¹³C NMR of the Tetrakis(phenylethynyl)borate Anion and of Some Phenylethynyl Boranes

Bernd Wrackmeyer

Institut für Anorganische Chemie
der Universität München,

Meiserstraße 1, D-8000 München 2

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The ¹³C NMR parameters of the title compounds are assigned by heteronuclear triple resonance experiments ¹³C{¹H,¹¹B}. The magnitude of the coupling constants $J(^{13}\text{C}^{11}\text{B})$ corresponds roughly with $J(^{13}\text{C}^{13}\text{C})$. The chemical shifts $\delta^{13}\text{C}$ reveal B–C(pp) π bonding which is, however, rather weak when compared with C⁺–C(pp) π bonding in phenylethynyl carbocations.

Indirect nuclear spin-spin coupling between sp-hybridized carbon and boron (sp³) has been observed for H₃B–C $\equiv$ O (30.2 Hz) and for H₃B–C $\equiv$ N[–] (53.0 Hz) [1]. Although a considerable number of other coupling constants $^1J(^{13}\text{C}^{11}\text{B})$ with various states of hybridisation of carbon and boron are known [2] data for alkynyl borates are still missing. Considering the quadrupole moment of the ¹¹B nucleus tetrakis(alkynyl)borates [(R–C $\equiv$ C)₄B][–] should be most suitable to obtain accurate values $J(^{13}\text{C}^{11}\text{B})$ by natural abundance ¹³C NMR spectra. Another interesting aspect is the question for B–C(pp) π interactions. The comparison of relevant $\delta^{13}\text{C}$ data for the borate with those for corresponding boranes is expected to shed some light on this problem.

Therefore, we have studied the tetrakis(phenylethynyl)borate anion (**1**) [Li⁺[(C₆H₅–C $\equiv$ C)₄B][–] · 4 THF] which was prepared by the method of Krüerke [3], and some phenylethynyl boranes (**2**, **3**) by ¹³C NMR. The data for the title compounds are given in Table I together with the data for two phenylethynyl carbocations (**5**, **6**) for comparison.

The resonances of carbon atoms linked to boron are in general severely broadened due to partially relaxed scalar coupling $J(^{13}\text{C}^{11}\text{B})$ and they are, therefore, of low intensity. The symmetric surrounding of boron in **1** is responsible for a slow quadrupolar relaxation rate and the coupling $J(^{13}\text{C}^{11}\text{B})$ is resolved as shown in Fig. 1(a). The detection of the resonances of the alkyne carbon atoms in the trigonal boron compounds **2**, **3** is severely hampered (i) by the absence of an appreciable nuclear Overhauser effect (NOE), (ii) by long longitudinal relaxa-

tion times T₁(¹³C) and (iii) by the broadening effect mentioned above. However, simultaneous decoupling of ¹H and ¹¹B(¹³C{¹H,¹¹B}) can solve this problem [2]. The efficiency of this method is shown in Fig. 1(b). It allows the unambiguous assignment of the ¹³C _{α , β} resonances in **2** and **3**.

Fig. 1. 50.3 MHz ¹³C NMR spectra of [(C₆H₅–C $\equiv$ C)₄B][–]Li⁺ · 4 THF in CDCl₃, ethynylic carbon atoms.

(a) ¹³C{¹H-broad band};

(b) ¹³C{¹¹B, ¹H-broad band}.

The magnitude of $^1J(^{13}\text{C}^{11}\text{B})$ in **1** is in accord with the dominance of the Fermi contact contribution and agrees roughly with expectations based on the increase in s-character of the B–C bond under consideration:

$^1J(^{13}\text{C}^{11}\text{B})$ [Hz]			
[(CH ₃) ₄ B] [–]	[(C ₆ H ₅) ₄ B] [–]	[(C ₆ H ₅ –C $\equiv$ C) ₄ B] [–]	
39.4 [4]	49.4 [2]	70.0	

The analogous trend is also evident for trigonal boron. The difference in the magnitude of the coupling constants $^1J(^{13}\text{C}^{11}\text{B})$ corresponds to the change in the hybridisation of boron from sp³ to sp²:

$^1J(^{13}\text{C}^{11}\text{B})$ [Hz]		
(CH ₃) ₂ B–CH ₃	(CH ₃) ₂ B–CH=CH ₂	
46.7 [2]	≤ 75 [5]	
(CH ₃) ₂ B–C $\equiv$ C–CH ₃		
≤ 110 [6]		

The behaviour of $^1J(^{13}\text{C}^{11}\text{B})$ is reminiscent of the values $^1J(^{13}\text{C}^{13}\text{C})$ [7] at least as far as the borates are concerned [8]. Interestingly this analogy also holds for $^nJ(^{13}\text{C}^{11}\text{B})$ ($n > 1$) in tetraalkyl- and in tetraphenyl borate anions [2]. Similarly, the fairly large value $^2J(^{13}\text{C}^{11}\text{B})$ (14.0 Hz) in **1** compares well with $^2J(^{13}\text{C}^{13}\text{C})$ in propyne (11.8 Hz) [7].

Tab. I. $\delta^{13}\text{C}$ - and $\delta^{11}\text{B}$ values for **1**, some phenylethynyl boranes (**2** to **4**) and phenylethynyl carbocations (**5**, **6**).

Nr.	R							$\delta^{11}\text{B}^a$
		$\text{C}_{(\alpha)}$	$\text{C}_{(\beta)}$	$\text{C}_{(\gamma)}$	$\text{C}_{(\delta)}$	$\text{C}_{(\epsilon)}$	$\text{C}_{(\zeta)}$	
—	H^b	77.8	84.0	122.7	132.3	128.5	128.8	—
1	$(\text{C}_6\text{H}_5\text{C}\equiv\text{C}-)_3\text{B}^{-c}$	102.8	94.2	125.7	131.5	127.8	126.7	—31.0
2	$[\text{CH}_2(\text{CH}_3\text{N})_2\text{B}^{e,d}]$	90.6	105.2	123.2	131.7	127.9	128.1	24.4
3	$\text{C}_6\text{H}_5\text{C}\equiv\text{C}-\text{B}^{e,e}$	94.5	105.9	123.8	132.2	128.7	129.0	22.5
	$(\text{C}_2\text{H}_5)_2\text{N}$							
4	$[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2]_2\text{B}^f$	102.4	126.9	123.4	132.5	128.4	129.7	64.0
5	$(\text{CH}_3)_2\text{C}^{+g}$	123.5	199.4	119.9	141.7	131.4	145.5	—
6	$(\text{C}_6\text{H}_5)_2\text{C}^{+g}$	105.9	159.1	119.9	138.7	130.7	137.6	—

^a To high frequency of $(\text{CH}_3)_4\text{Si}$, $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$; ^b this work, in C_6D_6 ; ^c this work, in CDCl_3 ; ^d $\delta^{13}\text{C}(\text{NCH}_3)$ 34.0, (NCH_2) 51.4; ^e $\delta^{13}\text{C}(\text{NCH}_2)$ 44.5, (CH_3) 15.6; ^f N. M. D. Brown, F. Davidson, and J. W. Wilson, *J. Organomet. Chem.* **209**, 1 (1981); ^g ref. [11].

The chemical shifts $\delta^{13}\text{C}$ of $\text{C}_{(\beta)}$ and $\text{C}_{(\text{p})}$ (Table I) should be indicative of mesomeric interactions of the phenyl ethynyl group with the substituent R. The comparison between $\delta^{13}\text{C}$ data for **1** and for phenyl ethyne is not particularly instructive. However, there are striking differences between $\delta^{13}\text{C}_{(\beta)}$ for **1** and for the trigonal boranes **2** to **4**. The decrease in the shielding of the β -carbon atom in the latter compounds can be interpreted in terms of B-C(pp) π -interactions which are not of importance in case of the borate **1**. The same arguments apply to the $^{13}\text{C}_{(\beta)}$ resonances in alkenyl boranes [2] and to the $^{13}\text{C}_{(\text{p})}$ resonances in phenyl boranes [2, 9] with respect to their adducts with Lewis bases. The $\delta^{11}\text{B}$

data of alkynyl boranes [10] and the $\delta^{13}\text{C}_{(\beta)}$ data are tempting to overestimate B-C(pp) π -interactions. This is evident by comparison of $\delta^{13}\text{C}_{(\text{p})}$ for **1** with $\delta^{13}\text{C}_{(\text{p})}$ for **2** to **4**. The small deshielding observed for $^{13}\text{C}_{(\text{p})}$ in the latter is contrasted by a large deshielding of $^{13}\text{C}_{(\text{p})}$ in the carbocations **5** and **6** [11]. It is, therefore, concluded that boryl groups are rather weak π -acceptors [12] and it should be noted that the phenyl group may also act as a π -acceptor competing with the trigonal boron for the π -electron density of the ethyne unit [13].

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