ing is possible based on the logarithm of the rate constant for the reaction of various nucleophiles with *trans*-dichlorodipyridineplatinum(II).[3] It is also possible to get an ordering of softness[4] from the $C_{\mathrm{B}}/E_{\mathrm{B}}$ ratios of the Drago–Wayland equation,[5] where C_{B} and E_{B} are constants assigned to Lewis bases in a fashion designed to make C_{B} reflect the covalent contribution and E_{B} reflect the electrostatic contribution of the base to the enthalpy of formation of a molecular addition compound. Neither of these approaches is applicable to the determination of the hardness of metal ions. We wish to report here the use of α/β ratios of the Edwards equation[6] as a measure of the hardness of metal ions. Recent stability constant data,[7] β_{n}, were used along with what we felt to be the best assignments[8] of H (ligand $\mathrm{p}K_{\mathrm{a}} + 1.74$) and E_{n} (the ligand nucleophilicity parameter) to obtain α and β values of the Edwards equation. A computer program was used to fit a rearranged form of the Edwards equation

$$\log [\beta_{\mathrm{n}} + 1.74n]/H = \alpha E_{\mathrm{n}}/H + \beta$$

Although this method of fitting the Edwards equation has been questioned by Edwards,[9] its simplicity has led us and others[10] to use it. Our results are shown in Table I along with the Pearson classification. Hard acids in general have a low α (sensitivity to nucleophilic ligand character, or polarizability) and a high β (sensitivity to basicity of ligand toward protons). The α/β ratio allows simultaneous consideration of both factors and should be of value in assigning hardness to more metal ions as further stability constant data become available. Negative α or β values are interpretable as due to an overlap of the factors making up H and E_{n}.[8] Since these negative α or β values will always be small, the absolute value of α/β will unambiguously put metals with negative α values in the hard classification and metals with negative β values in the soft classification.

TABLE I

A COMPARISON OF α/β WITH HARDNESS

Metal ion	α	β	α/β^{a}	Hardness^{b}
Hg^{2+}	5.786	−0.031	187	S
Cu^{+}	4.060	0.143	28.4	S
Ag^{+}	2.812	0.171	16.5	S
Pb^{2+}	1.771	0.110	16.1	B
Sr^{2+}	1.382	0.094	13.0	H
Cd^{2+}	2.132	0.171	12.5	S
Cu^{2+}	2.259	0.233	9.7	B
Mn^{2+}	1.438	0.166	8.7	H
In^{3+}	2.442	0.353	6.9	H
Mg^{2+}	1.402	0.243	5.8	H
Zn^{2+}	1.367	0.252	5.4	B
Ga^{3+}	3.795	0.767	5.0	H
Ba^{2+}	1.786	0.411	4.4	H
Fe^{3+}	1.939	0.523	3.7	H
Ca^{2+}	1.073	0.327	3.5	H
Al^{3+}	−0.749	1.339	0.6	H
H^{+}	0.000	1.000	0.0	H

[a] Ratio from monoligated complex; sign neglected. [b] Pearson classification;[3] S = soft, H = hard, B = borderline. [c] Not classified by Pearson; predicted from α/β ratio.

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(3) R. G. Pearson, *Science*, **151**, 172 (1966).

(4) See ref 3, particularly footnote 29.

(5) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).

(6) J. O. Edwards, *ibid.*, **76**, 1541 (1954).

(7) L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1954.

(8) Sources the same as those cited for calculations in D. H. McDaniel and A. Yingst, *J. Am. Chem. Soc.*, **86**, 1334 (1964).

(9) J. O. Edwards, *ibid.*, **78**, 1819 (1956).

(10) R. E. Davis, R. Nehring, S. P. Molnar, and L. A. Suba, *Tetrahedron Letters*, 885 (1966).

A Correlation between the Boron–Hydrogen Stretching Frequency and the Boron–Hydrogen Nuclear Magnetic Coupling Constant

Sir:

It is well accepted that the ^{13}C–H spin coupling constants, J_{CH}, are mainly determined by the s character of the carbon orbital.[1] On the other hand, the CH stretching force constants have also been recognized to depend upon the hybridization of the carbon orbital.[2,3] These two facts suggest a simple correlation between the two variables, and, in practice, Brown and Puckett[4] have examined methyl groups attached to various atoms or groups to find a linear correlation. We have independently noticed a similar correlation between the two variables to hold for various types of B–H bond.[5] The infrared and nmr data obtained from literature sources are collected in Table I and shown graphically in Figure 1. Here, the stretching frequency, ν_{BH}, was used instead of the force constant which necessitates troublesome calculations to obtain, because the B–H stretching vibrations are highly localized within the B–H bonds. For molecules having more than one B–H bond are cited the weighted average values of the symmetric and asymmetric stretching frequencies calculated by the average rule.[6] The linearity of the plot is quite satisfactory except for the point of aluminum borohydride which will be referred to later. In contrast to the B–H bond, the inclusion of C–H bonds other than the methyl group, *e.g.*, aldehydes,

(1) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

(2) A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947).

(3) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p 200; L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958.

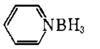
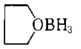
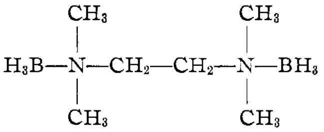
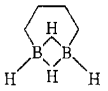
(4) T. L. Brown and J. C. Puckett, *J. Chem. Phys.*, **44**, 2238 (1966).

(5) This paper was presented at the 19th Annual Meeting of Chemical Society of Japan, Tokyo, April 3, 1966, Preprint part 1, IC305.

(6) W. J. Lehmann, *J. Mol. Spectry.*, **7**, 261 (1961).

TABLE I

INFRARED AND NMR DATA

No.	Compound	ν_{BH}, cm^{-1}	$J_{^{11}BH}$, cps
1	$LiBH_4$	2259[a]	75[k,l]
2	$(CH_3)_3NBH_3$	2337[b]	97[k-m]
3	H_3NBH_3	2306[c]	91[k]
4	$(C_2H_5)_3NBH_3$	2340[b]	97
5		2339[b]	96[k,l]
6		2360[d]	103[m]
7	$B_3H_6N_3H_3(CH_3)_3$	2326	101[k]
8	$B_3H_6N_3H_6$	2367	100[k]
9	$(CH_3HNBH\text{-}t\text{-}C_4H_9)_2$	2400[e]	106[k]
10	 $H_3B{-}N(CH_3)_2{-}CH_2{-}CH_2{-}N(CH_3)_2{-}BH_3$	2393[f]	96[f]
11	$CH_3B_2H_5$	2542[g]	127[k]
12		2510[h]	119[h]
13	$CH_3BH_2H_2BCH_3$	2519	131[k]
14	$(CH_3)_3B_2H_3$	2506	134[m]
15	$H_2B_2O_3$	2667[o]	169[k,l]
16	$(CH_3)_3N_3B_3H_3$	2515[i]	134[k]
17	$H_3N_3B_3H_3$	2530[i]	136[m]
18	B_2H_6	2555[j]	137[k]
19	$HB(OCH_3)_2$	2513	141[k,l]
20	$Al(BH_4)_3$	2520[n]	86[k,m]

[a] A. R. Emery and R. C. Taylor, *J. Chem. Phys.*, **28,** 1029 (1958). [b] B. Rice, R. J. Galiano, and W. J. Lehmann, *J. Phys. Chem.*, **61,** 1222 (1957). [c] J. Goubeau, *Z. Anorg. Allgem. Chem.*, **310,** 123 (1961). [d] B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59,** 650 (1955). [e] M. F. Hawthorne, *J. Am. Chem. Soc.*, **83,** 2671 (1961). [f] A. R. Gatti and T. Wartik, *Inorg. Chem.*, **5,** 329 (1966). [g] W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **32,** 1088 (1960). [h] H. G. Weiss, W. J. Lehmann, and I. Shapiro, *J. Am. Chem. Soc.*, **84,** 3840 (1962). [i] H. Watanabe, T. Totani, T. Nakagawa, and M. Kubo, *Spectrochim. Acta*, **16,** 1076 (1960). [j] W. J. Lehmann, J. F. Ditter, and I. Shapiro, *J. Chem. Phys.*, **29,** 1248 (1958). [k] H. Steinberg and A. L. McCloskey, *Progr. Boron Chem.*, **1,** 453 (1964). [l] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63,** 1533 (1959). [m] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81,** 4496 (1959). [n] W. C. Price, *J. Chem. Phys.*, **17,** 1044 (1949). [o] J. F. Ditter and I. Shapiro, *J. Am. Chem. Soc.*, **81,** 1022 (1959).

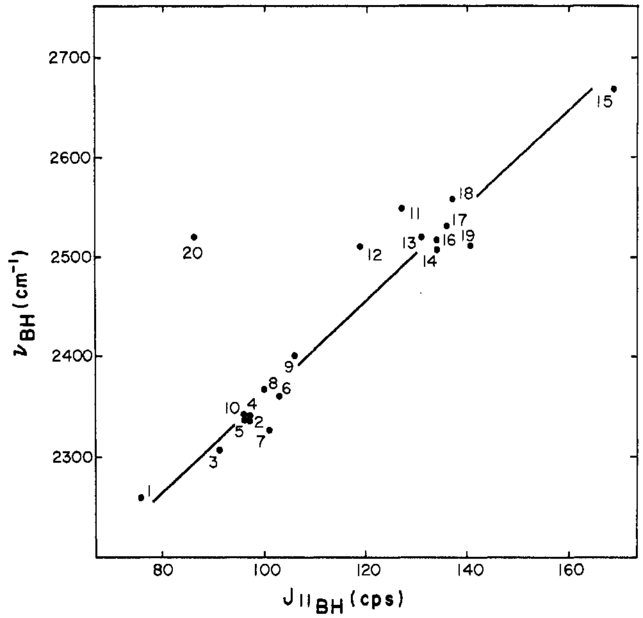


Figure 1.—ν_{BH} *vs.* $J_{^{11}BH}$.

formic acid, aromatic compounds, alkynes, alkenes, alkanes, etc., resulted in a wide spread in the J_{CH}–ν_{CH} plot. The range of ^{11}B–H coupling constants, J_{BH}, given in Figure 1 spans a large part of the range of observed values for various boron–hydrogen compounds. The lowest values of J_{BH} and ν_{BH} are those for the BH_4^- ion produced by the ionization of lithium borohydride, and similar data have been reported for sodium and potassium borohydrides which are not involved therein. Some boranes and carboranes afford larger coupling constants and higher infrared frequencies than $H_2B_2O_3$, and their plots roughly locate on the line, though lack of Raman data prevents the calculations of the average frequencies and their precise locations. For instance, pentaborane gives 168 (base) and 176 (apex) cps for J_{BH}[7] and 2595 cm^{-1} for ν_{BH} in infrared absorption,[8] 1-bromopentaborane[7,8] 161 cps and 2607 cm^{-1}, 1,5-dicarbaclovopentaborane(5)[9] 188 cps and 2620 cm^{-1}, and 1,6-dicarbaclovohexaborane(6)[10] 184 cps and 2657 cm^{-1}.

In the light of this correlation, some structural problems may be discussed; *e.g.*, the correlation can give a rationale of the deviation of the plot for aluminum borohydride,[11] in which the three boron hydrides are bonded to aluminum through six B–H–Al three-center orbitals as in diborane. When the spin coupling of proton aluminum is eliminated by a saturating field at the ^{27}Al, the resulting proton spectrum is a quartet suggesting that all protons are environmentally equivalent and equally coupled with the boron nucleus. The process producing the equivalence of hydrogen was explained as an intramolecular quantum mechanical tunneling through the potential barriers to BH_4 rotation, with a frequency greater than the nmr frequency separation of the bridge and terminal hydrogen signals. Thus the coupling constant of 86 cps is the average value for the four protons in the three BH_4^- ions. On the contrary, the B–H stretching frequency listed in Table I originates from the terminal B–H bonds and does not include the contribution from the bridge hydrogens.

The correlation permits immediate estimation of B–H stretching frequencies if the coupling constants are measurable and *vice versa*, although there are as yet insufficient data to predict the accuracy of such calculations. The stretching vibrations of borine carbonyl were observed at 2441 cm^{-1} (asymmetric) and 2379

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(7) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Am. Chem. Soc.*, **80,** 2670 (1958).

(8) B. Figgis and R. L. Williams, *Spectrochim. Acta*, **15,** 331 (1959).

(9) I. Shapiro, R. E. Williams, and C. D. Good, *J. Am. Chem. Soc.*, **84,** 3837 (1962).

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(11) R. A. Ogg, Jr., and J. D. Ray, *Discussions Faraday Soc.*, **19,** 392 (1955).

cm^{-1} (symmetric). The average value of 2427 cm^{-1} is located between that for sp^3 and sp^2 hybridization and is consistent with the observed bond angle of 113° 52′.[12] From the stretching frequency, one can predict a value of J_{BH} to be about 110 cps based on the correlation.

(12) W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.*, **78**, 512 (1950).

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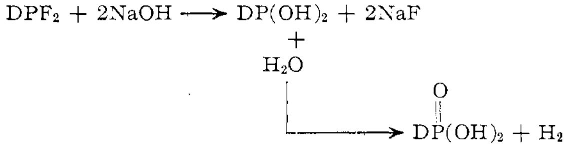
The Hydrolysis of Difluorophosphine

Sir:

In our original characterization of difluorophosphine[1] the following equation was suggested for the basic hydrolysis of the HPF_2

$$HPF_2 + H_2O \longrightarrow PF_2OH + H_2$$

Such an equation implies hydridic behavior for the hydrogen attached directly to phosphorus. The reaction would be comparable to that of the M–H linkages in the silanes[2] and boranes. More recently, however, evidence has been obtained which suggests that the hydrogen of the P–H linkage tends to be more protonic (or truly covalent) rather than hydridic in behavior; hence, the original equation is probably incorrect. The point has been investigated in a tracer study. If the above process were correct, hydrolysis of DPF_2 by H_2O should give HD. When the basic hydrolysis was conducted, a mass spectral analysis of the liberated hydrogen indicated that *no* deuterium was present. This observation can be rationalized by the following mechanism which retains the integrity of the P–H bond throughout the entire hydrolysis operation



$$DPF_2 + 2NaOH \longrightarrow DP(OH)_2 + 2NaF$$

$$DP(OH)_2 + H_2O \longrightarrow D\overset{O}{\overset{\|}{P}}(OH)_2 + H_2$$

Clearly H_2 is arising from reduction of water by the strongly reducing $DP(OH)_2$. There is no real evidence for hydridic behavior of the hydrogen in HPF_2.

Acknowledgment.—This work was supported by the Petroleum Research Fund of the American Chemical Society under Grant PRF2089A-3.

(1) R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

(2) D. T. Hurd, "Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952.

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