the ligands to be of the three-center, four-electron type, using the other two 5p orbitals. Molecular orbitals, constructed from the $(CH_3)_2Sn$ group and the ligands, would result in bonding, nonbonding, and antibonding orbitals. The four electrons from the ligand would occupy the bonding and nonbonding orbitals.

A relationship between the tin-proton coupling constants and the hybridization of the atomic orbitals on the tin has been noted[18] and has been used in correlating the amount of s character in a tin-carbon bond. Using the value given by McGrady and Tobias[6] for the ^{119}Sn-H coupling constants of $(CH_3)_2Sn(C_5H_7O_2)_2$ in deuteriochloroform leads to the prediction of approximately 50% s character in the Sn-CH_3 bond. This is in accordance with the proposed sp hybridization given in the molecular orbital scheme.

It should be clearly noted that the bonding of the 2,4-pentanedionate ligands to the $(CH_3)_2Sn$ moiety may involve a high percentage ionic character. Some involvement of the 5d orbitals in the bonding is also likely, but the extent of such involvement is not established.

The structure of $(CH_3)_2Sn(C_5H_7O_2)_2$ in solution and the solid state has been investigated[19] by Ramos and Tobias in a laser Raman study. The correlation between the single-crystal laser Raman data and those obtained in benzene solution suggest that the compound retains the trans arrangement of the methyl groups in solution.[20]

Registry No. $(CH_3)_2Sn(C_5H_7O_2)_2$, 19631-04-0.

(18) J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 83, 3903 (1961).

(19) V. R. Ramos and R. S. Tobias, *Spectrochim. Acta*, in press.

(20) The space group, unit cell dimensions, and trans configuration have been established independently by E. G. Miller and R. C. Fay, private communication.

Contribution from the Department of Chemistry, University
of South Carolina, Columbia, South Carolina 29208

High Resolution Boron-11 Nuclear Magnetic Resonance. IV. Boron-Boron Coupling Constants in Apically Substituted Pentaborane(9) Derivatives[1,2]

DOUGLAS W. LOWMAN, PAUL D. ELLIS,* and JEROME D. ODOM*

Received October 11, 1972

Substituent effects on ^{11}B-^{11}B coupling constants have been observed for apically substituted pentaborane(9) derivatives, 1-XB_5H_8, where X = H, Cl, Br, I, CH_3, C_2H_5, $CH(CH_3)_2$, and $Si(CH_3)_3$. The value of J_{BB} has been observed to vary from 13.8 to 25.1 Hz. The effect of the substituent on the coalescence temperature of the quartet is discussed. In general, for similar substituents, J_{BB} has been observed to be more sensitive than J_{CC}. Attempts to synthesize other 1-XB_5H_8 systems, where X = CN, C_2H, C_6H_5, $C(CH_3)_3$, and $CH(Br)CH_3$, are also discussed along with the reaction between acetonitrile and B_5H_9.

Introduction

Three important factors affecting nuclear spin-spin coupling constants between quadrupolar nuclei are the type of bonding involved, the substituents attached to one or both of the nuclei, and the temperature. We have previously discussed $J_{^{11}B^{11}B}$ values for three-center two-electron BHB bonds in diborane(6) and tetraborane (10).[1] In addition we have examined the temperature dependence of the value of J_{BB}[3] in pentaborane(9).[4] Numerous investigators have discussed the ^{11}B and ^1H nmr spectra of apically substituted pentaborane(9) derivatives.[5]

In 1959 Williams and coworkers[6] compared the line width of the resonance of the apex boron in B_5H_9 with the line width of the resonances of boron nuclei in analogous environments in several other boron hydrides. The resonance of the apex boron was observed to be broader than the other resonances studied. Thus, it became necessary to conclude that the broadening in the apical resonance of B_5H_9 is characteristic of the molecule and not of the ^{11}B nucleus. Therefore, it was concluded that unresolved boron-boron coupling and not nuclear quadrupole broadening was more important in the apex resonance broadening. Based on the apex resonance line width of *ca.* 160 Hz and considering only the apex boron connected to four ^{11}B nuclei in the base, Williams and coworkers[6] predicted that the ^{11}B (apex) to ^{11}B (base) coupling constant was "<13+ Hz."

From ^{11}B nuclear spin-lattice relaxation time, T_1, studies, Allerhand, Odom, and Moll[7] concluded that the expected ^{11}B line widths should be quite narrow at room temperature for B_5H_9—about 5 and 0.5 Hz for the base and apex, respectively. Complex unresolved splittings were postulated as an explanation for the observed broad line widths (over 40 Hz). Leach and Onak[8] proposed that the apex ^{11}B resonance in 1-methylpentaborane(9) should resolve into a 1:3:3:1 quartet from long-range coupling to the methyl hydrogens. This was not observed. A 1:1:1:1 quartet was observed by these authors in the ^1H nmr of 1-methylpentaborane(9) for the methyl hydrogens spin coupled to the apex boron, only upon decoupling the basal borons. The authors proposed that the expected 1:3:3:1 quartet might be obscured by unresolved homonuclear spin-spin coupling

(1) Part III: J. D. Odom, P. D. Ellis, D. W. Lowman, and M. H. Gross, *Inorg. Chem.*, 12, 95 (1973).

(2) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; this paper is based, in part, on the thesis submitted by D. W. L. to the Graduate School of the University of South Carolina in partial fulfillment of the requirements for the M.S. degree.

(3) Henceforth, J_{BB} will be used to represent $J_{^{11}B^{11}B}$.

(4) D. W. Lowman, P. D. Ellis, and J. D. Odom, *J. Magn. Resonance*, 8, 289 (1972).

(5) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, and references therein.

(6) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Amer. Chem. Soc.*, 81, 6164 (1959).

(7) A. Allerhand, J. D. Odom, and R. E. Moll, *J. Chem. Phys.*, 50, 5037 (1969).

(8) J. B. Leach and T. Onak, *J. Magn. Resonance*, 4, 30 (1971).

between the apex boron and the four basal borons.

More recently, homonuclear spin-spin coupling has been observed experimentally between the apex and base boron nuclei in B_5H_9.[9] The value of J_{BB} was observed to be 19.4 Hz at 25°. We wish to present here the results of a study on substituent effects on J_{BB} in apically substituted pentaborane(9) derivatives where the substituents are H, Cl, Br, I, CH_3, C_2H_5, $CH(CH_3)_2$, and $Si(CH_3)_3$.

For a more comprehensive study of the factors that influence J_{BB} the synthesis of several unknown apically substituted pentaborane(9) derivatives was attempted. The results of the attempted synthesis of several 1-XB_5H_8 derivatives, where X = CN, C_2H, C_6H_5, $C(CH_3)_3$, and $CH(Br)CH_3$, will be discussed.

Experimental Section

Instrumental Work. All ^{11}B nmr spectra were obtained on a Varian XL-100-15 nmr spectrometer operating at 32.1 MHz. Proton noise decoupling was accomplished by use of the Varian Gyrocode Decoupler. Standard variable-temperature accessories were employed. Field-frequency lock was provided by locking to ^{19}F in C_4F_8 in 3-mm o.d. capillaries placed inside 12-mm o.d. nmr tubes. The only exceptions were for 1-$(CH_3)_3SiB_5H_8$ where *sym*-$C_2F_4Br_2$ was used and for one B_5H_9 experiment where field-frequency lock was provided by ^2H in toluene-d_8. Proton nmr studies were obtained on a Varian A-60 nmr spectrometer operating at 60 MHz and a Varian XL-100-15 nmr spectrometer operating at 100 MHz.

The compounds studied were dissolved in CS_2, toluene-d_8, or a mixture of CS_2 and *sym*-$C_2F_4Br_2$. The sample concentrations ranged from 20 to 50% by volume except for 1-BrB_5H_8 which was less than 5%.

The precision of J_{BB} values is given in Table I for each compound, while that for J_{BH} is ±0.2 Hz. Chemical shifts, reported with respect to $BF_3 \cdot O(C_2H_5)_2$, are correct to within 0.1 ppm. Except where noted the nmr spectra were recorded at ambient temperature. The ^{11}B nmr spectra of 1-IB_5H_8 and 1-$(CH_3)_3SiB_5H_8$ were also recorded at elevated temperatures (1-IB_5H_8, 55 and 59°; 1-$(CH_3)_3SiB_5H_8$, 48°). Chemical shift data for 1-$(CH_3)_3SiB_5H_8$ were obtained at −25°.

Synthesis of Compounds. Standard high-vacuum techniques were employed on an all-glass vacuum system fitted with greaseless stopcocks.[10] Reactions were performed in either 500-ml standard wall bulbs or 75 ml thick wall tubes fitted with break-seals for removing the products. Photolytic brominations were performed using a 75-W sun lamp and a 2-in. deep Pyrex dish containing water placed between the sun lamp and the reaction tube as a heat filter. Purifications were accomplished either by trap-to-trap distillation or by using a modified version of the low-temperature vacuum distillation column described by Dobson and Schaeffer.[11]

Pentaborane(9) (Callery Chemical Co.) was purified using traps cooled to −60, −95, and −196°. Pure B_5H_9 (vapor pressure 66 mm at 0°) condensed at −95°. The material in the −60 and −196° baths was discarded. 1-Chloro-,[12] 1-bromo-,[13] 1-iodo-,[14] 1-methyl-,[15] 1-ethyl-,[16] 1-isopropyl-,[16] and 1-trimethylsilylpentaborane(9)[17] derivatives were prepared by previously published procedures. Other chemicals were obtained from commercial sources and used without further purification. Product purity was monitored by vapor pressure measurement, infrared analysis, mass spectroscopy, and ^{11}B and ^1H nmr spectra.

Attempted Syntheses of 1-Substituted Pentaborane(9) Derivatives. The attempted syntheses of several 1-XB_5H_8 derivatives, where X = CN, C_2H, C_6H_5, $C(CH_3)_3$, and $CH(Br)(CH_3)$, are presented below. Under each compound, several methods of synthesis may be given and are denoted as A, B, C, etc.

1-Cyanopentaborane(9). A. Potassium cyanide (0.4 g, 6.15 mmol) was allowed to react with 1-ClB_5H_8 (0.56 g, 5.7 mmol) at 60–70° for 2.25 hr. The reaction mixture had a yellow color at the end of the reaction period. Infrared analysis of the products collected at −196° showed the presence of a trace amount of B_2H_6, at −60° pure 1-ClB_5H_8 (0.50 g), and at −95° a trace amount of another species with infrared absorptions (±5 cm^{-1}) at 2960 (w), 2920 (w), 2625 (s), 1630 (s), 1620 (s), and 1600 (sh) cm^{-1}, with a very weak absorption at approximately 2150 cm^{-1} indicative of a nitrile group.[18] The product was so thermally unstable as to decompose while obtaining the infrared spectra. Thus, no further investigation was possible.

B. Potassium cyanide (0.95 g, 14.6 mmol) was allowed to react with 1-IB_5H_8 (1.4 g, 7.37 mmol) at 60° for 45 min. After this period, only a red-brown solid was observed in the reaction tube, indicative of decomposition of the 1-IB_5H_8. Infrared analysis of the trace quantity of volatile products condensed at −196° showed absorptions characteristic only of B-H (2620 cm^{-1}) and C-H (2900–2980 cm^{-1}). No absorption characteristic of a nitrile group was observed near 2200 cm^{-1}.[18]

1-Ethynylpentaborane(9). A. 1-Chloropentaborane(9) (1.0 g, *ca.* 10 mmol) was allowed to react with sodium acetylide (1.1 g, *ca.* 20 mmol) suspended in 8 ml of diethyl ether for 1.75 hr at −80°. The reaction vessel was not totally immersed in the low-temperature bath and the reactants in that portion of the vessel not at −80° turned brown in 15–30 min while the material at −80° developed no discoloration. Diethyl ether and sodium acetylide were found not to react under similar conditions. Separation of the volatile materials was accomplished using −60, −95, and −196° baths. Only 1-ClB_5H_8 and diethyl ether were obtained.

B. A mixture of 1-IB_5H_8 (0.95 g, 4.73 mmol) and sodium acetylide (1.8 g, 37.5 mmol) in 8 ml of *n*-pentane was left at 0° for 45 hr. Purification of the reaction mixture was accomplished using −40 and −196° baths. 1-Iodopentaborane(9) condensed at −40° while *n*-pentane condensed at −196°. No reaction occurred.

1-Phenylpentaborane(9). Phenyllithium (10 ml of a 1.84 *M* solution in diethyl ether–benzene solvent) was allowed to react with 1-ClB_5H_8 (1.1 g, 11.2 mmol) by warming the reaction mixture from −196° to melt the solvent. Upon immediate frothing and the formation of a yellow solution, the reaction was quenched in a −78° bath. The reaction was rewarmed and then finally quenched at −196°. This process required approximately 10 min. The mixture was purified by pumping the products from the reaction bulb at increasingly warmer temperatures from −78° to ambient temperature. Volatile materials consisted only of 1-ClB_5H_8 and solvent.

1-*tert*-Butylpentaborane(9). A. Pentaborane(9) (27.6 mmol) was allowed to react with isobutylene (20.0 mmol) in the presence of $FeCl_3$ (3.1 g, 19.1 mmol) and HCl (1.01 mmol) at 65° for 6.8 hr. The reaction mixture was purified using −60, −131, and −196° baths. Recovered B_5H_9 amounted to 25.8 mmol. Approximately 30 μl of 2-*tert*-butylpentaborane(9), identified by ^1H nmr spectra, was collected at −60°.

B. Pentaborane(9) (27.8 mmol) and isobutylene (20.1 mmol) were allowed to react at room temperature for 24 hr in the presence of HCl (1.0 mmol) and $FeCl_3$ (1.0 g, 6.2 mmol). Infrared analysis of the product condensed at −60° showed strong absorption (±5 cm^{-1}) characteristic of an organic species [2980 (s), 2790 (s), 1475 (br), 1380 (br), 1110 (w), 1060 (w), 1035 (sh), and 745 (s) cm^{-1}]. The ^1H nmr spectrum of this product gave no evidence for the presence of a B-H species. A weak absorption at 2620 cm^{-1} is indicative of the presence of a trace amount of B_5H_9 impurity. Pentaborane(9) condensed at −95° and HCl and C_4H_8 at −196°. In both reactions above, a clear thin film was noted inside the reaction bulb. This was possibly polyisobutylene.

C. A similar reaction between isobutylene (14.6 mmol) and B_5H_9 (15.8 mmol) in the presence of 6 μl of pyridine was left at room temperature for 24 hr. Upon purification approximately 300 μl of 2-*tert*-butylpentaborane(9) condensed at −65°, 7.46 mmol of B_5H_9 condensed at −112°, and 19.4 mmol of isobutylene condensed at −196°. The ^{11}B nmr spectrum of the product was in agreement with previously reported observations.[5]

D. A mixture of B_5H_9 (19.8 mmol), *tert*-butyl chloride (20.3 mmol), and $AlCl_3$ (0.3 g) was left at room temperature for 115 hr. After about 50 hr the reaction mixture appeared to become more

---

[9] J. D. Odom, P. D. Ellis, and H. C. Walsh, *J. Amer. Chem. Soc.*, 93, 3529 (1971).

[10] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[11] J. Dobson and R. Schaeffer, *Inorg. Chem.*, 9, 2183 (1970).

[12] D. F. Gaines and J. A. Martens, *Inorg. Chem.*, 7, 704 (1968).

[13] L. H. Hall, V. V. Subbanna, and W. S. Koski, *J. Amer. Chem. Soc.*, 86, 3969 (1964).

[14] A. B. Burg, *J. Amer. Chem. Soc.*, 90, 1407 (1968).

[15] T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, 1, 742 (1962).

[16] G. E. Ryschkewitsch, S. W. Harris, E. J. Mezey, H. E. Sisler, E. A. Weilmuenster, and A. B. Garrett, *Inorg. Chem.*, 2, 890 (1963).

[17] D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, 10, 1094 (1971).

[18] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967.

viscous. The reaction mixture was purified using −40, −60, −95, −131, and −196° baths. Material in −40 and −60° baths was further purified on a low-temperature vacuum distillation column.[11] Pentaborane(9), HCl, and *tert*-butyl chloride were the volatile materials recovered.

Photolytic Bromination of 1-Ethylpentaborane(9). 1-Ethylpentaborane(9) (5.54 mmol) and $BrCCl_3$ (7.46 mmol) were irradiated with ultraviolet light for 6 hr at 35°. The reaction products were separated using −40 and −196° baths. An unidentified nonvolatile viscous residue remained in the reaction tube after removing the products. A less volatile material (0.2 g) stopped in the −40° bath. The mass spectrum of this material had a *m/e* cutoff peak of 173. The infrared spectra had absorptions ($\pm 5\ cm^{-1}$) at 2960 (s), 2920 (sh), 2882 (sh), 2850 (w, sh), 2612 (s), *ca.* 1800 (br, w), 1570 (sh), 1390 (br), 1360 (br), 1030 (m), 889 (m), 790 (s), 742 (sh), and 739 (s) cm^{-1}. The ^{11}B nmr data gave resonances similar to those observed for 2-chloro-1-methylpentaborane(9).[19] The ^{11}B nmr at ambient temperature showed four resonances in the ratio of 1:2:1:1 with proton noise decoupling exhibiting chemical shifts (B–H coupling constants, ±5 Hz) of 9.3, 12.2 (185 Hz), 19.2 (158 Hz), and 40.4 ppm, respectively. From these data, the product is 2-bromo-1-ethylpentaborane(9). Found in the −196° bath were trace amounts of B_2H_6 and C_2H_6, $HCCl_3$ (~0.12 mmol), and an inseparable mixture of unreacted 1-ethylpentaborane(9) and $BrCCl_3$.

1-Ethylpentaborane(9) (4.97 mmol), upon irradiation with ultraviolet light, gave B_2H_6, C_2H_6, and noncondensable gases. The majority of the 1-ethylpentaborane(9) (4.09 mmol) was recovered. Pentaborane(9) had been shown not to react upon irradiation with ultraviolet light.[20]

Reaction of Acetonitrile and Pentaborane(9). Acetonitrile (1.2 ml, 22.9 mmol) was allowed to react with B_5H_9 (20.7 mmol) at 105° for 2.5 hr to give a red solution. The reaction products were purified using −70 and −196° baths. Approximately 0.02 mmol of 1-ethylpentaborane(9), mass spectral *m/e* cutoff peak 92, condensed at −70° and unreacted B_5H_9 at −95°. No acetonitrile was recovered.

Results and Discussion

A compilation of ^{11}B nmr parameters for the $1\text{-}XB_5H_8$ species studied is shown in Table I. The ^{11}B(basal)–^{1}H(terminal) coupling constants from this work are shown and compared to literature values, as are the chemical shifts for the apical and basal borons. The separations between the members of the quartet are tabulated in Table I. For these separations "L" denotes the separation between the two least shielded lines, "M" the separation between the central two lines, and "H" the separation between the two most shielded lines.

The relative precision of J_{BH} values was considerably better than that obtained for J_{BB}. For J_{BB}, the separations between the resonances of the quartet were not equal, an interesting feature previously noted by Leach and Onak[8] for the ^{1}H magnetic resonance of the methyl protons coupled to the apical ^{11}B in 1-methylpentaborane(9) under conditions of basal ^{11}B decoupling. The M separation was not always larger than H. The L separation was systematically less than that for the other two separations. Sweeping the frequency from the left or the right did not affect this separation difference. Further research is in progress to determine the nature of this phenomenon.

Besides varying resonance separations within a quartet, the 1:1:1:1 quartet was very slightly asymmetric. The peak heights observed for the quartet were not exactly as one would predict for a 1:1:1:1 quartet superimposed over a 1:1:1:1:1:1:1 septet from ^{11}B coupling to ^{10}B.[9] The outer members of the quartet were not of the same height; likewise the inner two members of the quartet were of different height. This asymmetry might also be accounted for by a small isotope effect where there is an inexact coincidence of ^{11}B–^{11}B and ^{11}B–^{10}B resonances,[21] as well as the temperature dependence of the coupling constant and line shape.[4] Suzuki and Kubo,[22] as well as Bacon, Gillespie, and Quail,[21] have analyzed line shape variations for spin $^{3}/_{2}$ nuclei. Theoretically, the quartet observed for a particular species coupled to a spin $^{3}/_{2}$ nucleus was shown to collapse by the M separation only slightly enlarging while the L and H separations decrease until a single resonance is observed. Separations L and H were always equal and smaller than M, while the resonance itself remained symmetric.

Table I lists the resonance separations L, M, and H observed for each compound. The boron–boron coupling constant is reported as the average of L, M, and H, *i.e.*, $J_{BB} = {}^{1}/_{3}(L + M + H)$. In general, J_{BB} was obtained to within 0.7 Hz. Within experimental error, no solvent dependence was observed for J_{BB}. The larger error for $1\text{-}ClB_5H_8$ was due to the difficulty in determining the value of the L separation. The error for $1\text{-}IB_5H_8$ did not seem to improve on raising the temperature, possibly due to the presence of the spin $^{7}/_{2}$ iodide. With $1\text{-}(CH_3)_3SiB_5H_8$ the individual members of the quartet appeared to broaden on raising the temperature.

Thermal Decoupling. The temperature dependence of J_{BB} in B_5H_9 has previously been noted.[4] The J_{BB} quartet was observed to coalesce at −51 ± 1°. Shore and coworkers[23,24] have shown the effect of varying counterions on the coupled ^{11}B nmr spectra of $B_5H_8^-$ and $B_6H_9^-$ salts at reduced temperatures. With the alkali metal cations,[23] different temperatures were required for each compound to obtain spectra in which the basal ^{11}B doublet had coalesced and the apical ^{11}B doublet had sharpened to the same extent. Much lower temperatures were required for the sodium and potassium salts than for the lithium salt.

Ambient-temperature ^{11}B nmr spectra of the 1-substituted pentaborane(9) derivatives gave well-defined quartets except for $1\text{-}IB_5H_8$ and $1\text{-}(CH_3)_3SiB_5H_8$. To obtain similarly well-resolved quartets for these two compounds, the probe temperature had to be elevated. That elevated temperature was required is an example of the dependence of the coalescence point upon the substituent for coupled quadrupolar nuclei.

Comparison of J_{BB} with J_{CC}. In organoboranes, where boron is attached to carbon by a two-center two-electron bond, boron–carbon coupling constants vary from 30 to 75 Hz.[25] For some of the same substituents as used in the J_{BB} study, carbon–carbon coupling constants through pure two-center two-electron bonds have been shown to vary from 33 to 36 Hz for ethyl derivatives,[26] from 41.8 to 48.5 Hz for isopropenyl derivatives,[27] and from 38.4 to 56.1 Hz for acetyl derivatives.[28]

If one assumes the Fermi contact term to be the dominant

---

[19] P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, 9, 1430 (1970).

[20] J. D. Odom and D. C. Moody, unpublished results.

[21] J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, 41, 3063 (1963).

[22] M. Suzuki and R. Kubo, *Mol. Phys.*, 7, 201 (1963).

[23] H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 9, 908 (1970).

[24] V. T. Brice, H. D. Johnson, II, D. L. Denton, and S. G. Shore, *Inorg. Chem.*, 11, 1135 (1972).

[25] P. D. Ellis, J. D. Odom, D. W. Lowman, and A. Cardin, *J. Amer. Chem. Soc.*, 93, 6704 (1971); D. W. Lowman, J. D. Odom, and P. D. Ellis, to be submitted for publication.

[26] V. J. Bartuska and G. E. Maciel, *J. Magn. Resonance*, 5, 211 (1971).

[27] V. J. Bartuska and G. E. Maciel, *J. Magn. Resonance*, 7, 36 (1972).

[28] G. A. Gray, P. D. Ellis, D. D. Traficante, and G. E. Maciel, *J. Magn. Resonance*, 1, 41 (1969).

Table I. ^{11}B Nmr Parameters for 1-XB_5H_8 Derivatives

		Resonance separations[a,d]								
X	J_{BB}[a,c,e]	L	M	H	J_{B-H}- (exptl)[a,e,f]	J_{B-H}- (lit.)[a]	δ_{apex}- (exptl)[b,e]	δ_{apex}- (lit.)[b]	δ_{base}- (exptl)[b,e]	δ_{base}- (lit.)[b]
H	19.2 ± 0.4	18.8[i]	19.4[i]	19.5[i]	164.0	161[h]	52.7[g]	51.8[h]	13.1[g]	12.5[h]
CH_3	18.9 ± 0.5	18.4	19.1	19.1	163.5	159[h]	43.1	44.5[h]	11.4	13.8[h]
C_2H_5	19.0 ± 0.7	18.3	19.4	19.4	162.2	160[h]	40.4	42.5[h]	11.7	14.2[h]
$CH(CH_3)_2$	18.6 ± 0.6	18.0	18.6	19.2	161.7	[j]	37.9	[j]	11.9	[j]
Cl	23.9 ± 1.1	22.8	24.5	24.3	165.8	~160[h]	28.5	30.6[h]	11.1	14.5[h]
						175 ± 5[k]		29.3[k]		11.9[k]
Br	25.1 ± 0.5	24.6	25.6	25.2	165.8	161 ± 5[l,u]	36.3	36.4[l]	10.5	12.5[l]
I	22.8 ± 1.5[m]	21.3	24.0	22.2	163.8	160 ± 5[l,u]	54.5	55.0[l,u]	9.6	11.8[l,u]
	23.4 ± 1.2[n]	22.2	24.4	23.7						
	23.8 ± 1.6[o]	22.2	24.6	24.5						
$Si(CH_3)_3$	13.8 ± 0.4[p,t]	13.4	14.0	14.0	164.6[r]	168[s]	57.3[r]	58.0[s]	11.5[r]	12.9[s]
	13.9 ± 1.1[q,t]	12.8	14.4	14.6						

[a] In Hz. [b] Chemical shifts reported in ppm with respect to external $BF_3 \cdot O(C_2H_5)_2$. [c] $J_{BB} = {}^1/_3(L + M + H)$. [d] "L" is the separation between the two least shielded lines of the quartet, "M" between the two central lines, and "H" between the two most shielded lines. [e] In CS_2 and at ambient temperature unless otherwise noted. [f] ±0.2 Hz. [g] Neat B_5H_9 in 12-mm o.d. nmr tube containing a 5-mm o.d. $BF_3 \cdot O(C_2H_5)_2$ capillary. [h] T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967). [i] Average value of separations in quartets of 3 B_5H_9 samples, each in different solvents. [j] Data not reported previously. [k] D. F. Gaines, *J. Amer. Chem. Soc.*, 88, 4528 (1966). [l] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959). [m] At 37°. [n] At 55°. [o] At 59°. [p] At 34°. [q] At 48°. [r] At −25°. [s] Reference 17. [t] In *sym*-$C_2F_4Br_2$ and CS_2. [u] In CS_2.

contribution to J_{BB},[25] then the expression for the coupling constant between the atoms A and B takes the form[29]

$$J_{AB} = (4/3)^2 h\beta^2 \gamma_A \gamma_B s_A{}^2(0) s_B{}^2(0)[(\partial {}^\rho s_A s_A(h_B)/\partial h_B]_{h_B} = 0 \qquad (1)$$

In this equation ${}^\rho s_A s_A(h_B)$ is the diagonal element of the spin density matrix (in the presence of the contact perturbation h_B), $s_A{}^2(0)$ is the value of the valence s-orbital electron density of the nucleus A, γ_A is the magnetogyric ratio of nucleus A, and β is the Bohr magneton. It is of interest to see if this equation can rationalize the magnitude of J_{BB} compared to other known coupling constants, *e.g.*, J_{CC}. This can be accomplished by examing the ratio of J_{BB} to J_{CC}, *i.e.*

$$J_{BB}/J_{CC} \simeq \left[\frac{\gamma_B s_B{}^2(0)}{\gamma_C s_C{}^2(0)}\right]^2 \qquad (2)$$

This, of course, assumes that the value of $\partial {}^\rho s_A s_A(h_B)/\partial h_B$ is comparable for both systems. Using the values of $s_C{}^2(0)$ and $s_B{}^2(0)$ given by Pople and coworkers,[29] one can calculate that $J_{BB} \simeq 0.52 J_{CC}$. In pentaborane(9) the bonding between the apical and basal borons can be described as a linear combination of two two-center two-electron BB bonds and a three-center two-electron BBB[30] bond. In a comparison of J_{BB} in 1-XB_5H_8 derivatives to J_{CC} (a two-center two-electron bond) values for similar substituents, it is interesting to note that the results of eq 2 are in qualitative agreement with the experimental data.[26-28] It appears that, within the limited amount of data presented here, the three-center two-electron bond in 1-XB_5H_8 compounds does not diminish the magnitude of the induced spin density on the basal borons due to the magnetic moment of the apical boron. Further research is in progress to assess the value of J_{BB} in a three-center two-electron bond.

From the limited number of substituents studied, boron-boron coupling constants seem to enjoy greater sensitivity to substituents than carbon-carbon coupling constants, except when a different functional group is involved such as the carbonyl group in the acetyl derivatives. The value of J_{BB} varies by about 25% while J_{CC} varies by 9% for the ethyl derivatives, 14% for the isopropenyl derivatives, and 32% for the acetyl derivatives.

Attempted Syntheses. All of the 1-organopentaborane(9) derivatives presently known contain saturated organic substituents. No unsaturated substituents are currently known. To fill this void and in order to observe the effect on J_{BB} of a carbon with a different hybridization attached to the apical boron, the synthesis of several 1-XB_5H_8 derivatives, where X = CN, C_2H, C_6H_5, $C(CH_3)_3$, and $CH(Br)(CH_3)$, was attempted.

Efforts by several authors have previously been directed toward a similar goal. Muetterties, *et al.*,[31] reported the synthesis of a salt of the type NaB_5H_8CN from the reaction of B_5H_9 with sodium cyanide. Schaeffer[32] mentioned the reaction between acetonitrile and B_5H_9 in 1957 but was unable to elucidate the nature of the products obtained. Onak has previously been unsuccessful in preparing 1-phenylpentaborane(9).[33] Ryschkewitsch has prepared an unidentified *tert*-butylpentaborane(9) from the reaction of B_5H_9 with excess isobutylene in the presence of either pyridine[34] or catalytic amines,[35] such as $(CH_3)_3N$.

Infrared analysis gave evidence for an unstable cyanopentaborane(9) species. Attempts to synthesize the other apically substituted pentaborane(9) derivatives were unsuccessful. The presence of a red color in the reaction mixture gave evidence that a reaction had taken place between B_5H_9 and acetonitrile. Trace quantities of 1-ethylpentaborane(9) were obtained from this reaction. Boron-11 nmr studies on the *tert*-butylpentaborane(9) prepared by the procedure of Ryschkewitsch[34] gave evidence that the product was 2-*tert*-butylpentaborane(9).

Brown and Yamamoto[36] have shown that mono(α-bromoethyl)diethylboron can be obtained from the reaction of triethylboron and $BrCCl_3$ in a 2:1 ratio upon irradiation with ultraviolet light. The yield was 78% based on reacted triethylboron. Only bromine was found to add to the α carbon and not attack the boron.

In the attempted bromination of the α carbon in 1-ethyl-

---

[29] J. A. Pople, J. W. McIver, Jr., and M. S. Ostlund, *J. Chem. Phys.*, 49, 2965 (1968).

[30] I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, 10, 1921 (1971).

[31] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **83**, 2471 (1961).

[32] R. Schaeffer, *J. Amer. Chem. Soc.*, 79, 1006 (1957).

[33] T. P. Onak, personal communication.

[34] G. E. Ryschkewitsch, U. S. Patent 2,971,031 (1961).

[35] G. E. Ryschkewitsch, U. S. Patent 3,030,417 (1962).

[36] H. C. Brown and Y. Yamamoto, *J. Chem. Soc. D*, 1535 (1971).

pentaborane(9), it was hoped that, in addition to obtaining a J_{BB} value for 1-CH(Br)(CH$_3$)B$_5$H$_8$, dehydrohalogenation of this product would be a successful route to the unknown species 1-vinylpentaborane(9). Instead, the product has been determined to be 2-bromo-1-ethylpentaborane(9) by infrared and mass spectral analysis and ^{11}B nmr spectra. This product would be expected from a free-radical bromination if halogenation of the basal position on B$_5$H$_9$ proceeds by a free-radical mechanism as proposed previously.[37]

Registry No. 1-IB$_5$H$_8$, 30624-33-0; 1-cyanopentaborane(9), 37768-70-0; 1-ethynylpentaborane(9), 37768-71-1; 1-chloropentaborane(9), 19469-13-7; 1-phenylpentaborane(9), 37768-72-2; 1-*tert*-butylpentaborane(9), 37768-68-6; pentaborane, 19624-22-7; 2-bromo-1-ethylpentaborane(9), 37768-69-7; potassium cyanide, 151-50-8; sodium acetylide, 1066-26-8; phenyllithium, 591-51-5; 1-ethylpentaborane(9), 23753-61-9; acetonitrile, 75-05-8.

Acknowledgment. J. D. O. and P. D. E. are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The XL-100-15 nmr spectrometer and a research assistantship to D. W. L. were made available through a National Science Foundation Department Development Grant.

[37] D. F. Gaines, *J. Amer. Chem. Soc.*, 88, 4528 (1966).

Contribution from the Department of Chemistry,
Georgetown University, Washington, D. C. 20007

Optical and Electron Spin Resonance Spectra of the 11-Tungstovanado(IV)phosphate Anion. A Heteropoly Blue Analog[1]

DOROTHY P. SMITH,[2] HYUNSOO SO, JOSEPH BENDER,[3] and MICHAEL T. POPE*

Received August 2, 1972

The anion $PV^{IV}W_{11}O_{40}{}^{5-}$ (I) may be prepared by electrolytic reduction of the corresponding vanadium(V) complex or by reaction of VO^{2+} with $PW_{11}O_{39}{}^{7-}$ at pH 4.5. The optical spectrum of the deep red-purple complex shows bands at 20 and 25 kK ascribed to V(IV) → W(VI) "intervalence" transitions, as well as ligand field bands for oxovanadium(IV) at 12.0 and 14.5 kK. The esr parameters, determined from a dilute solution of I in $K_5BW_{12}O_{40}\cdot{\sim}20H_2O$, are $g_{\parallel} = 1.910$, $g_{\perp} = 1.965$, $|A| = 167.0$, and $|B| = 59.3 \times 10^{-4}$ cm^{-1}. A single-crystal esr study confirms that the vanadium atom in I occupies one of the tungsten positions in a normal Keggin structure. The usual equations relating optical and esr parameters do not give internally consistent results for I, due principally to the low *g* values observed. Reasons for this are considered.

Introduction

We have recently reported the preparation and characterization of several 12-(tungstovanado)phosphates.[4] The complex $PVW_{11}O_{40}{}^{4-}$ undergoes a reversible one-electron reduction at +0.58 V *vs.* sce. This paper describes the preparation and optical and esr spectra of the reduced species $PV^{IV}W_{11}O_{40}{}^{5-}$, an intensely colored substance isoelectronic with the mixed-valence heteropoly blue $PW^{V}W_{11}O_{40}{}^{4-}$. The tungstovanado(IV)phosphate complex has apparently been made by Tourne and Tourne, who reported a partial absorption spectrum.[5]

Experimental Section

Preparation of 11-Tungstovanado(IV)phosphate Anion. Solutions containing this species could be prepared either by controlled-potential electrolysis at +0.4 V of a solution of $K_4PVW_{11}O_{40}$ in 1.0 *M* sodium sulfate, pH 2 on a platinum gauze electrode, or by adding a solution of $VOSO_4$ to one of $Na_3PW_{12}O_{40}$ buffered at pH 4.5. In the latter process the characteristic purple color of the anion formed instantaneously. Solutions prepared by both methods gave identical voltammograms and optical and esr spectra. A sample of the very soluble potassium salt was prepared as follows. Thirty grams of $Na_3PW_{12}O_{40}$, prepared as described elsewhere,[6] was dissolved in 25 ml of a 0.1 *M* acetate buffer, pH 4.5.[7] To this solution was added an equimolar amount of $VOSO_4$ as a *ca.* 1 *M* solution. The resulting solution was heated to near boiling and solid potassium acetate was added to the hot solution until no more white precipitate (probably potassium paratungstate) formed. The solution was filtered rapidly, 1 g further of potassium acetate was added and the solution placed in a refrigerator overnight. The resulting crystalline product was filtered and recrystallized from a boiling potassium acetate buffer, pH 4.5. *Anal.* Calcd for $K_5PVW_{11}O_{40}\cdot 6H_2O$: K, 6.42; V, 1.67. Found: K, 6.49; V, 1.71.

Dilute single crystals of the above salt were grown for esr purposes by slowly evaporating an acidic solution of $K_5BW_{12}O_{40}$[8] containing a small amount of an equimolar mixture of $Na_3PW_{12}O_{40}$ and $VOSO_4$ buffered at pH 4.5. A polycrystalline sample was prepared by grinding several dilute crystals.

Physical Measurements. The electrochemical equipment and techniques have been described previously.[4] Esr measurements were made as described elsewhere.[9] A homemade goniometer was used for the single-crystal measurements.

Results

Solution Properties. Visible and near-infrared absorption spectra of solutions taken during the course of controlled-potential electrolysis of 2.5 m*M* $K_4PVW_{11}O_{40}$ in 1.0 *M* sodium sulfate, pH 2.3, showed an isosbestic point at 455 nm (ϵ 520 M^{-1} cm^{-1}). Voltammograms of the fully reduced solution using rotating platinum or wax-impregnated graphite electrodes showed the expected oxidation wave or peak at +0.58 V *vs.* sce.[4]

---

[1] Presented in part at the 13th International Conference on Coordination Chemistry, Krakow and Zakopane, 1970.

[2] Holder of an NSF Summer Award to Secondary School Teachers, 1965-1966; NIH Predoctoral Fellow, 1966-1968.

[3] NSF Undergraduate Research Participant, 1969.

[4] D. P. Smith and M. T. Pope, *Inorg. Chem.*, 12, 331 (1973).

[5] C. Tourne and G. Tourne, *Bull. Soc. Chim. Fr.*, 1124 (1969).

[6] M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, 5, 1249 (1966).

[7] At this pH the 12-tungstate is converted to $PW_{11}O_{39}{}^{7-}$: see, for example, P. Souchay, "Ions Mineraux Condenses," Masson et Cie, Paris, 1969, p 93.

[8] Sample kindly supplied by D. R. Wexell.

[9] G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, 9, 662 (1970).