. As a case in point, $^{1}J_{PB}$ is greater for $F_2POPF_2 \rightarrow BH_3$ than for $F_2HP \rightarrow BH_3$, but the former is partially dissociated at 25°[12] whereas the latter is not.[10] Thus, although 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, it is not known if the correlation can be quantified, and it does not appear to be general for cases where the phosphine ligands belong to different series. Theoretical justification of the trends is not presently clear, but it is interesting to note that $^{1}J_{PB}$ is a much better indicator of P→B bond strength than is the bond length. For instance, the P–B bond lengths of $F_3P \rightarrow BH_3$ and $F_2HP \rightarrow BH_3$ are essentially identical (1.836 and 1.832 Å, respectively[13]) but $F_3P \rightarrow BH_3$ is less stable.[10] More strikingly, the dative bond distance in $Me_3P \rightarrow BH_3$ at 1.900 Å[14] is much longer than that for $F_3P \rightarrow BH_3$, yet the shorter bond is the weaker bond.

Nuclear spin–spin coupling in the P–B bond is probably dominated by the contact term;[2c] therefore, it is tempting to relate the magnitude of the interaction to the s character which each atom contributes to the coordinate bond. If the contribution by boron is held constant owing to the assumption that the BH_3 geometry is invariant, then the nature of the phosphine need only be considered. However, using the isovalent hybridization hypothesis,[15] there should be considerable s character in the dative bond when electronegative substituents are found on phosphorus. To the contrary, compounds like $F_3P \rightarrow BH_3$ and $ClF_2P \rightarrow BH_3$ have relatively small $^{1}J_{PB}$ values. Thus, it appears that the theoretical justification of the subject correlation will require more study.

Experimental Section

General. Vacuum-line techniques were used for the preparation, purification, and manipulation of reactants and products.[16] The samples used for $^{1}J_{PB}$ sign determination, $HF_2P \rightarrow BH_3$, $(Me_2N)F_2P \rightarrow BH_3$, $Me_3P \rightarrow BH_3$, and $Me_3P \rightarrow BF_3$, were prepared by direct combination of the ligand and the acid in the vacuum system, the excess reactant being removed by fractional condensation procedures.[16] The solids $Me_3P \rightarrow BH_3$ and $Me_3P \rightarrow BF_3$ were sublimed into the nmr tubes before distilling in the appropriate solvent. Chloroform served as both a solvent and lock signal for $Me_3P \rightarrow BH_3$. However, since CH_3CN was the solvent of choice for $Me_3P \rightarrow BF_3$, it was necessary to add $CFCl_3$ for a ^{19}F lock signal. Solvents were not necessary for the liquids $HF_2P \rightarrow BH_3$ and $(Me_2N)F_2P \rightarrow BH_3$, but TMS was added for a lock signal before sealing the tubes *in vacuo*.

Instrumentation. The nmr spectra were recorded with a Varian HA-100 instrument at 100 and 94.1 MHz for ^{1}H and ^{19}F, respectively. In order to effect heteronuclear spin tickling, the output of a General Radio 1164-AR7C frequency synthesizer was tied directly to the Varian V-4333 probe using the double-tuning scheme described by Burton and Hall.[17]

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