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A Nuclear Magnetic Resonance Investigation of the Nature of the Boron–Carbon Bond in Some Vinylboranes

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Abstract: The ^{13}C chemical shifts of the terminal vinyl carbons in trivinylborane, six vinylhaloboranes, and several Lewis acid–base adducts of the vinylboranes have been determined. Treatment of these compounds as monosubstituted ethylene derivatives indicates that in any of the tricoordinate boron species a vinyl group behaves as a mesomeric donor and in the vinylhaloboranes the ability of a vinyl substituent to supply π-electron density to boron is not very sensitive to the interchange of halogens (F, Cl, Br). Boron-11 NMR chemical shifts of the vinylboranes are also discussed. The preparation and properties of the new compound divinylbromoborane are presented. Some properties of several adducts of the vinylboranes are also presented.

Trivinylborane and the vinylhaloboranes are excellent examples of a chemically interesting group of compounds which contain an electron-deficient central atom that is directly bonded to electron-rich substituents. Since the boron atom possesses a low-lying vacant p_π orbital it could accept electron density by delocalization of the π systems of the vinyl groups, by p_π-p_π back-donation from the halogens to boron or by a combination of these two effects. Thus, mesomeric interactions could lead to contributions from the structure
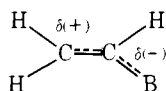
which could play a substantial role in the ground state properties in vinylboranes. The question of the occurrence of a significant amount of π-character in these boron–carbon bonds has received considerable attention and evidence both for and against such bonding can be found in the literature.

The earliest evidence suggesting mesomeric interaction between boron and vinyl substituents was based on the chemical stability of various vinylboranes[2] and (perfluorovinyl)boranes.[3] Evidence from NMR spectroscopy[4,5] has also been rationalized in terms of delocalization of π-electron density from the vinyl group to boron.

The infrared and Raman spectra of some vinylboranes[5-9] as well as the microwave spectrum of vinyldifluoroborane[6] have been investigated. The structural study of vinyldifluoroborane[6] has found that molecule to be planar in both the fluid and solid states with a barrier to internal rotation about the B–C bond of 4.17 kcal/mol. It is believed, however, that this apparently high value simply reflects the fact that the internal rotation involves a twofold barrier and is not indicative of any significant double-bond character in the B–C bond. A complete structural determination of the

molecule using isotopic substitution is currently in progress in our laboratories.[7] The photoelectron spectrum of trivinylborane[10] has been interpreted as suggesting that only a small amount of conjugation through the B–C bond can occur in this compound. The observation of absorption maxima in the ultraviolet spectra of several vinylborane species[5,11a] has also been interpreted to show that some electron delocalization occurs in these systems. The vinylboranes have also been the subject of several theoretical studies.[11a,12,13]

In order to obtain a better understanding of the nature of the B–C bond in vinylboranes as well as the effects of halogen substitution, an NMR investigation of trivinylborane, six vinylhaloboranes, and several adducts of the vinylboranes was undertaken. The results of this study are presented herein.

Experimental Section

All preparative work involved in the synthesis of trivinylborane and the vinylhaloboranes was carried out in a conventional high-vacuum system employing greaseless stopcocks. In general, the preparative routes followed were those of Brinckman and Stone.[14] Trivinylborane was obtained by two different synthetic methods, both of which have been previously described in detail.[9,15]

The preparation of $ClB(C_2H_3)_2$ and $Cl_2B(C_2H_3)$ involved the reaction of BCl_3 with $Sn(C_2H_3)_4$ in a 2:1 mole ratio. Boron trichloride was obtained commercially (Matheson) and was purified by trap-to-trap fractionation until the vapor pressure was 476 mmHg at 0°.[16] Tetravinyltin was also obtained commercially (Columbia Organic Chemicals, Inc.) and its purity was checked by ^{1}H NMR. The reaction of 27.9 mmol of $Sn(C_2H_3)_4$ with 56.4 mmol of BCl_3 in a sealed 1.0-l. bulb, at ambient temperature, for approximately 26 hr, yielded 16.6 mmol of $(ClB(C_2H_3)_2$ and 19.9 mmol of $Cl_2B(C_2H_3)$. These products were separated by distillation on a variable-temperature vacuum fractionation column.[17] Purity was determined by infrared[14] and ^{11}B NMR[11a] spectroscopy. A vapor pressure of 128 mmHg at 24.9° was found for $ClB(C_2H_3)_2$ (lit. value:[14] 126.7 mmHg at 24.9°). The vapor pressure of

Table I. [11]B Chemical Shifts for Vinylboranes and Analogous Ethylboranes[a]

Compound	[11]B chemical shift	Compound	[11]B chemical shift
$B(C_2H_3)_3$	−56.4 (−55.2)[b]	$B(C_2H_5)_3$	−85 ± 1[b]
$ClB(C_2H_3)_2$	−56.7 (−54.8)[b]	$ClB(C_2H_5)_2$	−78.0 ± 0.2[e]
$Cl_2B(C_2H_3)$	−53.5 (−52.4,[b] −53.2[c])	$Cl_2B(C_2H_5)$	−63.4 ± 0.2[e] (−63.0)[c]
$BrB(C_2H_3)_2$	−60.1	$BrB(C_2H_5)_2$	
$Br_2B(C_2H_3)$	−54.7 (−55.2)[d]	$Br_2B(C_2H_5)$	
$FB(C_2H_3)_2$	−42.4[f]	$FB(C_2H_5)_2$	−59.6 ± 0.2[e]
$F_2B(C_2H_3)$	−22.6 (−22.8)[c,g]	$F_2B(C_2H_5)$	−28.6 ± 0.2[e] (−28.1)[c]

[a] Shifts are reported in parts per million relative to $BF_3 \cdot O(C_2H_5)_2$ and values are converted from the external reference $B(OCH_3)_3$, by the equation $\delta(BF_3 \cdot O(C_2H_5)_2) = \delta(B(OCH_3)_3) − 18.1$ ppm. Negative values denote decreased shielding. The shifts given are for neat samples. [b] Reference 11a. [c] Reference 10. [d] Reference 18. [e] H. Nöth and H. Vahrenkamp, Chem. Ber., 99, 1049 (1966). [f] J_{B-F} = 104.0 Hz. [g] J_{B-F} = 60.0 Hz.

Table II. [13]C Chemical Shifts for Vinylborane Terminal Carbons[a]

Compound	Vinyl substituent	δ C_β relative to $H_2C=CH_2$ 10% solutions	Neat samples
$B(C_2H_3)_3$	$(C_2H_3)_2B$	+14.7[b]	+15.2
$FB(C_2H_3)_2$[d]	$F(C_2H_3)B$	+18.1[b]	+18.1
$ClB(C_2H_3)_2$	$Cl(C_2H_3)B$	+18.3[b]	+18.7
$BrB(C_2H_3)_2$	$Br(C_2H_3)B$	+19.2[b]	+20.3
$F_2B(C_2H_3)$[e]	F_2B	+22.2[c]	+20.9
$Cl_2B(C_2H_3)$	Cl_2B	+22.5[c]	+21.7
$Br_2B(C_2H_3)$	Br_2B	+23.2[c]	+23.5

[a] Shifts are reported in parts per million relative to $H_2C=CH_2$ and values are converted from internal and external TMS and internal C_6D_6 by the following equations: $\delta(C_2H_4) = \delta(TMS) − 122.8$ ppm and $\delta(C_6D_6) = \delta(TMS) − 128.7$ ppm. Spectra were obtained with ^{1}H noise decoupling and positive values denote decreased shielding. [b] 10% solution in TMS. [c] 10% solution in C_6D_6. [d] $^3J_{C-F}$ = 15.0 Hz. [e] $^3J_{C-F}$ = 8.5 Hz.

$Cl_2B(C_2H_3)$ is 124 mmHg at 0° (lit. value:[14] 134.3 mmHg at −0.4°).

The trimethylamine adduct of $Cl_2B(C_2H_3)$ was prepared by condensing equimolar amounts of each compound into a reaction tube at −196° and then allowing the tube to slowly warm to room temperature. Trimethylamine was obtained commercially from Matheson and purified by trap-to-trap fractionation until it exhibited a vapor pressure of 680 mmHg[16] at 0°. The ^{1}H NMR spectrum of the thermally stable, white solid adduct was obtained in C_6D_6. The vinyl protons appear as a broad unresolved signal centered at approximately τ 4.5 while the methyl protons appear as a singlet at τ 8.22. The integrated intensities of the methyl to vinyl proton signals are in the expected 3:1 ratio. The ^{11}B NMR spectrum consists of a single resonance at −8.7 ppm. The adduct, $Cl_2(C_2H_3)BN(CH_3)_3$, exhibits a melting point of 84°. The melting points of all the adducts were obtained on a Büchi melting point apparatus with samples contained in evacuated, sealed capillaries.

Divinylfluoroborane was obtained from the reaction of $ClB(C_2H_3)_2$ with SbF_3 (Alfa), which had previously been "activated" by heating the reaction apparatus with a cold flame while pumping. A reaction mixture consisting of approximately 250 mmol of SbF_3 and 12.6 mmol of $ClB(C_2H_3)_2$ was allowed to stand for approximately 15 hr at −50°. At several intervals during this period the apparatus was cooled to −95° (toluene slush) and $FB(C_2H_3)_2$ was removed. The reaction yielded $FB(C_2H_3)_2$, 10.5 mmol; $B(C_2H_3)_3$, 0.9 mmol; and $F_2B(C_2H_3)$, 1.0 mmol. Products were separated by distillation on a variable-temperature vacuum fractionation column. The infrared spectrum of $FB(C_2H_3)_2$ was in excellent agreement with that of Brinckman and Stone.[14] A vapor pressure of 283 mmHg is exhibited by $FB(C_2H_3)_2$ at 0° (lit. value:[14] 303.8 mmHg at −0.3°).

Vinyldifluoroborane was obtained either by the reaction of BF_3 (Matheson) with $Sn(C_2H_3)_4$[14] or as a product in the thermal decomposition of $FB(C_2H_3)_2$. In one reaction, 6.4 mmol of

$FB(C_2H_3)_2$ was allowed to stand in a sealed bulb at ambient temperature for approximately 20 hr. The tube was then opened, and the volatile products were separated by fractionation on the low-temperature column. The products obtained were: $FB(C_2H_3)_2$, 0.6 mmol; $B(C_2H_3)_3$, 2.6 mmol; and $F_2B(C_2H_3)$, 2.8 mmol. The purity of the $F_2B(C_2H_3)$ was checked by infrared[14] and ^{11}B NMR[5] spectroscopy. It has a vapor pressure of 19 mmHg at −95° (lit. value:[14] 18.5 mmHg at −95.5°).

The 1:1 adduct, $F_2(C_2H_3)BN(CH_3)_3$, was prepared by the reaction of equimolar amounts of the Lewis acid and base. The ^{1}H NMR, obtained in C_6D_6, consists of a singlet for the methyl protons at τ 8.51 and a broad unresolved signal for the vinyl protons centered approximately at τ 4.7. The integrated intensities of the methyl to vinyl proton signals are in the expected 3:1 ratio. The ^{11}B NMR spectrum shows a triplet, centered at −3.9 ppm (J_{B-F} = 58.5 Hz). The adduct exhibits a melting point of 33°.

The new compound, divinylbromoborane, was obtained from the reaction of equimolar amounts of BBr_3 (Columbia Organic Chemicals Co., Inc.) and $Sn(C_2H_3)_4$ at room temperature.[15] Boron tribromide was purified by trap-to-trap fractionation until its vapor pressure was 19 mmHg[16] at 0°. The volatile products of this reaction are $BrB(C_2H_3)_2$ and $B(C_2H_3)_3$, which can be separated with considerable difficulty by low temperature column fractionation. The infrared and ^{11}B, ^{13}C, and ^{1}H NMR spectra of $BrB(C_2H_3)_2$ were obtained. The [11]B and ^{13}C (^{1}H noise decoupled) NMR spectra consist of single resonance signals (see Tables I and II). In the case of the ^{13}C spectrum, only the terminal carbons were observed, with the coupled spectrum consisting of a triplet of doublets, with the following coupling constants: J_{CH} = 160 Hz, $^2J_{CH}$ = 8 Hz. Divinylbromoborane exhibits the following vapor pressures: 52 mmHg at 24°, 26 mmHg at 0°, 14 mmHg at −20°, and 8 mmHg at −40°. The compound melts at −98°, as determined by use of a Stock-type melting-point apparatus.[16] The $N(CH_3)_3$ adduct of $BrB(C_2H_3)_2$ was prepared by condensing equimolar amounts of each compound into a reaction tube at −196°, and then allowing the tube to slowly warm to room temperature. The ^{1}H NMR spectrum of the thermally stable, white solid adduct was obtained in C_6D_6. The vinyl protons appear as a broad unresolved signal centered at approximately τ 4.8 while the methyl protons appear as a singlet at τ 8.46. The integrated intensities of the methyl to vinyl proton signals give the expected 3:2 ratio. The adduct $Br(C_2H_3)_2BN(CH_3)_3$ thermally decomposed in vacuo around 190°. Its ^{11}B NMR spectrum is comprised of a single resonance at −6.0 ppm.

Vinyldibromoborane was obtained from the reaction of BBr_3 with $Sn(C_2H_3)_4$ in a 4:1 molar ratio, at room temperature, in the presence of Hg.[18] The $Br_2B(C_2H_3)$ obtained in this manner was purified by fractionation on the low-temperature column. The ^{11}B NMR spectrum of neat $Br_2B(C_2H_3)$ consists of a single resonance at −54.7 ppm (lit value:[18] −55.2 ppm). The ^{1}H noise decoupled ^{13}C NMR spectrum exhibits a single resonance, due to the terminal vinyl carbon. The coupled spectrum consists of a triplet of doublets, with the following coupling constants: J_{CH} = 161 Hz, $^2J_{CH}$ = 8 Hz. Vinyldibromoborane exhibits the following vapor pressures: 63 mmHg at 24°, 26 mmHg at 0°, 16 mmHg at −20°, and 10 mmHg at −40°. The compound melts at −95°, as determined by use of a Stock-type melting-point apparatus.[16] The ir spectrum of $Br_2B(C_2H_3)$ was in poor agreement with the published spectrum.[19] The ir spectrum (gas phase, 10 mmHg, 10-cm cell, KBr windows) of $Br_2B(C_2H_3)$ exhibits the following peaks: 3070 (m), 3025 (w), 2990 (w), 2955 (w), 1978 (w), 1610 (s), 1424 (d, vs), 1348 (w), 1273 (b, vs), 1095 (f, b, s), 991 (f, b, vs), 924 (w), 906 (sh, w), 845 (ms), 813 (vs), 686 (b, vs), 624 (sh, m), 616 (m), 478 (m), 464 (sh, m) cm^{-1} (d = doublet, f = unresolved fine structure). The reaction of $Br_2B(C_2H_3)$ with an equimolar amount of $N(CH_3)_3$ led to the formation of a thermally stable white solid adduct. The ^{1}H NMR of this 1:1 adduct was obtained in C_6D_6. The vinyl protons appear as a broad unresolved signal centered at approximately τ 4.5 and the methyl protons appear as a singlet at τ 7.92. The integrated intensities of the methyl to vinyl proton signals give the expected 3:1 ratio. The ^{11}B NMR spectrum consists of a single resonance at −5.7 ppm. When heated in vacuo, the adduct $Br_2(C_2H_3)BN(CH_3)_3$ decomposes around 260°.

Adducts of trivinylborane were prepared by condensing equimolar amounts of $B(C_2H_3)_3$ and the respective bases into a reaction tube at −196° and allowing the tubes to gradually warm to room

temperature. In this manner, stable 1:1 adducts were formed with NH_3, $N(CH_3)_3$, and $P(CH_3)_3$. These adducts could be sublimed in vacuo with no noticeable decomposition. They were characterized by their ^{13}C, [11]B, and [1]H (with ^{11}B noise decoupling) NMR spectra (see Table III). The ^{11}B NMR spectrum of $(C_2H_3)_3BP(CH_3)_3$ consists of a doublet centered at +17.5 ppm (J_{BP} = 47.0 Hz) while the spectra of the NH_3 and $N(CH_3)_3$ adducts consist of single resonances at +9.5 and +3.0 ppm, respectively. No isolable adducts were formed between $B(C_2H_3)_3$ and PH_3 or PF_3. These bases were quantitatively recovered from the reaction flask below $-80°$. The adducts exhibit the following melting points: $(C_2H_3)_3BP(CH_3)_3$, 83°; $(C_2H_3)_3BN(CH_3)_3$, 61°; and $(C_2H_3)_3BNH_3$, 54°.

Carbon-13 (25.2 and 20.0 MHz), boron-11 (32.1 MHz), and proton (100.1 MHz) NMR parameters were obtained on Varian Associates XL-100-15 or CFT-20 spectrometers. Boron-11 chemical shifts were obtained using $B(OCH_3)_3$ as an external reference with subsequent conversion of these values to a $BF_3 \cdot O(C_2H_5)_2$ reference by a conversion factor of -18.1 ppm; $\delta(BF_3 \cdot O(C_2H_5)_2) = \delta(B(OCH_3)_3) - 18.1$ ppm. The ^{13}C chemical shifts of the neat samples were referenced to external TMS, while the solutions were referenced internally to either C_6D_6 or TMS. These values were calculated relative to C_2H_4 using the following conversions from TMS: $\delta(C_2H_4) = \delta(TMS) - 122.8$ and $\delta(C_6D_6) = \delta(TMS) - 128.7$ ppm.

Results and Discussion

The technique of nuclear magnetic resonances spectroscopy has previously been employed to investigate the nature of the B–C bond in vinylboranes. Correlations of ^{19}F chemical shifts with electron density at fluorine atoms in organodifluoroboranes[4] and [11]B chemical shifts with electron density at boron in ethyl- and vinylhaloboranes[5] have been used to support delocalization of vinyl systems in vinylboranes. An extended list of [11]B chemical shifts of analogous ethyl- and vinylboranes is given in Table I. Two features of these values should be noted: (1) in every case the boron nucleus in the vinyl compound is more shielded than its ethyl counterpart, and (2) the trends observed are consistent with the generally accepted ideas of halogen-boron p_π–p_π backbonding increasing in the order Br < Cl < F.

Although the evidence from [11]B chemical shift data is consistent with the occurrence of B–C π-bonding and halogen-boron back-bonding, no hard conclusions can be made at this time about π conjugation through the B–C bond based on this information alone. This is because a clear separation of σ and π contributions to the boron chemical shifts cannot be made since the boron atom is directly bonded to substituents which are giving rise to both σ and π interactions.

Carbon-13 NMR, however, does provide a valuable technique for detecting possible mesomeric interactions between the boron atom and a vinyl group, as well as the effects of other substituents on the nature of the B–C bond. The monosubstituted ethylenes are a group of compounds whose ^{13}C chemical shifts have been extensively studied. The overall trends in the ^{13}C chemical shifts of some simple vinyl systems have been rationalized in terms of mesomeric arguments which reflect the competition between the carbon bearing the substituent, C_α, to engage in multiple bond formation with the substituent or with C_β; as well as taking into account the possible ionic character of these bonds.[20-23] These treatments are of particular interest here since trivinylborane and the vinylhaloboranes can be viewed as monosubstituted ethylene derivatives. Savitsky and co-workers[22] employed the Karplus and Pople[24] formulation of ^{13}C chemical shifts to derive expressions for the local paramagnetic terms for the α- and β-carbon atoms of monosubstituted ethylenes, for the cases where the substituents were either mesomeric donors or acceptors. These expressions established a reasonable correlation between the experimentally determined chemical shifts of the vinyl carbon atoms

and the mesomeric donor or acceptor ability of the substituents.

Mesomeric interactions between substituents and the π-electron system of an unsaturated framework are expected to be felt most effectively at carbon atoms more remote from the substituent than the actual point of substitution. The following resonance structures for monosubstituted ethylenes indicate why the effects of either a mesomeric donor (X_d) or acceptor (X_a) would be most dramatically reflected by the chemical shift changes of the β-carbon.
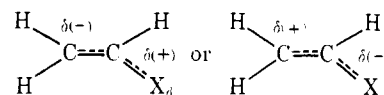
Interpretation of the α-carbon chemical shift changes is not as straightforward since C_α is the direct site of both inductive and mesomeric effects. Thus, as was the case with the boron-11 chemical shifts for the vinylboranes, a clear partitioning of σ and π contributions to these shifts is not possible at this time. However, for the series of vinylhaloborane compounds investigated, the terminal carbon resonance is the only ^{13}C resonance that can be observed for all members of the series. In most of the spectra, C_α is not observed due to the influence of the directly bound quadrupolar boron nucleus. An example in which the ^{13}C resonance of C_α is observed and extensively broadened is that of $B(C_2H_3)_3$ whose ^{13}C spectrum is shown in Figure 1. The broadening undoubtedly arises from T_2 scalar coupling caused by the boron quadrupole. Therefore, only the chemical shift changes of the β-carbon atoms that occur throughout the series will be considered and the various vinylboranes will be treated as monosubstituted ethylene derivatives. The chemical shifts for C_β in these systems, relative to the reference compound ethylene, are given in Table II. The most dramatic feature of these values is that for all the vinylboranes studied, the boron substituents act as mesomeric acceptors. This is indicated by the decreased shielding observed for the terminal carbons in every case. The sizable decrease, as much as 23.2 ppm for a solution of $Br_2B(C_2H_3)$, suggests that π-conjugation between the vinyl groups and boron does occur in all these compounds.

The fact that the relatively large deshielding observed for the terminal carbons can be attributed mainly to mesomeric effects is supported by the ^{13}C chemical shift data for the Lewis base adducts of the vinylboranes, given in Table III. In all cases it is found that complexation results in a dramatic shielding of C_β relative to the analogous tricoordinate

Table III. [13]C Chemical Shifts for the Terminal Vinyl Carbons of 1:1 Adducts[a]

Compound[b]	Vinyl substituent	δ vinyl C_β relative to $H_2C=CH_2$
$(CH_3)_3NB(C_2H_3)_3$	$(CH_3)_3NB(C_2H_3)_2$	+1.6
$(CH_3)_3PB(C_2H_3)_3$[c]	$(CH_3)_3PB(C_2H_3)_2$	+0.2
$H_3NB(C_2H_3)_3$	$H_3NB(C_2H_3)_2$	-3.4
$(CH_3)_3NBBr(C_2H_3)_2$	$(CH_3)_3NBBr(C_2H_3)$	+4.6
$(CH_3)_3NBF_2(C_2H_3)$[d]	$(CH_3)_3NBF_2$	+4.7
$(CH_3)_3NBCl_2(C_2H_3)$	$(CH_3)_3NBCl_2$	+4.9
$(CH_3)_3NBBr_2(C_2H_3)$	$(CH_3)_3NBBr_2$	+6.1

[a] Shifts are reported in parts per million relative to $H_2C=CH_2$, and values are converted from internal C_6D_6 reference by the equations: $\delta(C_2H_4) = \delta(TMS) - 122.8$ ppm and $\delta(C_6D_6) = \delta(TMS) - 128.7$ ppm. Positive values denote decreased shielding. Spectra were obtained with ^{1}H noise decoupling. [b] C_6D_6 was employed as solvent for all adducts. [c] J_{C-P} = 33.0 Hz, $^3J_{C-P}$ = 13.9 Hz. [d] $^3J_{C-F}(CH_3)$ = 2.0 Hz, $^3J_{C-F}$(vinyl C_β) = 5.2 Hz.
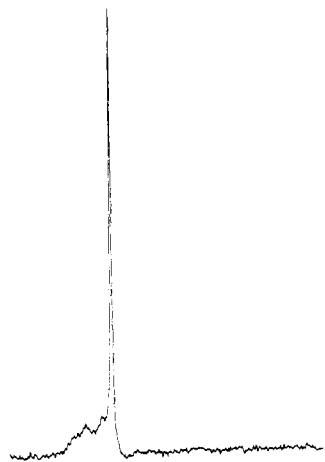
Figure 1. ^1H noise-decoupled ^{13}C FT spectrum of neat $B(C_2H_3)_3$. The sharp singlet is the resonance of the terminal carbons. The poorly resolved multiplet (least shielded) is that of the carbons directly bonded to boron. The spectrum is the result of 11,000 pulses with an acquisition time of 0.4 sec and no pulse delay.

boron compounds. It should be noted here that it has been suggested that multiple bonding may occur in some tetrahedral boron compounds,[25] analogous to that postulated to occur in the halomethanes.[26,27] For the vinylboranes, adduct formation is only viewed as changing the hybridization of boron so that it no longer contains an available p_π orbital. The evidence from ^{13}C NMR strongly suggests that some π-conjugation occurs in all the vinylboranes studied.

Further support for the occurrence of some π-delocalization in these systems comes from the ^{13}C NMR spectra of $B(C_2H_3)_3$ and $(CH_3)_3NB(C_2H_3)_3$. In both of these compounds the resonances of the vinyl carbon atoms that are directly bonded to boron can be observed, although the absorptions are broad and poorly resolved[15] (see Figure 1). In the case of neat $B(C_2H_3)_3$ the ^{13}C chemical shifts observed are $C_\alpha = +18.9$ and $C_\beta = +15.2$ ppm, both values relative to ethylene. For the adduct $(CH_3)_3NB(C_2H_3)_3$ the chemical shifts for the vinyl carbons are $C_\alpha = +25.6$ ppm and $C_\beta = +1.6$ ppm, again relative to ethylene. These results are consistent with the idea that the mesomeric pathway for delocalization through the vacant p_π orbital of boron, which is present in $B(C_2H_3)_3$, is removed upon adduct formation, leaving the inductive mechanism for removal of electron density from the vinyl groups. While C_α is sensitive to both inductive and mesomeric interactions, C_β is expected to be primarily affected by mesomeric interactions with the substituent.

The varying degrees of deshielding found for the vinylboranes suggest that the degree of B–C conjugation in these systems is sensitive to the nature of the other substituents on boron. Such conjugation appears to occur to the least extent in trivinylborane and to the greatest extent in the monovinylhaloboranes. Trivinylborane contains three vinyl groups bound to a central boron atom that contains just one vacant p_π orbital. Therefore, even optimal conjugation would give rise to B–C bonds with only 0.33 π character. In the vinylhaloboranes there are fewer vinyl groups per molecule to compete for boron's vacant p_π orbital; however, the ability of the halogens to back-bond to boron could become a factor. Strong π back-donation by a halogen to boron in the vinylhaloboranes could affect the demand for electron density placed on the remaining vinyl π systems. This competition might influence the ability of individual BY_2 substituents, where Y = F, Cl, Br, or $-CH=CH_2$, to behave as mesomeric acceptors. Several factors, however, could give

rise to the variation in terminal carbon shifts observed in Table II. The trends could reflect the changing ability of the boron substituents to act as mesomeric acceptors. The changes could also be at least partially caused by the fact that different BY_2 groups will exert unique inductive effects on the vinyl system. Also, a combination of mesomeric and inductive effects may be responsible for these changes, and indeed this is the most likely explanation. In the case of the adducts, changing a substituent on boron causes a variation in $^{13}C_\beta$ chemical shifts, indicating that these shifts are sensitive to inductive effects.

Another factor which must be considered when interpreting the trends found in Table II is whether they might arise because the various vinylboranes, containing both acidic and basic sites, could self-associate to significantly different degrees. Therefore, the ^{13}C chemical shifts for these compounds were determined for both neat samples and 10% solutions, in either benzene-d_6 or TMS. The trends are similar in both cases and there are no unexpected solvent effects. Self-association, therefore, does not appear to be a major contributor to the overall deshielding observed for the ^{13}C resonances in these systems or to the general trends found within the series. Also, since line broadening was not observed in going from the gaseous to liquid states in our vibrational study of $B(C_2H_3)_3$,[9] such association does not appear to be significant, at least for this compound.

In comparing the chemical shifts of the various vinylboranes, steric effects must also be considered. Nonbonded H···H repulsions of the terminal CH_2 groups could be significant in trivinylborane, especially since a nonplanar conformer is present in the fluid phases.[9] Such repulsions would be expected to be lessened in the divinylboranes and absent in the monovinylboranes. Since parallel changes occur within the divinyl- and monovinylborane series, however, steric factors do not appear to significantly affect the chemical shifts observed.

The 10% solutions of the monovinylhaloboranes have a $^{13}C_\beta$ chemical shift range of 1.0 ppm, and the range for solutions of the divinylhaloborane series is 1.1 ppm. The $^{13}C_\beta$ chemical shifts for the trimethylamine adducts of the monovinylhaloboranes encompass 1.4 ppm. In the latter case the changes should be attributable primarily to inductive effects. Since the range for this series of adducts is approximately equal to that found for either of the tricoordinate boron series, it appears that there is little difference in the relative ability of the halogens within a given series to affect the capacity of the vinyl substituents to act as mesomeric donors. The range of shifts within both the mono- and divinylhaloborane series is small enough so that purely inductive changes could account for them.

For the dihalogen compounds the terminal vinyl carbons are more deshielded in all cases than those of any monohalogen compound, and a similar trend in shifts is observed as in the monohalogen series. The $^{13}C_\beta$ resonances in both series are in turn more deshielded than in trivinylborane. To obtain a qualitative idea of the relative contributions of the inductive and mesomeric effects to the observed trend in $^{13}C_\beta$ chemical shifts in these series, it is helpful to compare these chemical shifts with the analogous shifts in the trimethylamine adducts of some of these compounds. In the free compounds the $^{13}C_\beta$ chemical shifts encompass 8.5 ppm in going from the least deshielded case, $B(C_2H_3)_3$, to the most deshielded, $Br_2B(C_2H_3)$. For the analogous trimethylamine adducts the chemical shift change is 4.5 ppm. Also, while the $^{13}C_\beta$ resonance of $Br_2B(C_2H_3)$ is 4.0 ppm more deshielded than that of $BrB(C_2H_3)_2$, the difference in chemical shifts for the terminal vinyl carbons between the analogous trimethylamine adducts is only 1.5 ppm. These values suggest that for the tricoordinate boron compounds the in-

creased deshielding that occurs in going from tri- to di- to monovinyl compounds reflects in part an increasing capacity for the respective boron substituents to act as mesomeric acceptors. The greatest degree of π conjugation through the B–C bond would therefore be expected in the monovinyl compounds. It is interesting that the fluorine compounds follow this trend and do not exhibit any anomalous behavior. Even though halogen back-bonding to boron is expected to be significant in the fluorine compounds, as suggested by ^{11}B NMR data, the BF_2 group appears to place a greater demand on the ethylene π system for electron density than a $BF(C_2H_3)$ or a $B(C_2H_3)_2$ substituent. When vinyl groups are replaced by any of the halogens the demand on the remaining vinyl π systems for electron density increases, as indicated by increased deshielding of $^{13}C_\beta$. The greatest degree of π conjugation through the B–C bond should therefore occur in the monovinylhaloboranes. The approximately equal values obtained for the $^{13}C_\beta$ chemical shifts for analogous fluorine and chlorine compounds could be viewed as arising from the fortuitous balancing out of different inductive and mesomeric effects for the two halogens. However, the fact that the changes in $^{13}C_\beta$ chemical shifts in going from $F_2B(C_2H_3)$ and $Cl_2B(C_2H_3)$ to their respective trimethylamine adducts are almost identical suggests that the two halogens exert similar effects on the ability of the vinyl systems to transfer electron density to boron's vacant p_π orbital. These data do not provide a direct measure of the ability of the halogens to back-bond to boron by the p_π–p_π mechanism. The terminal vinyl carbon chemical shifts for $F_2B(C_2H_3)$ and $Cl_2B(C_2H_3)$, relative to ethylene, are +22.2 and +22.5 ppm, respectively. Upon adduct formation with trimethylamine these resonances are shifted to +4.7 and +4.9 ppm, respectively.

It should be noted that from SCF–MO calculations,[12] the electron density for C_β in $Br_2B(C_2H_3)$ is greater than that calculated for either of the terminal carbons in $BrB(C_2H_3)_2$ or for those in $B(C_2H_3)_3$. From the ^{13}C NMR data it is found that the order of increasing shielding of the terminal vinyl carbons is $Br_2B(C_2H_3) < BrB(C_2H_3)_2 < B(C_2H_3)_3$. There is little agreement between the calculated electron densities and the relative electron distribution changes for the terminal vinyl carbons as indicated by their ^{13}C NMR parameters.

It would be tempting at this point to try to rationalize the patterns of ^{11}B chemical shifts exhibited by these compounds in view of the ^{13}C data presented here. It is essential to point out that the ^{13}C chemical shifts of C_β in these systems allows for a relatively easy separation of σ and π effects because of its "isolation" from the point of substitution. However, this is far from the case for C_α and boron. Hence, any arguments based solely on inductive mechanisms or mesomeric interactions are going to be significantly clouded by the present inability to unambiguously separate these effects. Therefore, such a discussion will not be attempted until better theoretical methods are developed to aid in the analysis of this complex problem.

In terms of quantities such as barriers to rotation, any π conjugation occurring through the B–C bonds of the vinylboranes is apparently small since the value of 4.17 kcal/mol in $F_2B(C_2H_3)$ is not an unexpectedly large twofold barrier.[6] Also, the planar conformation in the fluid states of $B(C_2H_3)_3$ where conjugation of the vinyl π system would be

optimal is only 0.73 kcal/mol more stable than a nonplanar conformer.[9]

Summary and Conclusions

An analysis of the ^{13}C chemical shifts of the terminal vinyl carbons of the vinylboranes clearly indicates that the vinyl groups behave as mesomeric donors toward boron in all the tricoordinate boron compounds studied even though evidence from other studies[6,9,10] indicates that such conjugation through the B–C bond is limited. Thus it appears that ^{13}C NMR spectroscopy provides a very sensitive technique for detecting limited delocalization of electron density in these systems.

The differences between the terminal vinyl carbon chemical shifts for the vinylboranes studied suggest the B–C π conjugation is greatest in the monovinylhaloboranes and least in $B(C_2H_3)_3$. As the number of vinyl substituents on a boron atom decreases, the demand placed on each remaining vinyl system for π-electron density increases. In the vinylhaloboranes, the interchange of halogens (F, Cl, Br) appears to have little effect on the ability of a vinyl substituent to act as a mesomeric donor.

References and Notes

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