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^{13}C NMR SPECTRA OF ALLYLIC BORON "ATE" COMPLEXES. RELATIVE IMPORTANCE OF σ-π CONJUGATION BETWEEN THE DOUBLE BOND AND THE CARBON-BORON BOND

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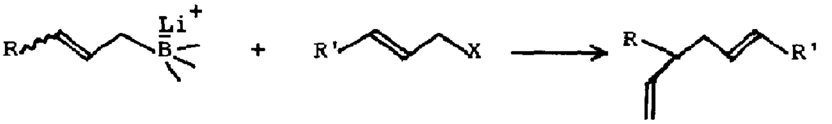
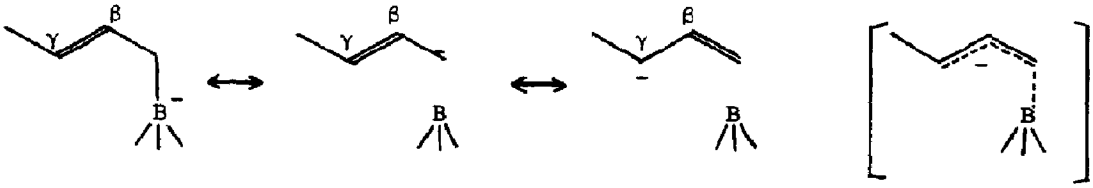
Summary: Carbon-13 NMR spectra of allylic boron "ate" complexes clearly indicate, for the first time, the relative importance of σ-π conjugation between the double bond and the carbon-boron bond.

We recently reported that allylic boron "ate" complexes undergo a facile and regioselective haid-to-tail coupling with allylic halides,[1] while the corresponding trivalent allylic borons do not react with such halides (eq 1).



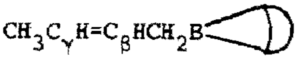
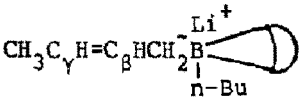
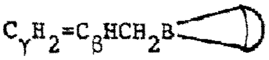
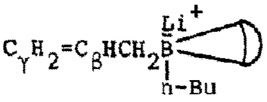
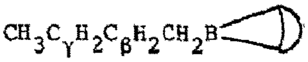
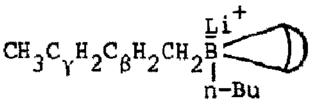
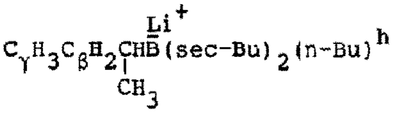
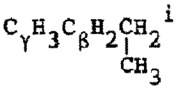
(1)

This result suggests that the C_γ of the "ate" complexes must bear negative charge as is shown by a pair of resonance structures (eq 2). We here report the first evidence for the presence of such a conjugation with the aid of ^{13}C NMR spectra.



(2)

Table I. Carbon-13 Chemical Shifts and Substituent Effects of Tri- and Tetravalent Boron Atoms[a]

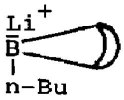
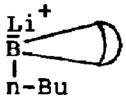
Compound	Chemical Shift[b]		Substituent Effec	
	δC_β	δC_γ	$\Delta\delta C_\beta$	$\Delta\delta C_\gamma$
	138.3 [136.6][d]	e	12.5[12.3]	e
	140.5 [139.1]	122.6[122.3]	14.7[14.8]	-3.2 [-2.0]
	136.6	(114.0)[f]	3.5	(-1.0)
	149.3	109.5	16.2	-5.5
	28.2	27.5	3.2	2.5
	29.9	28.9	4.9	3.9
$C_\gamma H_3C_\beta H_2CH_2B(n\text{-}Pr)_2$[g]	18.1	17.6	2.0	2.0
 $C_\gamma H_3C_\beta H_2\underset{CH_3}{CH}\overset{Li^+}{\bar{B}}(sec\text{-}Bu)_2(n\text{-}Bu)$[h]	27.1	15.2	2.1	2.0
$CH_3C_\gamma H=C_\beta HCH_3$[i]	125.8[124.3]	125.8[124.3]		
$C_\gamma H_2=C_\beta HCH_3$[i]	133.1	115.0		
$CH_3C_\gamma H_2C_\beta H_2CH_3$[i]	25.0	25.0		
 $C_\gamma H_3C_\beta H_2\underset{CH_3}{CH_2}$[i]	25.0	13.2		
$C_\gamma H_3C_\beta H_2CH_3$[i]	16.1	15.6		

[a] All spectra were assigned by noise-modulated proton decoupling. Single-freque off-resonance decoupled spectra were used to assign the resonance in questiona

Table 1. (continued)

cases. [b] In parts per million (± 0.1)(downfield positive) from Me_4Si, conver using $\delta(C_6D_6)$ 128.7. Chemical shifts of other carbons, not important in the present discussion, are omitted. [c] In parts per million with respect to the corresponding hydrocarbons (2-butene, propene, butane, and propane). Higher values correspond to lower shielding. [d] [cis isomer]. [e] Not obvious owing t the rapid allylic rearrangement. [f] Estimated value from a broad peak. [g] D. J. Hart and W. T. Ford, J. Org. Chem., 39, 363 (1974). [h] Several assumptions are made owing to the lack of an appropriate sample. For example, $CH_3CH_2(CH_3)CH-$ is used instead of $CH_3CH_2CH_2-$.  refers to 9-borabicyclo[3.3.1]nonane.

Table 2. Difference in Substituent Effect between Tri- and Tetravalent Boron Atoms[a]

Compound	Substituent		$\Delta\Delta\delta C_\beta$	$\Delta\Delta\delta C_\gamma$
$CH_3C_\gamma H{=}C_\beta HCH_2{-}B<$	Trivalent		9.3 [9.1][b]	-
	Tetravalent		9.8 [9.9][b]	-7.1 [-5.9][b]
$C_\gamma H_2{=}C_\beta HCH_2{-}B<$	Trivalent		1.5	(-3.0)[c]
	Tetravalent		14.1	-7.5

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[a] $\Delta\Delta\delta C_n = \Delta\delta C_n$ (allylic boron or borate) - $\Delta\delta C_n$ (alkylboron or borate).
[b] [cis isomer]. [c] Estimated value.

The carbon-13 chemical shifts of C_β and C_γ of allylic borons, allylic borates, alkylborons, alkylborates, olefins, and alkanes are summarized in the Table 1. The substituent effects of tri- and tetravalent boron atoms, listed in the Table 1, are obtained as previously described.[2] Table 2 summarizes the difference in substituent effect between tetra- and trivalent boron atoms. Comparison of the data leads to the following conclusions; i) the γ-carbons are shielded, while the β-carbons are deshielded by both tri- and tetravalent boron atoms; ii) the extent of the shielding and deshielding is greater in the tetravalent borons (ate complexes) than in the trivalent borons. Consequently the present work clearly indicates the relative importance of the σ-π conjugation between the $\mathrm{C{-}\bar{B}}\leqq$ bond and the π system in allylic boron "ate" complexes.[3]

Acknowledgment.

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References and Notes

1) a) Y. Yamamoto and K. Maruyama, J. Am. Chem. Soc., 100, 6282 (1978).
   b) Y. Yamamoto, H. Yatagai, and K. Maruyama, J. Chem. Soc. Chem. Commun., 157 (1979).
   c) Y. Yamamoto, H. Yatagai, and K. Maruyama, Chem. Lett., 385 (1979).
   d) Y. Yamamoto, H. Yatagai, and K. Maruyama, J. Org. Chem., 45, 195 (1980).
2) Y. Yamamoto and I. Moritani, J. Org. Chem., 40, 3434 (1975).
3) For a leading reference on σ-π conjugation on allylic organometallics and related compounds, see the following articles.
   a) G. Hartman and T. G. Traylor, Tetrahedron Lett., 939 (1975).
   b) A. Hosomi and T. G. Traylor, J. Am. Chem. Soc., 97, 3682 (1975).

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