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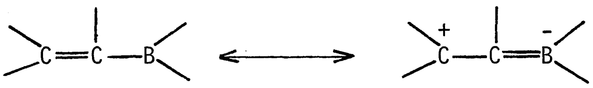
^{13}C NMR SPECTRA AND BONDING SITUATION OF THE B-C BOND IN ALKYNYLBORANES

Yoshinori YAMAMOTO and Ichiro MORITANI
Department of Chemistry, Faculty of Engineering Science
Osaka University, Toyonaka, Osaka 560

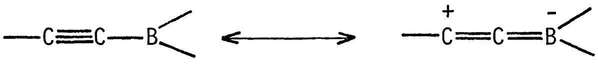
^{13}C NMR spectra of boron substituted alkynes reveal that the β-carbon is deshielded by ca. 21 ppm by a $B(O\text{-}\underline{n}\text{-}C_4H_9)_2$ group. This clearly indicates the presence of a B-C π-bonding in alkynylboranes.

Boron is less electronegative than carbon, as is evident from Pauling's electronegativities (2.0 for boron and 2.5 for carbon).[1) Therefore, a boron atom should exert an electron donating inductive effect toward a neighboring carbon atom. On the other hand, the vacant p-orbital of boron should accept electrons from a neighboring π-electron system. Accordingly, the π-electron withdrawing effect is opposed by the electron donating inductive effect. It is well known that, in the case of vinylboron derivatives, the withdrawing effect overcomes the donating one, as is shown by a pair of resonance structures (eq 1).[2)



(1)

These results lead to a postulation that a similar B-C π-bonding must exist in alkynylboron derivatives (eq 2). In fact, a one-sentence description on such a conjugation has appeared previously.[2a) However, a curious thing is that any experimental evidence has not been demonstrated there.[2a) To our best knowledge, there is no literature on the evidence for such a B-C π-bonding.



(2)

As a part of our broad study on organoboranes, we have obtained ^{13}C NMR spectra of alkynylboranes and wish to report here clear evidence for the presence of the B-C π-bonding (eq 2). Di-$\underline{n}$-butyl acetyleneboronate (I) and di-$\underline{n}$-butyl 1-hexyne-1-boronate (II) were prepared according to the known procedure.[3) ^{13}C signals were assigned by the method previously described.[2c) The data are

Table. ^{13}C Chemical Shifts for Acetylene Derivatives.[a] R-$C_\beta \equiv C_\alpha$-R'

Compound	R	R'	δ C_β (ppm)	δ C_α (ppm)	$J_{C_\beta H}$ (Hz)
I	H	B(O-*n*-$C_4H_9)_2$	91.4	[b]	240
II	*n*-C_4H_9	B(O-*n*-$C_4H_9)_2$	104.9	[b]	
III	H	H	70[c]	70[c]	249[c]
IV	*n*-C_4H_9	H	84.0[c](85.7)[c]	68.6[c](70.0)[c]	
			83.0[d]	66.0[d]	

[a] ^{13}C FT NMR spectra were examined with a Varian XL-100-15 spectrometer at 25.2 MHz; compounds were dissolved in C_6D_6, which was served as an internal standard and an internal lock. Chemical shifts were converted to δ_c, using $\delta_c^{C_6D_6}$ 128.7; errors were ± 0.1. [b] The signal was not obvious owing to the neighboring boron.[2c] [c] Ref. 4 and references cited therein. [d] Ref. 5 and references therein.

summarized in the Table. Evidently, the β-carbon is strongly deshielded by the boron substituent; 21.4 ppm for I and 20.9 (otherwise 19.2 or 21.9) ppm for II.

The effect of the boron substituent in saturated alkylboranes is weak on the β-position, as is exemplified by the chemical shifts of $(CH_3CH_2)_3B$ (δC_β 7.9[6] or 9.3[7]) and ethane (δC_β 5.9).[4] The α-effect of the boronate group for the triple bond, which was not available from the present study, is estimated to be ca. 5 ppm from the data on the corresponding saturated and unsaturated boranes. Consequently, the present results evidently indicate that the resonance structure of the B-C π-bonding (eq 2) contributes considerably to the ground state of alkynylboranes.

References

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7) Our result is somewhat, but not essentially, different from the reported value.[6] This must be due to the difference of experimental conditions (private communication from Prof. W. T. Ford).

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