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DYNAMIC NMR SPECTROSCOPY OF TETRAVALENT ORGANOBORATE COMPOUNDS. SYNTHESIS AND SOME UNIQUE FEATURES OF ORGANOBORATES CONTAINING THE $C_6H_4CH_2NMe_2$-2 LIGAND *

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Summary

Novel borates $(ArBMe_3)Li \cdot OEt_2$ (I), $(ArBEt_3)Li \cdot OEt_2$ (II) and (BArPh-9-BBN)Li $\cdot$ OEt_2 (III) ($Ar = C_6H_4CH_2NMe_2$-2, 9-BBN = 9-borabicyclo[3.3.1]nonyl) were synthesized in the reactions of ArLi with BMe_3, BEt_3 and BPh-9-BBN, respectively. Detailed studies were made of ^1H, ^{13}C, ^{11}B NMR, IR and molecular weight measurements. For I, II and III an alkyl and/or aryl bridged structure is proposed. The following order of stability of the aryl bridges has been established: (BArPh-9-BBN)Li $\cdot$ OEt_2 > $(ArBMe_3)Li \cdot OEt_2$ > $(ArBEt_3)Li \cdot OEt_2$.

Introduction

The polynuclear organometallic compounds containing boron and lithium atoms are widely used in the field of organic chemistry. Several reviews concerning the range of their synthetical application have recently been published [1–4]. In most cases they act as strong nucleophiles and therefore they are considered to be an ion pair Li^+ BR_4^-. The BR_4^- anion is assumed to be responsible for the course of the reactions of $LiBR_4$ with electrophiles. The role of the metal cation is usually neglected. However, in the light of recent investigations of multinuclear systems, e.g. $Li_4B_4Me_8$ [5], Li_4Ar_4 [6], $Li_2Ar_2 \cdot 4THF$ [6], $Li_2Ag_2Ar_4$ [7], $Li_2Cu_2Ar_4$ [7,8], $Li_2Au_2Ar_4$ [8], having an $Ar = C_6H_4CH_2NMe_2$-2 or $C_6H_4CH_2NMe_2$-2-Me-5 ligand we presume that certain organoborate compounds should contain covalent Li–C–B bond. The borates I, II and III having the above mentioned $C_6H_4CH_2NMe_2$-2 ligand were chosen for our investigation.

Results and discussion

It has been known since 1938 [9] that organoboranes can react with organolithium compounds. This complexation reaction is considered to be a very convenient route

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* Dedicated to Prof. O.A. Reutov on the occasion of his 65th birthday.

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for the preparation of organoborates [1–4]. A suspension of aryllithium dissolves very easily in the presence of a stoichiometric amount of an organoboron compound, giving a colourless solution.

$$\mathrm{ArLi + BRR'_2 \xrightarrow[\text{room temp.}]{Et_2O} (ArBRR'_2)Li \cdot OEt_2} \qquad (1)$$

(I: $R = R' = Me$; II: $R = R' = Et$; III: $R = Ph, BR'_2 = $ 9-borabicyclo[3.3.1]nonyl, $Ar = C_6H_4CH_2NMe_2$-2)

The organoborate compounds were crystallized from ether solutions at low temperatures. The organoborates I, II and III are thermally stable white solids, which can be crystallized from diethyl ether, and are soluble in aromatic hydrocarbons, chloroform and pyridine. They are extremely sensitive to moisture, and were separated as solvate with a diethyl ether molecule. Even long drying at 323 K under vacuum does not remove the strongly coordinated ether molecules. Raising the temperature causes the formation of completely insoluble glasses, which are probably the result of polymerization processes.

Our attempts to synthesize an organoborate compound with two aryl ligands failed (eq. 2). This unreactivity of BAr-9-BBN towards ArLi is probably due to the

$$\mathrm{ArLi + BAr\text{-}9\text{-}BBN \xrightarrow{Et_2O}\!\!\!\!\!\!\!/\;\; (BAr_2\text{-}9\text{-}BBN)Li \cdot OEt_2} \qquad (2)$$

strong N → B coordination. Only a BAr-9-BBN substrate was separated from the reaction mixture.

The physical properties of I, II and III and the results of elemental analysis are listed in Table 1. The agreement between experimental and theoretical values is not good presumably because of the extremely high reactivity of the investigated compounds towards moisture (see footnotes Table 1). Molecular weight measurements in benzene show that these compounds are undissociated monomers.

^1H NMR

The structure and dynamic properties of I, II and III in noncoordinating solvents were investigated. Their ^1H NMR spectra are solvent and temperature dependent (Table 2). The presence of the $C_6H_4CH_2NMe_2$-2 ligand in the molecule allows the determination of the configuration at nitrogen and at the C(1) carbon atom of the aromatic system in solution from the spectral properties of the NCH_2 and NCH_3 protons. At low temperature the protons of both groups have nonequivalent magnetic environments. The NCH_2 protons exhibit an AB pattern and the NCH_3 protons appear as two singlets. Raising the temperature results in coalescence of both sets of signals to singlets (Fig. 1).

These changes observed as a function of temperature in the ^1H NMR spectra were assigned to the dynamic behaviour of the $C_6H_4CH_2NMe_2$-2 ligand [8]. Splitting of the NCH_3 singlet into two singlets at lower temperatures is due to the coordination of the free electron pair of nitrogen to the metal atom. It was reported that the polynuclear molecules containing the $C_6H_4CH_2NMe_2$-2 ligand can be additionally stabilized by the coordination of the free electron pair of nitrogen to the metal atom. In the compounds investigated I, II and III the free electron pair of nitrogen can coordinate either to the lithium or to the boron atom. Coordination to

(Continued on p. 125)

TABLE 1

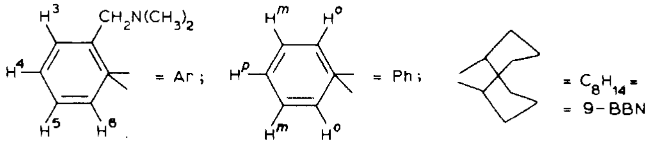
THE ANALYTICAL DATA FOR COMPOUNDS I, II AND III

Compound	Yield (%)	Colour	M.p. [a] (°C)	Analysis (Found (calcd.)(%))				M.w. [d] (Found (calcd.))	Degree of association
				C	H	N	B [c]		
$(ArBMe_3)Li \cdot OEt_2$	59	white	50–53 [e]	66.72 (70.90)	9.72 (11.45)	5.66 (5.17)	3.04 (3.95)	300.8 (270.7)	1.1
$(ArBEt_3)Li \cdot OEt_2$	51	white	55–57	68.20 (72.93)	10.67 (11.83)	5.21 (4.47)	2.61 (3.45)	289.7 (312.6)	0.93
$(BArPh\text{-}9\text{-}BBN) \cdot LiOEt_2$	60	white	162–168	72.01 (78.50)	8.95 (9.21)	3.41 (3.39)	1.9 (2.61)	454.5 (417.7)	1.1

[a] m.p. measured in a capillary under argon. [b] We assume that the results of elemental analyses differ from theoretical values because of the extremely high sensitivity of I, II and III to water, and the only available technique of measurements does not protect the compounds against exposition to air. [c] The amount of boron was found after oxidative hydrolysis by titration with NaOH in the presence of mannitol. [d] Mol-wt measured cryoscopically in benzene. [e] At about 50°C the compounds become "wet" most probably releasing ether molecules.

TABLE 2

^{1}H NMR DATA OF I, II, III, BPh-9-BBN AND BAr-9-BBN



Compound	Solvent	Temperature	δ(ppm) [a]										
			H(6)	H^o	H_{arom}	NCH_2	NCH_3	OCH_2	OCH_2CH_3	C_8H_{14} [b]	BCH_2 [c]	BCH_2CH_3 [c]	BCH_3
$ArB(CH_3)_3Li \cdot O(CH_2CH_3)_2$	$CDCl_3$	r.t.	7.86 m		6.83 m	3.80 bs	2.53 s	3.54 q	1.40 t				0.37 s
	tol-d_8	323 K	7.95 dd		6.83 m	3.42 bs	1.85 s	2.83 q	0.58 t				
	tol-d_8	r.t.	7.90 dd		6.83 m	3.41 bs	1.80 s	2.79 q	0.50 t				~ 0.13 s
	tol-d_8	243 K	7.90 dd		6.83 m	4.31 br n.o.	1.6 br 1.99 br	2.33 q	0.23 t				~ 0.13 s ~ 0.05 s
$ArB(CH_2CH_3)_3Li \cdot O(CH_2CH_3)_2$	$CDCl_3$	r.t.	8.08 dd		7.14 m	3.60 bs	1.96 s	2.21 q	0.69 t		0.89	1.20 m	
	tol-d_8	323 K	8.13 dd		7.17 m	3.58 bs	2.0 s	2.93 q	0.7 t		0.7 m	1.0 m	
	tol-d_8	r.t.	8.15 dd		7.15 m	3.55 bs	1.95 s	2.80 q	0.65 t		0.6 m	0.93 m	
	tol-d_8	223 K	8.15 dd		7.18 m	4.33 br n.o.	1.78 b	2.58 q	0.48 t		0.6 m	0.90 m	
	CH_2Cl_2	r.t.	7.83 dd		7.06 m	3.60 s	2.20 s	3.20 q	0.85 t		0.60 m	0.27 m	
$(BArPh\text{-}9\text{-}BBN)Li \cdot O(CH_2CH_3)_2$	$CDCl_3$	r.t.		7.61 m	7.27 m	3.88 s	2.66 s [d]	3.26 q	1.10 t	1.92 m			
	tol-d_8	353 K	8.38 dd	7.93 m	7.15 m	3.80	1.78 s	2.53 q	0.53 t	1.8 m			
	tol-d_8	r.t.	8.48 dd	8.03 m	7.28 m	4.85 br	1.95	2.40 q	0.45 t	2.10 m			
	tol-d_8	249 K	8.50 dd	7.88 m	7.28 m	5.03 br n.o.	2.0	2.40 q	n.o.	1.9 m			
	pyrid	r.t.	masked with solvent			3.46 s	2.00 s	3.21 q	0.87 t	2.20 m			
BPh-9-BBN	$CDCl_3$	r.t.		8.1 m	7.41 m					1.92 m			
BAr-9-BBN	$CDCl_3$		7.78 dd		7.16 m	3.97 s	2.45 s			1.8 m			
	tol-d_8		8.00 dd		7.25 m	3.38 s	2.10 s			1.9 m			

[a] δ(ppm) relative to internal TMS. [b] C_8H_{14} appears as a broad multiplet with the maximum given here. [c] Signals of ethyl groups from BR_4^- compounds appear as A_3B_2X patterns (A.G. Massey, E.W. Randall and D. Shaw, Spectrochim. Acta, 20 (1964) 379). [d] The protons of the $N(CH_3)_2$ group can interchange since they give the resonance in the range of C_8H_{14} protons.

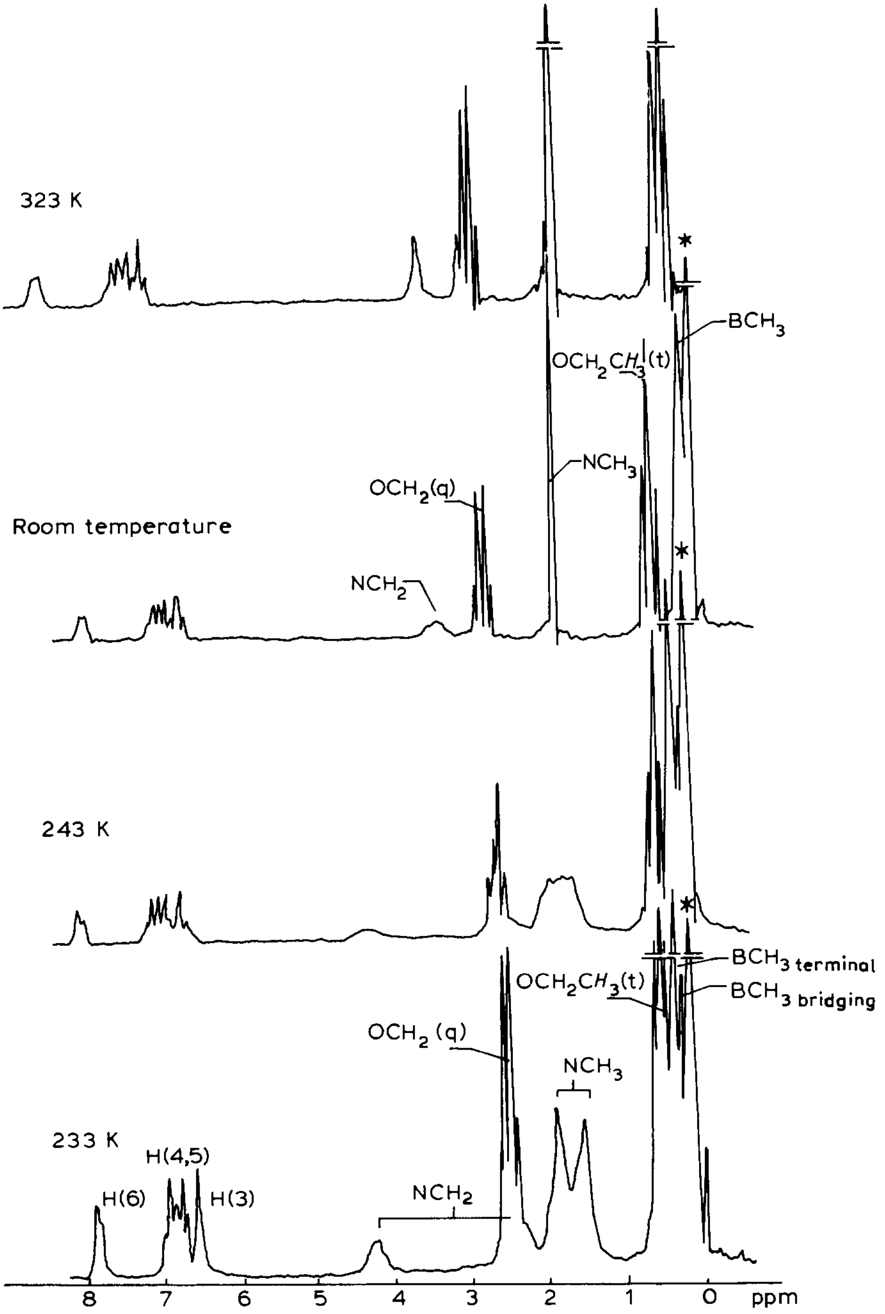


Fig. 1. ^{1}H NMR spectra (δ, ppm) of (ArBMe$_3$)Li·OEt$_2$ in toluene-d_8, at various temperatures, ★ internal TMS signal.

boron may be excluded since donor–acceptor complexes with five-coordinated boron are not known. Moreover, if the nitrogen atom were bonded to boron, the AB pattern of the NCH$_2$ protons would appear at lower fields [10,11]. Raising the

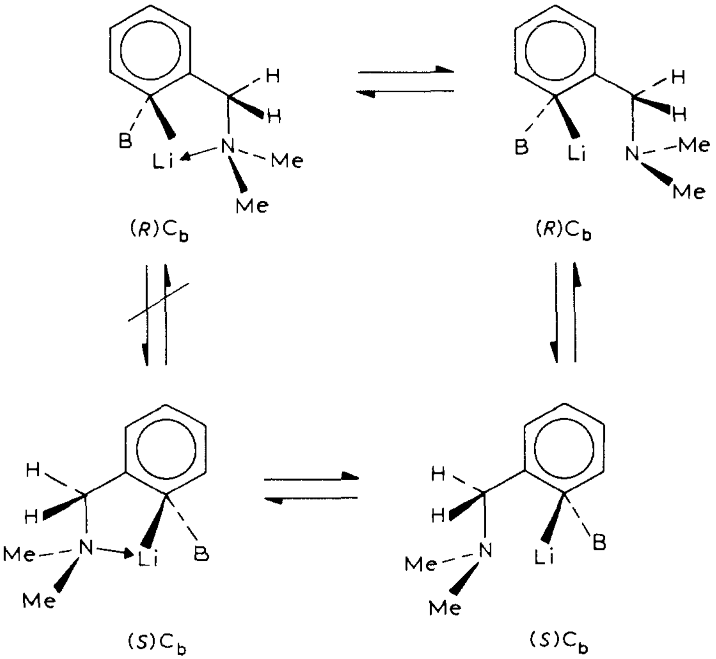


Fig. 2. The possible mechanism and sequence of the processes of Li–N dissociation and inversion at C(1).

temperature causes dissociation of a N–Li bond, simultaneous inversion of configuration at the nitrogen atom while free rotation around the C–N bond (Fig. 2) starts. Two singlets of magnetically nonequivalent methyl groups coalesce, giving a broad signal, when the rotation rate is low, and a sharp singlet, when rapid inversion occurs.

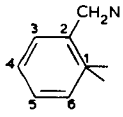
Another dynamic property of the ligand $C_6H_4CH_2NMe_2$-2 is reflected in the range of signals of NCH_2 protons in the temperature-dependent ^1H NMR spectra.

At low temperature NCH_2 protons are observed as an AB pattern, and it can be concluded that the CH_2 group is attached to a chirality center. A C(1) carbon atom from the aromatic ring bonded to two different metal atoms via a 3 center-2 electron (*3c–2e*) bond is asymmetrical. At lower temperatures the configuration around the C_{bridging} carbon is frozen and that implies that the AB resonance pattern of the NCH_2 protons is observed as a doublet of doublets. The structure with aromatic carbon bridges between the metal atoms has been confirmed for the solids of Ar_4Cu_4 [12], Ar_4Li_4 [6] and $Ar_4Cu_6Br_2$ [13]. Raising the temperature results, upon dissociation of the N–Li bond, in rapid changes of configuration at the chiral C(1) atom. Both enantiomers isomerize via an intermediate state with a planar configuration at C(1). If the inversion rate of the configuration is fast enough the CH_2 protons are observed as a singlet in the ^1H NMR spectra.

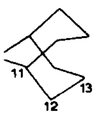
Similar spectral phenomena have been reported for $Ar_4Cu_2Li_2$ [7,8], Ar_4Li_4[6] and $Ar_4Ag_2Li_2$ [7], and were assigned to rotation around the C(1)–C(4) axis of the aromatic ring. This is achieved via an intermediate state with planar configuration at C(1), as outlined by us for boron–lithium compounds. The ^{13}C NMR spectra of the $Ar_4Ag_2Li_2$ grouping [8] provided evidence that during rotation both metal–C(1)

TABLE 3

^{13}C NMR SPECTRA OF I, II, III, BAr-9-BBN AND BPh-9-BBN



= Ar;



= C_8H_{14} = 9-BBN

Compound	δ(ppm) [a]									
	C_{arom}	C(NCH$_2$)	C(NCH$_3$)	C(7) [b]	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)
$ArB(C^7H_3)_3Li \cdot O(C^9H_3C^{10}H_3)_2$	139.92–124.69	65.5	44.54	16.7q $J(^{13}C-^{11}B)$ 39 Hz		65.16	14.03			
$ArB(C^7H_2C^8H_3)_3Li \cdot O(C^9H_3C^{10}H_3)_2$	141.2–121.6	64.97	44.6	16.0q $J(^{13}C-^{11}B)$ 38 Hz	11.63	65.6	14.19			
$(BArPh\text{-}9\text{-}BBN)Li \cdot O(C^9H_3C^{10}H_3)_2$	138.23–121.22	69.48	48.31			65.81	15.49	n.o. [c]	30.98 30.98 34.21	24.31 24.31 24.56
BAr-9-BBN	138.23–121.3	69.9	49.20					n.o.	30.68 33.98	23.99
BPh-9-BBN	134.7–128.1							n.o.	34.32	23.6

[a] In C_6D_6, concentration about 20%, δ(ppm) relative to C_6D_6. [b] Carbons in our borate compounds appear as a multiplet of broadened resonances which is due to interaction with ^{11}B($J(^{13}C-^{11}B)$ 39.7–40.8 Hz), and probably with ^7Li ($J(^{13}C-^7Li)$ 7 Hz). [c] n.o. = not observed.

bonds do not dissociate. Both coupling constants $J(^{13}C-^{7}Li)$ and $J(^{13}C-^{107}Ag)$ remain unaltered even at higher temperatures, when ^{1}H NMR spectra already show rotation. These considerations are in agreement with the semi-empirical MNDO calculations performed for alkyllithium [14] and aryllithium compounds [15]. It has been calculated that planar configuration at C(1), required for the rotation around the C(1)–C(4) axis is more stable than tetrahedral configuration.

Comparison of the coalescence temperatures of the AB patterns of I, II and III (233 K, 163 K and 263 K, respectively) shows that the stability of the aryl bridges decreases in the order: $(BArPh\text{-}9\text{-}BBN)Li \cdot OEt_2 > (ArBMe_3)Li \cdot OEt_2 > (ArBEt_3)Li \cdot OEt_2$. This sequence shows that the stability of the aromatic carbon bridges has to be considered together with the stability of the BC_2Li core (Fig. 6), depending also on the stability of the second carbon bridge in the borate molecule. The spectra of I provides evidence (Fig. 1) that the B and Li atoms are not only bonded by a C(1) aromatic bridge but also by a methyl bridge. At 243 K two singlets for BCH_3 protons are visible which were assigned to bridging and terminal methyl groups, respectively. At room temperature only one slightly broadened signal is visible, which means that the exchange process of the methyl groups bonded to boron takes place.

The spectra of II and III are not so clear because of the complicated nature of the 9-BBN and BPh protons (see footnotes, Table 2). Nevertheless we propose an alkyl bridge in II and a phenyl bridge in III.

Comparison of the stability of an aryl bridge in the LiC_2B core and the multinuclear $Ar_4M_2Li_2$ ($M = Cu^I$, Ag^I, Au^I) shows that the LiC_bB bridge is the least stable. The coalescence temperatures of the NCH_2 protons are 233, 163 and 263 K for I, II and III, 363 K for $Ar_4Cu_2Li_2$, and $Ar_4Ag_2Li_2$ and 353 K for $Ar_4Au_2Li_2$, respectively.

Finally from ^{1}H NMR spectra we deduce that at low temperatures I, II and III have the boron and lithium atoms bonded via two carbon bridges and are additionally stabilized with the acceptor–donor bond formed between nitrogen and lithium. Raising the temperature results in exchange of the alkyl groups bonded to boron, and rotation of the aryl ring around C(1)–C(4) axis upon dissociation of the $N \rightarrow Li$ bond.

^{13}C NMR

In the ^{13}C NMR spectra large similarities between compounds I and II and between III and BAr-9-BBN were observed. The ^{13}C NMR data are compiled in Table 3.

For I and II a very similar complicated signal at about 17 ppm was observed (Table 3, Fig. 3). This signal is split with one coupling constant about 38 Hz and the other one, observed rather as a broadening, which cannot be exactly deduced from the spectra measured with a frequency of 24.07 MHz.

It has been assigned to the aliphatic α-carbon C(7) atoms bonded either to boron or to boron and lithium via a *3c–2e* bond. The ^{13}C nucleus couples with ^{11}B ($J(^{13}C-^{11}B)$ 38–41Hz) and ^{7}Li ($J(^{13}C-^{7}Li)$ 7Hz). The aromatic C(1) carbons were not observed.

The resonance of the NCH_2 and NCH_3 carbons appear very close to the resonance of the parent amine. Only the carbons of the NCH_2 and NCH_3 groups of III are deshielded by about 4 ppm compared to I and II.

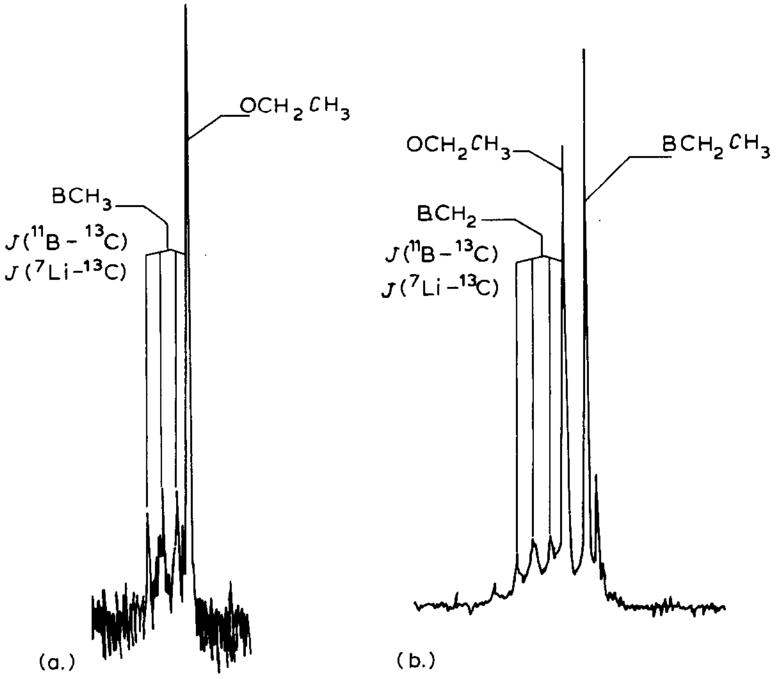


Fig. 3. ^{13}C NMR spectra (a) of I and (b) of II in the region of $C_{bridging}$ carbons. Chemical shifts are listed in Table 3.

The compound containing 9-borabicyclo[3.3.1]nonyl shows resonance signals at 24.56, 24.31, 30.98 and 39.21 ppm assigned to the carbons of the bicyclic aliphatic ring. This set of signals is strikingly similar to the peaks of BAr-9-BBN. The comparison of the spectra of BPh-9-BBN, BAr-9-BBN and (BArPh-9-BBN)Li · OEt$_2$ leads to the conclusion that the peaks at 30.68 and 34.98 ppm should be assigned to the β-carbons of the aliphatic ring numbered C(12), instead of to the NCH$_3$ carbons, as was previously been reported [11]. Two different pairs of the C(12) carbons can be found in compounds III and BAr-9-BBN in the presence of the $C_6H_4CH_2NMe_2$ ligand. In molecule III the carbons above the LiC$_2$B plane, under the strong influence of the CH$_2$NMe$_2$ substituent field differ from those below the plane (Fig. 4), analogically, in BAr-9-BBN two carbons neighbouring the CH$_2$NMe$_2$ substituent above the BC$_3$ plane, differ from those below.

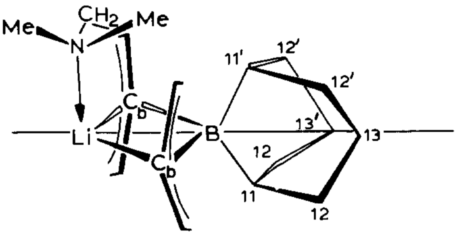


Fig. 4. The fragment of III containing the LiC$_{b2}$B core and the 9-BBN ligand with respect to the CH$_2$NMe$_2$ substituent.

TABLE 4

^{11}B NMR CHEMICAL SHIFTS OF CHOSEN ORGANOBORON COMPOUNDS

No	Compound	δ(ppm) [a]
1	BEt_3	86.5 [11]
2	BPh-9-BBN	80.35
3	BPh_3	68
4	BAr-9-BBN	7.48
5	$(ArBEt_3)Li \cdot OEt_2$	−12.8
6	$(BArPh\text{-}9\text{-}BBN)Li \cdot OEt_2$	−12.85

[a] $BF_3 \cdot OEt_2 = 0$ ppm; in C_6D_6.

^{11}B NMR

The resonance of ^{11}B for I and II was found at −12.8 ppm. This signal is strongly shifted to higher fields compared to the resonance of trivalent borane compounds (Table 4). It is reported that this phenomenon can be used as a tool for distinguishing between *sp*^{2} and *sp*^{3} organoboron species [16].

The difference between the chemical shifts of the trialkylborane compounds and the tetravalent organoborates is 100 ppm. This value is extremely high in comparison with the difference between the chemical shifts of BEt_3 and BPh-9-BBN or BPh_3 (Table 4). The presence of one aromatic ring in the molecule results in an upfield shift of about 6 ppm. The BPh_3 molecule with three phenyl rings has its resonance shifted about 16 ppm to higher fields with respect to BEt_3. If an aromatic ring contains a substituent with coordinating properties e.g. CH_2NMe_2, a resonance of ^{11}B is observed at 7.48 ppm. (see also ref. 17). The electron density on the boron nucleus in this compound is enriched due to coordination of the electron pair of nitrogen to the boron atom.

In this case II and III have boron atoms with the largest negative charge. This phenomenon confirms our proposal of a four coordinated *sp*^{3} boron atom.

TABLE 5

FT IR SPECTRA [a] OF II AND III IN THE RANGE 2700–2900 cm^{-1}

$(ArBEt_3)Li \cdot OEt_2$	$(BArPh\text{-}9\text{-}BBN)Li \cdot OEt_2$	$(BBu_4)Li$ [18]
2716.1 vw		2770
	2790w	
	2810	
	2817.9	
2820.5		
	2829.7	
	2832.9	
	2864.3	
		2870
	2916.2	
		2940

[a] Spectra were recorded in an fluorinated oil mull.

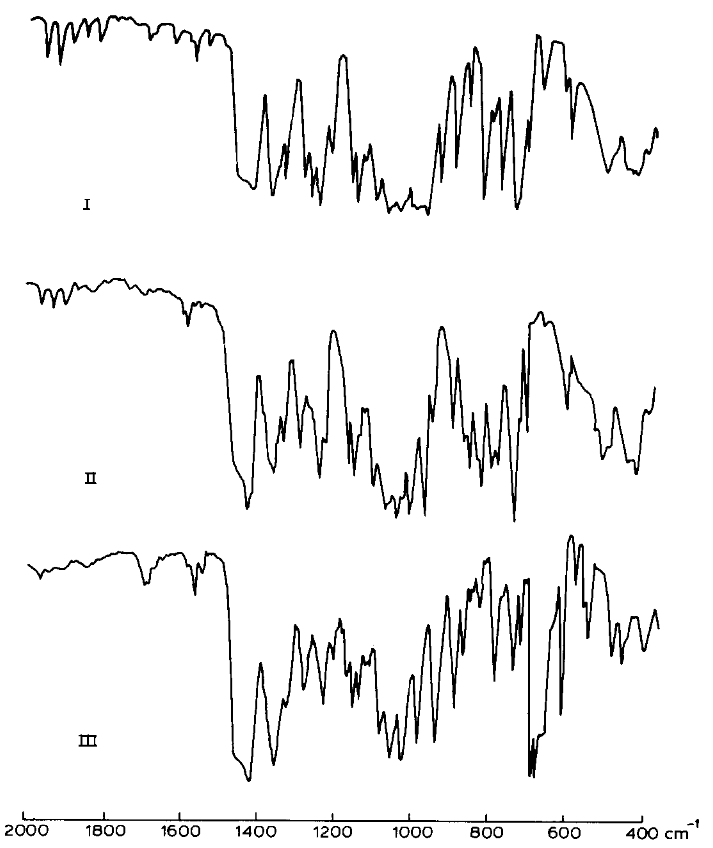


Fig. 5. The IR spectra of I, II and III in the range 2000–400 cm^{-1}, Nujol mull in polyethylene bags.

IR

The IR spectra of borates I, II and III (Fig. 5) were recorded in the range 4000–400 cm^{-1} and they were carefully examined for II and III in the range 2700–2900 cm^{-1} by means of FT IR spectroscopy. It was reported by Damico [18] for $Li(BR_{4-n}R'_n)$ (R, R' = Et, Bu) that the C–H bands are shifted about 100–150 cm^{-1} to lower values from typical C–H frequencies. They have been assigned to vibrations of the carbon–hydride hydrogen bond [19]. For compounds II and III only weak and very weak peaks at 2716vw and 2790w cm^{-1} were observed (Table 5). It leads to the conclusion that for II and III, electron transfer to H_α (with respect to boron) is negligible.

Conclusions

The measurements show that the following formulas: $(ArBMe_3)Li \cdot OEt_2$, $(ArBEt_3)Li \cdot OEt_2$ and $(BArPh\text{-}9\text{-}BBN)Li \cdot OEt_2$ can be assigned to compounds I, II and III, respectively. In non-coordinating solvents they exist as monomeric species. The multinuclear magnetic resonance measurements show that the borate molecules with a $C_6H_4CH_2NMe_2$-2 ligand contain a BC_2Li core with carbons bounded to

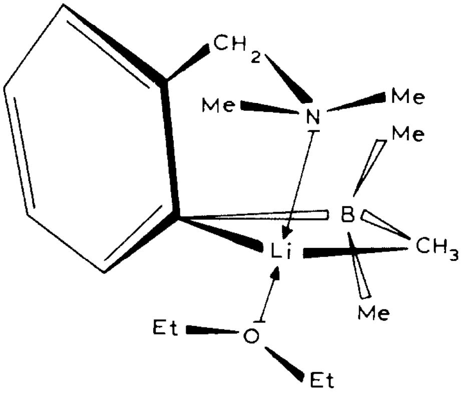


Fig. 6. The proposed structure of the $(ArBMe_3)Li \cdot OEt_2$ molecule.

boron and lithium via *3c–2e* bonds. Both metals are four coordinated. Four positions around the boron atom are occupied by two σ bonds and two electron deficient bonds. In the case of the lithium atom two coordination sites are occupied by two electron deficient bonds, the others are occupied by acceptor–donor N → Li and O → Li (coordination of the Et_2O molecule) bonds. These coordinations are stable and can easily be observed at low temperatures. Raising the temperature causes dynamic processes to begin (1) dissociation of the N–Li coordinative bond; (2) inversion of configuration at the nitrogen atom; (3) free rotation around the N–C bond; (4) inversion of configuration at the C(1) carbon atom, which probably proceeds via a planar intermediate configuration around C(1).

The proposal for the structure of the organoborates containing the $C_6H_4CH_2NMe_2$-2 ligand is shown in Fig. 6. Compound I has been chosen as a model for this drawing.

The dynamic model of this type of borate leads us to the assumption that the reactions with electrophiles can proceed via a different pathway than the attack of a BR_4^- anion at the electron deficient site. It may be assumed that in some cases the first step of the reaction is exchange of donors at the lithium atom, formation of donor–acceptor complexes with lithium and then anchorage of a substrate is followed by intramolecular rearrangement.

Experimental

All experiments were carried out under deoxidized and dried argon. Solvents were deoxidized and dried prior to use.

The elemental analyses for C, H, N were performed using a Perkin–Elmer 240 apparatus, IR spectra were recorded with a Perkin–Elmer 527 spectrometer in Nujol mulls. FT IR spectra were recorded with a NICOLET 7199 B FT-IR Interferometer with a liquid nitrogen cooled Hg, Cd, Fe detector. ^1H NMR spectra were recorded with JNM-100-H (JEOL) and Tesla 80 MHz spectrometers, ^{13}C NMR spectra were recorded with a Varian 100 MHz spectrometer, ^{11}B NMR spectra were recorded with a Bruker WM 250 apparatus.

$Li_4[C_6H_4CH_2NMe_2\text{-}2]_4$ was synthesized as reported by Noltes et al. [12,20]. BAr-9-BBN was synthesized as previously described [11] and 9-BBN was synthesized at the Max-Planck-Institute in Mülheim (F.R.G.).

Preparation of $(ArBMe_3)Li \cdot OEt_2$. BMe_3 was generated [21] in a reaction apparatus immediately before use. A suspension of $AlCl_3$ (3.2 g, 0.016 mol) and of B_2O_3 (2.14 g, 0.030 mol) in $Me_3Al_2Cl_3$ (15 g 0.074 mol) was heated with a reflux condenser. Me_3B evolved from the reaction mixture and was passed through a dry ice/acetone trap to a suspension of ArLi (2.9 g, 0.021 mol) in Et_2O, during a period of 3 h. Then the amount of Me_3B which condensed in the trap was slowly distilled into the suspension of ArLi, which dissolved. The apparatus was flused with Ar and an excess of Me_3B burnt in the air. The reaction was performed with extreme caution because of the inflammable and explosive properties of Me_3B.

Preparation of $(ArBEt_3)Li \cdot OEt_2$. To ArLi (3.5 g, 0.025 mol) in Et_2O (50 ml), a solution of BEt_3 (25 ml, 0.1 *M*) in hexane was added dropwise during 20 min. The reaction mixture immediately becomes clear. The reaction mixture was concentrated to 50% of the starting volume. Then the mixture was cooled to −78°C and a white solid precipitate crystallized. The white solid was separated, washed three times with cold diethyl ether and dried in vacuo. The solid was identified as compound II.

Preparation of BPh-9-BBN: BPh-9-BBN was synthesized according to a modified procedure reported by Brown et al. [22]. In the first stage PhLi was prepared in an equimolar reaction of PhI with BuLi/hexane and separated from the reaction mixture, then a suspension of PhLi (2.1 g/0.025 mol) in Et_2O (10 ml) was added dropwise to a solution of 9-BBN (3.06 g, 0.025 mol) in THF (40 ml) at 0°C. CH_3SO_3H (1.6 ml) was then added dropwise by means of a syringe. The approximately stoichiometric amount of H_2 evolved; the salt was allowed to settle and the clear solution was transferred to a distillation flask. BPh-9-BBN was separated as a viscous colorless oil and its purity was checked by ^1H NMR. Yield 81%.

Preparation of $(BArPh\text{-}9\text{-}BBN)Li \cdot OEt_2$. To a suspension of ArLi (1.61 g, 0.011 mol) in Et_2O (40 ml), a solution of BPh-9-BBN (2.32 g, 0.011 mol) in 30 ml of Et_2O was added dropwise. Then the procedure described above for II was applied.

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