The Haloboration of Tri-*tert*-butylazadiboriridine NB_2R_3: Ring Opening versus NB_3 Cluster Formation

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Dedicated to Professor Heinrich Vahrenkamp on the Occasion of his 60th Birthday

Abstract. The azadiboriridine [–BR–NR–BR–] (**1**; R = *t*Bu) is bromoborated at the B–B bond by alkyldibromoboranes R′BBr_2 to give the products Br–BR–NR=BR–BR′–Br (**8a–g**: R′ = Me, Bu, *i*Bu, Bzl, CH_2CHEt_2, CH_2Cy, $CH_2(4\text{-}C_6H_4t\text{Bu})$). Two isomers of each of the products **8a–g** are formed and attributed to a *cis*/*trans* isomerism at the BN double bond; the isomerization is followed thermodynamically and kinetically by NMR methods with **8a–d**. The analogous chloroboration of **1** with BCl_3 yields Cl–BR–NR=BR–BCl_2 (**8h**), which at ambient temperature undergoes a degenerate exchange of the ligands Cl and BCl_2 along the B–N–B skeleton. At room temperature, the isomer Cl–BR–NR=BCl–BR–Cl (**8h′**) is slowly formed by an irreversible exchange of R and Cl along the B–B bond of **8h**. Different from BCl_3, the chloroborane BH_2Cl is simply added to the B–B bond of **1** under formation of the aza-*nido*-tetraborane $NB_3R_3H_2Cl$ (**2b**). The chloroborane $BHCl_2$ gives a mixture of **8h′** and **2b** upon addition to **1**, apparently according to a preceding dismutation into BCl_3 and BH_2Cl. The configuration at the B3 atom of the *nido*-clusters $NB_3R_3H_2X$ (X = H, Cl) is discussed on the basis of the corresponding model molecules $NB_3Me_3H_2X$, whose structure and NMR signals are computed by the B3LYP method. The boranes **8b–g** can be debrominated with Li in the presence of tmen on applying ultrasound. The products are found to be the B-borylated azadiboriridines [–BR–NR–B(BRR′)–] (**9b–g**). The 2-borylazadiboriridines NB_3H_4 (**9h**) and NB_3Me_4 (**9i**) were found as local minima on the energy hyperface by the B3LYP method, but minima for structural isomers with lower energy were also found; the tetrahedral clusters NB_3R_4 give high-energy minima with triplet ground states. Computations of the ^{11}B NMR shifts of **9h** and **9i** support the proposed structures of **9b–g**.

Keywords: Boron; Azadiboriridine; Haloboration; Azatetraboranes; *exo*/*endo* Configuration; Ab initio computations

Die Haloborierung von Tri-*tert*-butylazadiboriridin NB_2R_3: Ringöffnung oder Bildung von NB_3-Clustern

Inhaltsübersicht. Das Azadiboriridin [–BR–NR–BR–] (**1**; R = *t*Bu) läßt sich mit Alkyldibromboranen R′BBr_2 an der B–B-Bindung unter Bildung der Produkte Br–BR–NR=BR–BR′–Br (**8a–g**: R′ = Me, Bu, *i*Bu, Bzl, CH_2CHEt_2, CH_2Cy, $CH_2(4\text{-}C_6H_4t\text{Bu})$) bromoborieren. Zwei Isomere werden für jedes der Produkte **8a–g** beobachtet und einer *cis*/*trans*-Isomerie an der BN-Doppelbindung zugeschrieben; im Falle von **8a–d** wurde die Isomerisierung mit NMR-Methoden kinetisch und thermodynamisch verfolgt. Die analoge Chloroborierung von **1** mit BCl_3 ergibt Cl–BR–NR=BR–BCl_2 (**8h**), das bei Raumtemperatur einem entarteten Austausch der Liganden Cl und BCl_2 entlang dem B–N–B-Gerüst unterliegt. Bei Raumtemperatur bildet sich aus **8h** langsam das Isomere Cl–BR–NR=BCl–BR–Cl (**8h′**) durch einen irreversiblen Austausch von R und Cl entlang der B–B-Bindung von **8h**. Anders als BCl_3 addiert sich das Chlorboran BH_2Cl lediglich an die B–B-Bindung von **1**, wobei das Aza-*nido*-tetraboran $NB_3R_3H_2Cl$ (**2b**) gebildet wird. Das Chlorboran $BHCl_2$ ergibt bei der Addition an **1** eine Mischung von **8h′** und **2b**, der offenbar eine Dismutierung von $BHCl_2$ in BCl_3 und BH_2Cl vorausgeht. Die Konfiguration am Atom B3 der *nido*-Cluster $NB_3R_3H_2X$ (X = H, Cl) wird auf der Grundlage von Modellmolekülen $NB_3Me_3H_2X$ diskutiert, deren Struktur und NMR-Signale mit dem B3LYP-Verfahren berechnet wurden. Die Borane **8b–g** können mit Li in der Gegenwart von tmen und unter Anwendung von Ultraschall debromiert werden; dabei entstehen die B-borylierten Azadiboriridine [–BR–NR–B(BRR′)–] (**9b–g**). Die 2-Borylazadiboriridine NB_3H_4 (**9h**) und NB_3Me_4 (**9i**) wurden mittels der B3LYP-Methode als lokale Minima auf der Energiehyperfläche gefunden, allerdings neben den Minima geringerer Energie von Isomeren anderer Struktur; die tetraedrisch gebauten Cluster NB_3R_4 entsprechen Minima hoher Energie mit Triplett-Grundzustand. Die für **9h** und **9i** berechneten NMR-Verschiebungen bestätigen die für **9b–g** angenommene Struktur.

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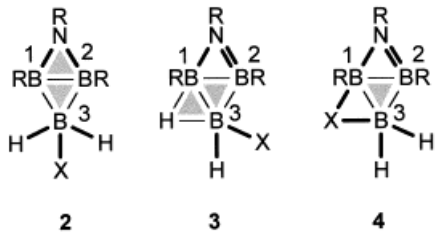
Introduction

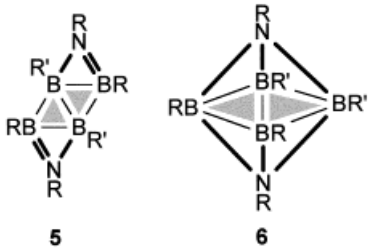
The azadiboriridine NB_2R_3 (**1**; R = *t*Bu) adds Lewis acids A across its basic B–B bond under formation of a bent bicyclic NB_2A skeleton [1]. In terms of localized molecular orbitals, the B–B (2c2e) σ-bond of **1** is transformed into a (3c2e) BBA σ-bond. The octet rule is obeyed, when a (3c2e) BNB π-bond is present in NB_2R_3 as well as in the adduct NB_2R_3A, but the π-bonding in the adduct is mixed with some σ-bonding because of the bent NB_2A skeleton.

In the case of boranes XBH_2 as the Lewis acids A, three types of adducts have been observed: the simple adduct **2** (X = H: **2a**) [2], the H-bridged adduct **3** (X = Ph, *s*Bu) [3], and the X-bridged adduct **4** is formed, when a lone pair is available at X (X = NHPr, NH*t*Bu, NMe_2, NEt_2, SPr) [3, 4]. The ^{11}B NMR signals had turned out to be characteristic for each of the three types (Table 1). Note that the (3c2e) BNB π-bond in **1** and **2** must be replaced by a (2c2e) BN π-bond in **3** and **4** in order to meet the octet rule.

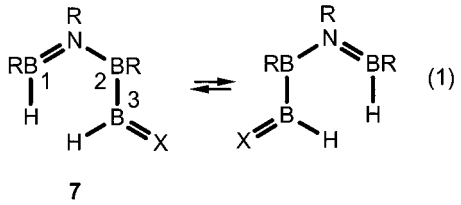


Equilibria between type **2** and **3** adducts were detected in solution with X = alkyl R′ (R′ = Me, *t*Bu, CMe_2CHMe_2) [3] and also between a type **2** and **4** adduct with X = SPh [4]. The type **3** compound $NB_3H_2R_4$ (R = *t*Bu) was crystallized from the mixture at low temperature and structurally analyzed; upon dissolving, the equilibrium mixture was promptly formed again [3].

Azadiboriridines NB_2R_2R', in which at least one group R = *t*Bu is replaced by a stericly less demanding group R′, are unstable with respect to a dimerization. The B–B bond of one molecule NB_2R_2R' is attacked by the BR′ moiety of a second molecule, which acts as the Lewis acid, followed by the same reaction of the two starting molecular units with reversed roles, giving finally the tetracyclic molecule **5** (R′ = CH_2CMe_3) [5]. With a series of ligands R′ (e. g. R′ = *i*Pr), the product **5** may undergo an antarafacial intramolecular (2 + 2) cycloaddition at the two BN double bonds to yield the *nido*-cluster **6** in a sterospecific way [5–7].



Finally, a Lewis acid XBH_2 with a stericly demanding and π-electron donating group X might completely open the B–B bond of **1** to yield a B–N–B–B–X open-chain product of type **7**; the degenerate rearrangement (1) was observed by NMR measurements at elevated temperature, which includes an exchange of the groups H and BHX along the B–N–B chain (X = N*i*Pr_2) [3].



In the present paper, we first report on the reaction of **1** with haloboranes and discuss the products in terms of the above mentioned products **2**, **3**, **4**, and **7**, using NMR spectra as the source of structural information (Table 1). We then discuss the configuration of the atom B3 in type **2** and **3** products, making use of density functional calculations on model molecules. Final-

Table 1 ^{11}B NMR shifts of the atoms B1, B2, B3 in the cluster molecules **2**, **3**, **4**, **7** [2–4]

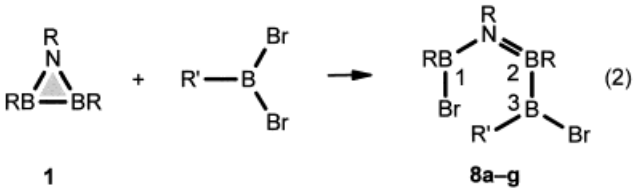
2	X	H	Me	*t*Bu	CMe_2CHMe_2		SPh
	B1, B2	32.9	29.0	28.0	27.6		29.6
	B3	–14.1	–2.6	6.8	8.0		–3.4
3	X	Me	*t*Bu	CMe_2CHMe_2		Ph	*s*Bu[a]
	B1	22.6	22.6	24.7		20.7	24.3/24.7
	B2	32.5	38.7	40.1		31.7	31.6/31.6
	B3	1.9	12.8	8.0		6.0	3.3/4.5
4	X	SPh	SPr	NHPr	NH*t*Bu	NMe_2	NEt_2
	B1	2.6	–0.9	–0.8	–7.7	–6.1	–5.3
	B2	35.4	34.5	37.4	38.9	37.1	36.7
	B3	–22.1	–20.3	–22.4	–27.4	–15.7	–17.5
7	X	N*i*Pr_2 (65 °C)		N*i*Pr_2 (–10 °C)			
	B1, B2	34.4		30.4, 41.0[b]			
	B3	45.1		44.6			

[a] Diastereomers. [b] Assignment B1/B2 uncertain.

ly, we report on molecules NB_3R_3R', formed from the bromoboration products by debromination, and again we discuss the structure by comparing to computed models.

Reaction of NB_2R_3 with Bromoboranes $R'BBr_2$

Dibromoorganoboranes give a quantitative 1 : 1 addition to NB_2R_3 (**1**) under opening of the B–B bond [Eq. (2)].



1 **8a–g**

	R'		R'
8a	Me	**e**	CH_2CHEt_2
b	Bu	**f**	CH_2Cy
c	*i*Bu	**g**	$CH_2(4\text{-}C_6H_4t\text{Bu})$
d	Bzl		

Upon mixing the components at –78 °C, an intermediate product of unknown structure is formed, that exhibits a single broad ^{11}B NMR signal at ca. 54 ppm. It is transformed into the products **8** after hours at room temperature or, in the case of **8c**, **e**–**g**, in refluxing pentane. The raw material is obtained with ca. 95% yield in a purity of more than 90%, according to the NMR spectra. The products **8a**, **c**, **d** are pure after crystallization from hydrocarbons at –78 °C, and the thermally most stable among the products, **8b**, can be purified by high vaccuo condensation at 120 °C. Long-term storing is only possible at low temperature.

Two sets of ^1H and ^{13}C NMR signals are observed with intensities that depend on temperature. This points to an equilibrium between isomers. We observed the ^1H and ^{13}C NMR spectra in [D_8]toluene (ca. 0.25 mol/l) in the temperature range –40 to 35 °C (**8a**), –10 to 70 °C (**8b**), and 24 to 90 °C (**8c**, **d**); lower temperatures than the mentioned ones make the isomerization too slow for reaching the equilibrium state within reasonable time. Equilibrium constants can be concluded from the intensity ratios at different temperatures. The isomerization is endothermic and endotropic when going from the majority to the minority isomer. The corresponding $\Delta H/\Delta S$ values are (in kJ mol^{-1} and J mol^{-1}, respectively): 4.7/7.7 (**8a**), 3.5/6.6 (**8b**), 3.6/3.6 (**8c**), and 2.9/8.1 (**8d**).

The structures of **8a–g** are deduced from the NMR spectra. The NMR signals of the Br(R)B–N(R)–B(R)–BBr– fragment, common to all members of **8a–g**, are presented in Table 2, those of the varying R′ fragments in Tables 3 and 4. The assignment of the R′ NMR signals is straight forward, in accordance with general experience. Noteworthy is that the two methylene protons of *i*Bu, Bzl and $CH_2(C_6H_4t\text{Bu})$ (**8c**, **d**, **g**; Bzl = Benzyl) are not equivalent (^1H NMR); the same is true for the methyl groups of *i*Bu (**8c**), the ethyl groups of CH_2CHEt_2 (**8e**), and the CH_2 couples 2/6 and 3/5 of Cy (**8f**; Cy = Cyclohexyl) (^{13}C NMR). The ^{11}B NMR signals are found at about $\delta = 64$, 42, and 88. These are assigned to the atoms B1, B2, B3 in the chain Br–B1(R)–NR=B2(R)–B3(R′)–Br. The formulation of a single bond B1–N implies that the bond planes around B1 and N should be almost orthogonal to one another. A comparable situation had been assumed for diborylamines Hal–B1(R′)–N(R″)–B2(R‴)–Hal with stericly demanding organic groups, exhibiting ^{11}B NMR signals for B1 of about $\delta = 64$ [7]. The signal assigned to B2 of **8** can be compared to the signal of B2 in H–NR=B(2)(R)–B(3)(R)–Br (R = *t*Bu) at $\delta = 47.5$ [8], whereas the signal assigned to B3 of **8** fits to the signal $\delta = 88.0$ of Br–BR–BR–Br (R = *t*Bu) [9]. Moreover, the atoms B2 and B3 are related by cross-peaks in the 2 D-$^{11}B/^{11}B$ NMR spectra, detected at 80 °C in [D_8]toluene with **8a–d**. (Half widths of 500–900 Hz of the ^{11}B NMR signals of **8** hinders the observation of 2 D peaks at room temperature.)

Table 2 ^1H, ^{11}B, and ^{13}C NMR shifts of the Br(R)B–N(R)–B(R)–BBr– fragment of both isomers of **8a–g** at 24 °C (majority isomer noted first)

	8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**
$^1H(R)^{a)}$	1.14/1.16	1.15/1.17	1.13/1.16	0.77/0.87	1.13/1.12	1.12/1.11	1.10/1.16[b)]
$^1H(R)^{a)}$	1.09[c)]	1.12/1.13	1.11/1.12	1.11/1.05	1.15/1.18	1.13/1.16	1.17/1.21
$^1H(R)^{a)}$	1.18/1.19	1.20/1.22	1.21/1.22	1.16/1.12	1.22/1.24	1.22/1.25	1.25/1.26
^{11}B(B1)	64.7	64.6	64.2	63.9	63.8	64.0	63.9
(B2)	42.7	42.5	42.3	40.9	42.0	42.2	40.6
(B3)	87.6	88.4	89.2	86.3	89.8	89.5	87.0
$^{13}C(Me)^{a)}$	29.41/29.32	29.29/29.33	29.13/29.32	29.26/28.94	29.28/29.25	29.21/29.29	28.94/29.28[b)]
$^{13}C(Me)^{a)}$	29.36[c)]	29.53/29.73	29.38/29.23	29.79/29.55	29.32/29.35	29.31/29.34	29.66/29.85
$^{13}C(Me)^{a)}$	32.83/33.02	32.68/32.82	32.56/33.00	32.25/32.52	32.67/33.01	32.56/32.99	32.16/32.50
(NC)[d)]	58.56/58.70	59.49/58.65	58.30/58.48	58.66/58.57	58.27/58.54	58.29/58.45	58.53/58.64

[a)] No assignment of R to B1, B2, N possible. [b)] Because of the isomer ratio 1 : 1, the three signal couples for R in **8g** are noted in the order of increasing shift values without assignment to isomers. [c)] Broad signals, close to coalescence. [d)] ^{13}C NMR signals of BC not detected.

The opening of the B–B bond of **1** by bromoboration, according to Eq. (2), is comparable to the mentioned formation of **7** by hydroboration of **1** with H–BHN*i*Pr$_2$, but the B=N double bond seems to be in a different position: B1 = N in **7**, but N=B2 in **8**, presumably caused by differences in the steric situation.

Table 3 ^{1}H NMR shifts of the groups R′ of both isomers of **8c**, **d**, **g**[a] (majority isomer noted first)

8c	**8d**	**8g**
–CH_2CHMe_2	–CH_2Ph	–$CH_2C_6H_4R$
dd mc d	d m	d m s
1.66/1.67 dd[b]	2.81/2.73 d[c]	2.74/2.85 d[d]
1.14 (dd)[e]	3.04/3.04 d[c]	3.06/3.08 d[d]
2.13 mc	6.95–7.22 m	7.09–7.30 m
1.02/1.03 d		0.77/0.91 s

[a] In addition **8a**: δ = 0.98/1.00 (s); **8b**: δ = 0.80–1.78; **8e**: δ = 0.8–1.9; **8f**: δ = 0.8–2.1. [b] ^2J = 16.0/17.0 Hz, ^3J = 9.5/9.5 Hz. [c] ^2J = 16.2/16.8 Hz. [d] ^2J = 16.5/16.5 Hz; the four doublets of **8g** are noted arbitrarity without assignment to isomers (1 : 1 ratio). [e] Hidden under *t*Bu peak, but observable as 2 D-^{1}H/^{1}H cross-peak with δ = 1.66, 1.67.

Table 4 ^{13}C NMR shifts of the groups R′ of both isomers of **8b–g** (majority isomer noted first)

8b[a]	**8c**	**8d**[a]
–$CH_2CH_2CH_2Me$	–CH_2CHMe_2	–$CH_2C(CHCH)_2CH$
t t q	br d q	s d d d
30.64/30.95 t	40.16 br	142.66/143.00 s
22.60/26.57 t	28.39/28.46 d	125.15/124.88 d
14.00/14.16 q	25.53/25.63 q	128.93/128.63 d
	27.36/27.20 q	128.93/129.19 d

8e[a]	**8f**	**8g**[b]
–$CH_2CH(CH_2Me)_2$	–$CH_2CH(CH_2CH_2)_2CH_2$	–$CH_2C(CHCH)_2CCMe_3$
d t q	br d t t t	br s d d s s q
40.40/40.94 d	38.47 br	25.09 br
28.53/28.74 t	37.98/38.02 d	34.25/34.28 s
28.83/29.03 t	26.55/26.55 t	139.67/139.93 s
11.10/11.20 q	26.75/26.92 t	147.38/147.70 s
11.31/11.49 q	27.05/27.23 t	125.53/125.90 d
	36.35/36.38 t	128.56/128.92 d
	37.73/37.70 t	31.55/31.55 q

[a] ^{13}C NMR signal of BC not detected. [b] Notation of shift couples with increasing values and without assignment (1 : 1 isomer ratio).

Table 5 Coalescence temperature T_c (°C), shift difference $\Delta\nu$ (Hz) of isomers at –80 °C, equilibrium constants K at T_c, and free activation enthalpies $\Delta G^{\#}$ (kJ mol^{-1}) in both directions of the isomerization of **8a** with respect to four selected chemical shifts δ (measured at T_c)

	T_c	$\Delta\nu$	K	$\Delta G^{\#}$
$\delta(^1H)$ = 1.18	45	17.5	2.34	70.9/68.6
$\delta(^1H)$ = 0.99	50	33.0	2.28	70.2/68.0
$\delta(^{13}C)$ = 68.63	50	30.4	2.28	71.4/68.3
$\delta(^{13}C)$ = 32.99	57	38.3	2.19	71.2/69.2

There are at least four reasonable possibilities how the structures of the two isomers of **8** could be described. An exchange of Br and BR′Br along the B1–N–B2 chain of **8**, corresponding to the H/BHX exchange of **7**, can be excluded, because the isomerization would then be degenerate with K = 1 at any temperature. a) An exchange of Br and the amino group NR(BRBr) along the B2–B3 skeleton cannot be excluded. b) Conformational isomers could be described by the obvious assumption, that the two boryl groups BRBr and BR′Br define bond planes orthogonal to the central plane B1–N–B2–B3. The normal ligand conformation in diborane(4) derivatives is staggered and the same is true for one of the aminoborane fragments in stericly crowded diborylamines, as mentioned above. The groups R (at B1) and R′ in *syn* or *anti* position of **8** then cause conformational isomerism. c) An exchange of the boryl groups BRBr and BR′Br along the N=B2 skeleton can also not be excluded. d) A fourth possibility, the most likely one, is the *cis*/*trans* isomerism with respect to the B=N double bond, well established in the aminoborane chemistry for a long time.

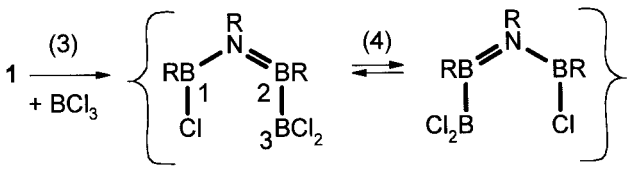
With respect to the NMR time scale, the isomerization rate is rapid enough to cause an observable coalescence of the corresponding NMR signals above room temperature in the case of products **8** with the less bulky ligands R′ (**8a–d**). We followed the kinetics of the isomerization with four signals of **8a** and calculated the free activation energy in both directions (Table 5) by an established method (Treatment of Unequally Populated Doublets [10]). The resulting average values, $\Delta G^{\#}$ = 70.9 and 68.5 kJ mol^{-1} in the two directions, are in agreement with a *cis*/*trans* isomerization, which is found in normal aminoboranes in a range of 70–100 kJ mol^{-1} [11, 12].

We tried to react the azadiboriridine **1** with boranes R′BBr_2, whose alkyl groups R′ are either α-branched or tertiary in β-position (R′ = *i*Pr, *t*Bu, CH_2*t*Bu, CH_2SiMe_3). No reaction took place at low temperature and decomposition into unknown products was observed upon long-term heating.

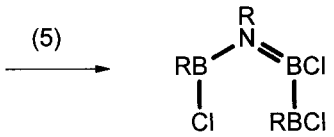
Reaction of NB_2R_3 with Chloroboranes

Trichloroborane BCl_3 quantitatively chloroborates NB_2R_3 (**1**) at low temperature according to Eq. (3), comparable to the bromoboration (2). The raw material contains the product **8h** in more than 95% purity, according to the NMR spectra; the product decomposes on attempts of further purification. The ^{11}B NMR signals at –60 °C (δ = 56.6, 49.6, 71.3 for B1, B2, and B3) are not far away from those of the dibromo species **8** (Table 2). There are no indications for isomers like in the case of the dibromo species, but a degenerate isomerization is concluded from the NMR

spectra at room temperature giving, e. g., one ^{11}B NMR signal at $\delta = 51.4$ for B1 and B2. We suggest that a BCl_2/Cl exchange takes place [Eq. (4)], comparable to the BHX/H exchange in the case of **7** (X = N*i*Pr$_2$ [3]). A bicyclic NB_3 cluster of type **2** would be a reasonable intermediate of that exchange.



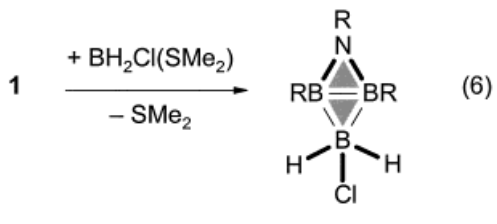
8h



8h'

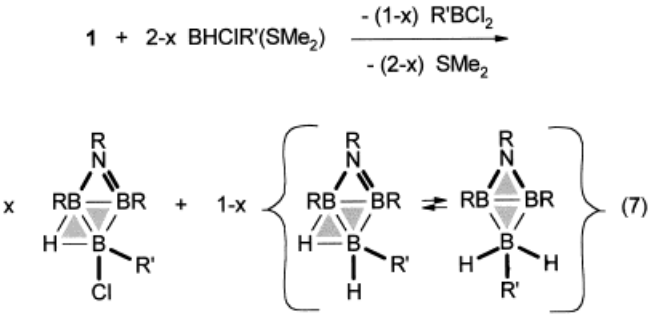
The product **8h** is not stable at room temperature. It rearranges to give **8h′** by an irreversible R/Cl exchange at the B2–B3 chain fragment [Eq. (5)]. The molar ratio of **8h**/**8h′** is 0.8 after 60 min at 24 °C, and the rearrangement is complete after 60 min at 60 °C. The ^{11}B NMR signals ($\delta = 64.3$, 39.1, 80.5) agree with those typical for **8**, and the signals of B2 ($\delta = 39.1$) and B3 ($\delta = 80.5$) are related by a 2 D-$^{11}B/^{11}B$ cross-peak. No indications for isomers like in the case of the dibromo species of type **8** were found.

Different from BCl_3, the addition of BH_2Cl (applied as the SMe_2 adduct) to **1** gives the simple 1 : 1 adduct of type **2** ($NB_3R_3H_2X$, X = Cl: **2b**), isolated as a glassy colourless solid at –75 °C, which undergoes slow decomposition at room temperature. The purity is ca. 80%. The structure can be deduced from the NMR spectra: *t*Bu groups and B atoms in the ratio 2 : 1 and an ^{11}B NMR triplet for the BH_2 group with a coupling constant in the typical range of cluster *endo*-H atoms (85 Hz) are observed. A 2 D-$^{11}B/^{1}H$ cross-peak is found for B3, but not for B1 and B2, indicating that the H atoms of BH_2 are not in a bridging position. The two ^{11}B NMR signals are related by a cross-peak; they fit well to the corresponding signals of the comparable type **2** product $NB_2R_3H_3$ (Tables 1, 6).



2b

The reaction of **1** with $BHCl_2$ (added as the SMe_2 adduct) gives a mixture of $NB_3R_3Cl_3$ (**8h′**) and $NB_3R_3H_2Cl$ (**2b**), showing that BCl_2H undergoes a dismutation into BCl_3 and BH_2Cl during this reaction. The product **8h′** can be purified by crystallization from hexane. A partial dismutation is also observed during the reaction of $BHClR'(SMe_2)$ (R′ = CMe_2CHMe_2) with **1**. A part of this borane gives the type **3** adduct $NB_3R_3R'HCl$ with H in a bridging position; another part gives a dismutation into BH_2R' and BCl_2R'. We could not detect BCl_2R' among the products, but BH_2R' adds to **1** in the known manner to give a 13 : 1 equilibrium mixture of the corresponding type **3** and type **2** adduct [3]. The type **3** product $NB_3R_3R'HCl$ could clearly be identified in a mixture with those two BH_2R' adducts by typical NMR shifts. The three ^{11}B NMR shifts of $NB_3R_3R'HCl$ correspond closely to $NB_3R_3R'H_2$ of type **3** (Table 1). The 2 D-$^{11}B/^{1}H$ cross-peaks between the signals of μ-H and both, B1 and B3, prove the bridging character of this H atom.

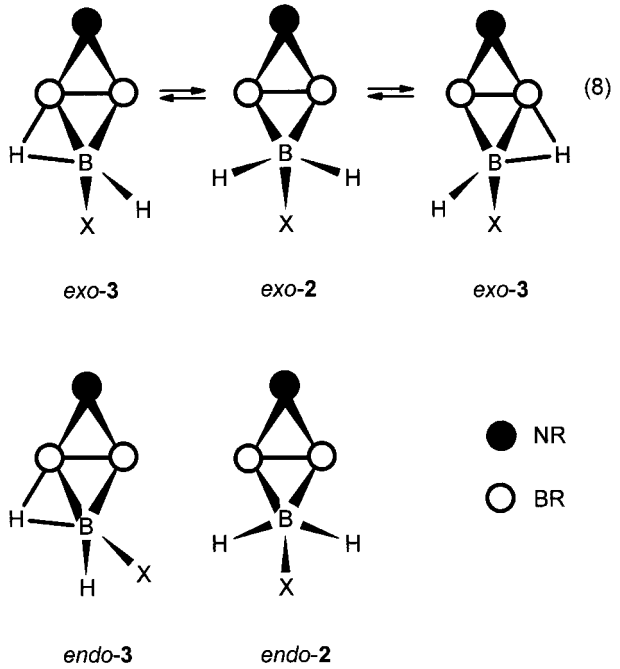


Attempts to react BHClR(thf) with **1** yielded BCl_2R and the known adduct $NB_3R_4H_2$ in the known type **2**/type **3** equilibrium [3] in the course of a complete dismutation of BHClR into BH_2R and BCl_2R (R = *t*Bu).

The Configuration at B3 of the Clusters $NB_3R_3H_2X$

The NB_3 skeleton of the *nido*-clusters $NB_3R_3H_2X$ of type **2** and **3** forms a bent bicyclobutane-type structure, which is typical for four-vertex *nido*-species derived from the corrresponding trigonal bipyramidal *closo*-structure. Interplanar angles between the two skeletal triangles of 137.4° (X = H, type **2**) and 139.8° (X = R, type **3**) were found in the crystal [2, 3]. The bent structure defines an *exo*/*endo* alternative for the position of X. An *endo*-structure of type **2** (C_s) includes two *exo*-H atoms at one cluster vertex, which means an unfamiliar situation in oligoborane chemistry. In the case X = H, type **2**, we define *exo*/*endo* with respect to the H atom in the mirror plane, whereas the *exo*/*endo*

alternative remains undefined in the case of X = H, type **3**.



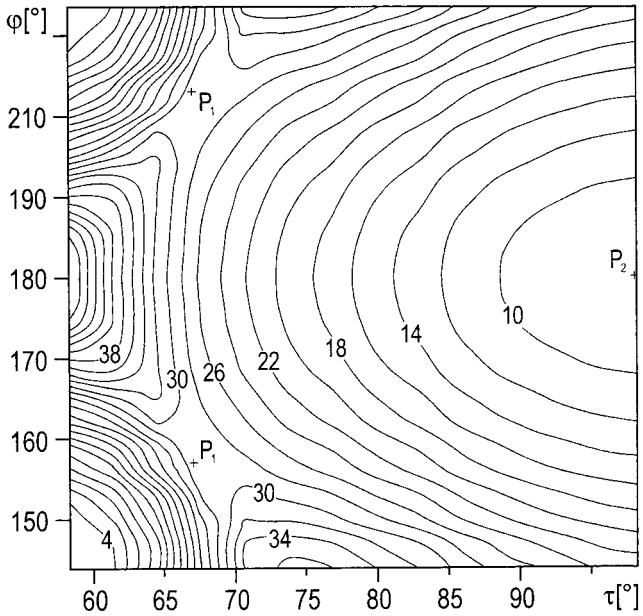


Fig. 1 Calculated potential energy surface (kJ mol^{-1}) of NB_3H_6 as depending from the interplanar angle (φ) and the ring angle B1–B2–B3 (τ) relative to the energy minimum in the type **3** structure ($\varphi = 145°$, $\tau = 58°$).

We calculated the molecules $NB_3Me_3H_3$ (**2c**, **3c**) and $NB_3Me_3H_2Cl$ (**2d**, **3d**), the formal adducts of BH_3 and BH_2Cl to the azadiboriridine NB_2Me_3, by density functional methods. Optimizations of geometry and calculations of frequency were performed at the B3LYP/6–31++G(d,p) level [13]. It turned out in both cases that the hydrogen-bridged isomers **3c** and **3d** represent minima on the potential energy hyperface, with the Cl ligand in the *exo*-position of **3d**. The type **2** *exo*-structures, which had been deduced from NMR data for $NB_3R_3H_2X$ (**2a**: [2]; **2b**: preceding section), were found as very low lying transition states, 3.5 (**2c**) and 5.6 kJ mol^{-1} (**2d**) apart from the corresponding ground states **3c**, **d**. (These ground states exhibit a staggered conformation of *N*-CH_3 with respect to BH_2X; the eclipsed conformation of these groups is represented by a second order saddle point at 5.3 and 7.5 kJ mol^{-1}, respectively.) Apparently, the type **2** *exo*-transition states (C_s) allow the rapid enantiomerization of the chiral type **3** *exo*-molecules [Eq. (8)], making clear that the products formulated earlier as **2a** and **2b** actually exhibit C_s *pseudo*-symmetry, even at low temperature, and should better be designated **3a** and **3b** in the free molecules, although the *exo*-**2a** structure is established in the crystal [2]. Interestingly, a type **4** isomer of the compound NB_3H_5Cl with Cl in a bridging position is also found as a minimum on the energy hyperface, which is 35.4 kJ mol^{-1} apart from the corresponding type **3** *exo*-ground state.

A type **3** *endo*-structure, undefined for **3c**, represents a minimum of potential energy in the case of **3d**, 23.2 kJ mol^{-1} apart from the *exo*-ground state. We thoroughly tried to find a type **2** *endo*-structure on the energy hyperface in the case of the parent compound **2c**, but could not find any stationary point; this corresponds to the mentioned general lack of finding two *exo*-H atoms at one vertex of borane clusters. How do we then explain the observed equilibria between $NB_3R_3H_2R'$ of type **2** and **3** [3] (R = *t*Bu; for alkyl groups R′ see X in Table 1)? The observed type **2** isomers should actually be type **3** *exo*-isomers, which undergo a rapid enantiomerization, as pointed out [Eq. (8)]. The observed type **3** isomers, on the other hand, are actually present as type **3** *endo*-isomers, established in the crystal by X-ray analysis. Obviously, they cannot undergo an enantiomerization, since an adequate transition state of the type **2** *endo*-configuration is not easily available. The question remains, how the type **3** molecules $NB_3R_3H_2R'$ can switch from the *endo*- into the *exo*-configuration and vice versa in an equilibrium, observed on changing the temperature or dissolving crystalline *endo*-isomer, slowly enough to make both of the isomers observable by NMR methods. A reasonable isomerization path seems to be the inversion of the interplanar angle φ between the NB_3 skeletal triangles via a planar structure. We therefore calculated the change in energy, when the type **3** structure of the parent molecule NB_3H_6 is planarized, starting from $\varphi = 145°$ at the minimum geometry. It turned out that $\varphi = 180°$ is approached at about 48 kJ mol^{-1}, but the reaction path becomes more favourable, when simultaneously the ring angle B1–B2–B3 (τ; B1–B3 is the H-bridged edge) is widened, starting from the minimum value of 58°. The

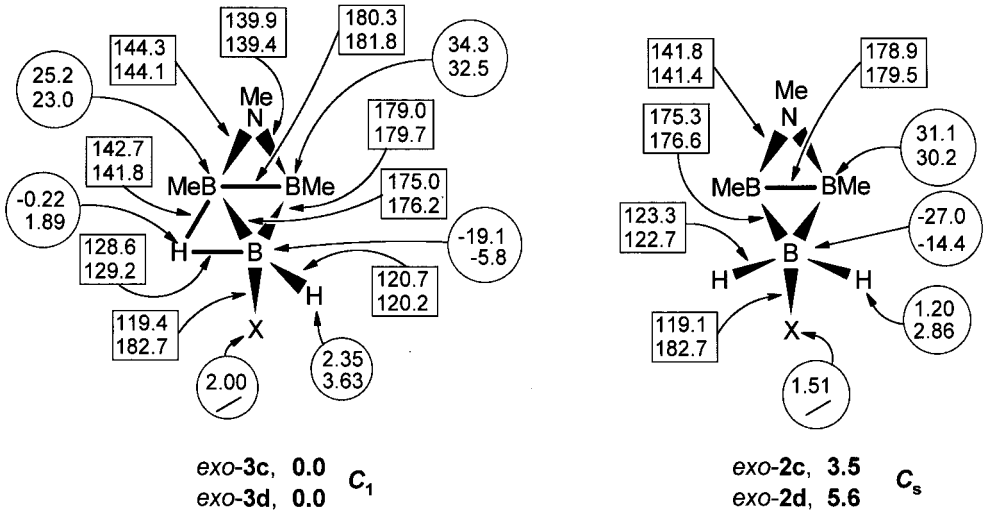


Fig. 2 Calculated structures of $NB_3Me_3H_2X$ in the *exo*-**3** ground state and in the *exo*-**2** transition state (X = H, **3c**, **2c** upper values; X = Cl, **3d**, **2d** lower values): relative energies (kJ mol^{-1}; bold); BN, BB and BX distances (pm; in rectangles); ^1H and ^{11}B NMR shift values (ppm; in circles; GIAO) [B3LYP/6–31++G(d,p) level for geometry and NMR data]

situation is illustrated in Fig. 1. The energy map was obtained by a relaxed potential energy surface scan with constrained angles φ and τ, proceeding with steps of 2°. A saddle point of ca. 30 kJ mol^{-1} is reached at about $\varphi = 157°$ and $\tau = 67°$ (P_1 in Fig. 1). Though the system could go down to an energy of 8.3 kJ mol^{-1} at $\varphi = 180°$ and $\tau = 97°$ (P_2 in Fig. 1), the real pathway from the saddle point to the planarized structure ($\varphi = 180°$) could be reached on a higher energy level ($\tau < 97°$) at the temperature of experiment. Anyhow, widening of τ corresponds to opening of the B1–B3 bond. We conclude that the *endo*/*exo* isomerization of the experimental molecules $NB_3R_3H_2R'$ is likely to proceed through some B–B opening via a structure, which is close to the products of type **8**. The reaction path from the minimum of type **3** via P_1 to P_2 was additionally confirmed by the method of Intrinsic Reaction Coordinates.

The optimized geometry data of *exo*-**2c**, **d** and *exo*-**3c**,**d** were used as a basis for the calculation of the NMR signals using the GIAO method [14]. Part of the results are presented in Fig. 2.

In Table 6, we compare the observed data of $NB_3tBu_3H_3$ (*exo*-**2a** [2], obviously better formulated as the rapidly enantiomerizing isomer **3a**) to the data calculated for $NB_3Me_3H_3$ in the ground state (**3c**, the shift values of μ-H/*endo*-H and B1/B2, Fig. 2, are averaged) and transition state (*exo*-**2c**), and we do the same for $NB_3tBu_3H_2Cl$ (*exo*-**2b**, see Exp. Sect.) and $NB_3Me_3H_2Cl$ (*exo*-**3d**, *exo*-**2d**, Fig. 2). The calculated ^{11}B NMR signals of B3 of **3c**,**d**/**2c**,**d** are somewhat high-field shifted as compared to the observed signals, but the difference between the ligands Me and *t*Bu makes such shift differences reasonable. Altogether, the observed and the calculated values are in good concordance.

Table 6 Comparison of NMR shift values observed for $NB_3R_3H_2X$ (X = H: **2a**; X = Cl: **2b**) and calculated for $NB_3Me_3H_2X$ (X = H: **3c**, **2c**; X = Cl: **3d**, **2d**; ground state **3**, transition state **2**)

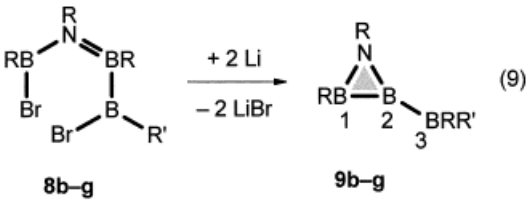
		2a	**3c**	**2c**	**2b**	**3d**	**2d**
^1H NMR,	δ(*exo*-H)	2.03	2.00	1.51	/	/	/
	δ(*endo*-H)	0.92	1.06	1.20	2.76	2.76	2.86
^{11}B NMR,	δ(B1/B2)	32.9	29.8	31.1	30.0	27.8	30.2
	δ(B3)	–14.1	–19.1	–27.0	–5.6	–5.8	–14.4

The products $NB_3R_3H_2X$ can be considered to be derivatives of the parent *nido*-cluster NB_3H_6, which is member of an isoelectronic series B_4H_8, CB_3H_7, and NB_3H_6. Recently, we reported on *tert*-butyl derivatives of B_4H_8 [15] and CB_3H_7 [16]. The configurational situation of B_4H_8 is comparable to that of NB_3H_6, but – different from NB_3H_6 and its derivatives – a transition state analogous to the *endo*-**2** type of NB_3H_6 is detected for B_4H_8 by theory.

Formation of NB_3R_3R' by Debromination of 8b–g

Upon applying ultrasound, the reduction of the boranes Br–BR–NR=BR–BR′–Br (**8b–g**) with lithium in hexane in the presence of $Me_2NCH_2CH_2NMe_2$ (tmen) gives products NB_3R_3R' (**9b–g**), according to Eq. (9). The application of ultrasound as well as of lithium and tmen turned out to be essential. The oily products are thermally labile, extremely sensitive to traces of air, and are obtained in about 90% purity; the product

9c (R′ = *i*Bu), however, can be purified by slow high vacuo condensation at room temperature.



The structures are concluded from the NMR spectra. The NB_3R_3 fragment of NB_3R_3R', common to all members in the series **9b–g**, exhibits ^{1}H, ^{11}B, and ^{13}C NMR shifts, whose concordance shows that the same type of structure is present (Table 7). The ^{1}H and ^{13}C NMR signals of the R′ fragment can be unequivocally assigned, according to general experience, in the case of **9c** additionally by applying special NMR techniques (see Exp. Sect.). It is evident from the spectra, that the two fragments BR are not equivalent and that there is a fragment NR. The ^{11}B NMR signal at δ = 99.1–99.7 points to a B atom, that is coordinated by two alkyl and one boryl group, comparable to the situation in diboranes $R'_2B–BR'_2$ (δ ca. 105 [17, 18]). The B atoms at $\delta(^{11}B)$ = 49.8–50.3 and 54.1–55.1 seem to be similarly coordinated as both of the B atoms of **1** (δ = 51.9 [6]). There are two cross-peaks in the 2 D-^{11}B/^{11}B NMR spectrum of **9c** (65 °C), a weak one between the signals of B1 and B2 and a strong one between the signals of B2 and B3; a weak cross-peak is expected for B atoms that are bound together by a direct bond and additionally by a bridging N atom [19]. All the given data are in accord with a 2-borylazadiboriridine-type structure of **9b–g**.

The two ^{13}C/^{1}H-HETCOR correlations for the ^{13}C/^{1}H shift couples δ = 31.14/1.18 (J = 145 Hz) and 56.19/1.18 (J = 5 Hz) of **9c** allow to distinguish the ^{1}H and ^{13}C NMR signals of N*t*Bu from those of B*t*Bu, since the ^{13}C NMR peak at δ = 56.19 clearly marks the C1 atom of N*t*Bu, whereas the signals for C1 of B*t*Bu, as usual, could not be detected in the spectra. The ^{13}C/^{1}H HETCOR couples δ = 28.32/1.06 and 29.24/1.20, observed with **9c**, prove, which of the ^{1}H and ^{13}C NMR signals of BR belong together (line 2 to line 8 and line 3 to line 9 values in Table 7), but an assignment of the two BR groups to B1 and B3 is not possible on the basis of the data presently available.

Table 7 ^{1}H, ^{11}B, and ^{13}C NMR shifts of **9b–g** (without shifts of R′)

	9b	**9c**	**9d**	**9e**	**9f**	**9g**
^{1}H (NR)	1.19	1.18	1.08	1.19	1.19	1.17
(BR)	1.05	1.06	0.94	1.07	1.07	1.11
(BR)	1.20	1.20	1.12	1.19	1.21	1.22
^{11}B (B1)	50.3	50.1	49.8	50.2	50.2	49.9
(B2)	55.1	54.9	54.3	54.9	54.9	54.1
(B3)	99.7	99.2	99.1	99.6	99.5	99.6
^{13}C (Me, NR)	31.24	31.14	30.84	31.15	31.15	30.73
(Me, BR)	28.47	28.32	28.47	28.48	28.33	28.40
(Me, BR)	29.28	29.24	29.29	29.25	29.23	29.24
(NC)	56.19	56.19	55.91	56.57	56.19	55.76

The room temperature NMR spectra do not give evidence for non-equivalent methylene protons in the corresponding groups R′ or for non-equivalent Me groups in the case of R′ = *i*Bu. We cannot explain this by a bond plane around B3, which is coplanar with the ring plane (C_s symmetry), having in mind that the two bond planes around boron in diborane(4) derivatives are mostly arranged more or less orthogonally. We instead assume an orthogonal position of these planes in the ground state (C_1 symmetry) and a rapid rotation around the B2–B3 bond, thus inducing C_s *pseudo*-symmetry with respect to the NMR observation. In order to support this assumption, we cooled **9c** down to –60 °C (in [D_8]toluene) and found a splitting of the methylene proton signals into δ = 1.57 (dd, ^2J = 17.4 Hz, ^3J = 9.5 Hz) and δ = 1.27 (dd, ^2J = 17.4 Hz, ^3J = 4.5 Hz). The methyl proton signal remained a broad *pseudo*-singlet on cooling, but the methyl ^{13}C NMR peak was transformed into two peaks at δ = 26.87 and 25.52 (–60 °C). Even the methyl ^{1}H NMR pseudo-singlet could be resolved into two shift values by ^{1}H/^{13}C HETCOR measurements at –80 °C, giving the ^{1}H/^{13}C couples δ = 25.50/1.07 and δ = 26.90/1.04. Coalescence of the two ^{13}C NMR methyl signals is observed at 0 °C ($\Delta\nu$ = 176 Hz at –80 °C) and, hence, an activation barrier of $\Delta G^{\#}$ = 53 kJ mol^{-1} can be estimated [20].

A plausible explanation, by which mechanism the debromination of type **8** products, Eq. (9), might proceed, starts from the exchange of Br and R′ along the B2–B3 bond of **8**, which completely parallels the exchange of Cl and R, Eq. (5), in the case of the rearrangement of **8h** into **8h′**. The Wurtz-type debromination would then be the plausible second step in the formation of the type **9** products. The products **9b–g** are derivatives of a parent molecule NB_3H_4, formally, what on naive consideration counts for a *closo*-cluster, presumably with the C_{3v} structure of a trigonally distorted tetrahedron. We have concluded quite a different structure for **9b–g** from NMR-based arguments. So reasonable these arguments might be, they do not finally prove the structure. Since crystals are not available, we studied the structure of the parent compound NB_3H_4 (**9h**) and of NB_3Me_4 (**9i**) by *ab initio* calculations and derived the ^{11}B NMR shifts by the GIAO method.

Theoretical Model of NB_3H_4 (9h) and NB_3Me_4 (9i)

We found local minima on the potential energy hyperface for the six structures **A–F** of **9h,i** at the B3LYP/6–31++G(d,p) level [13]. The calculated relative energies, bond distances and NMR shifts are presented in Fig. 3.

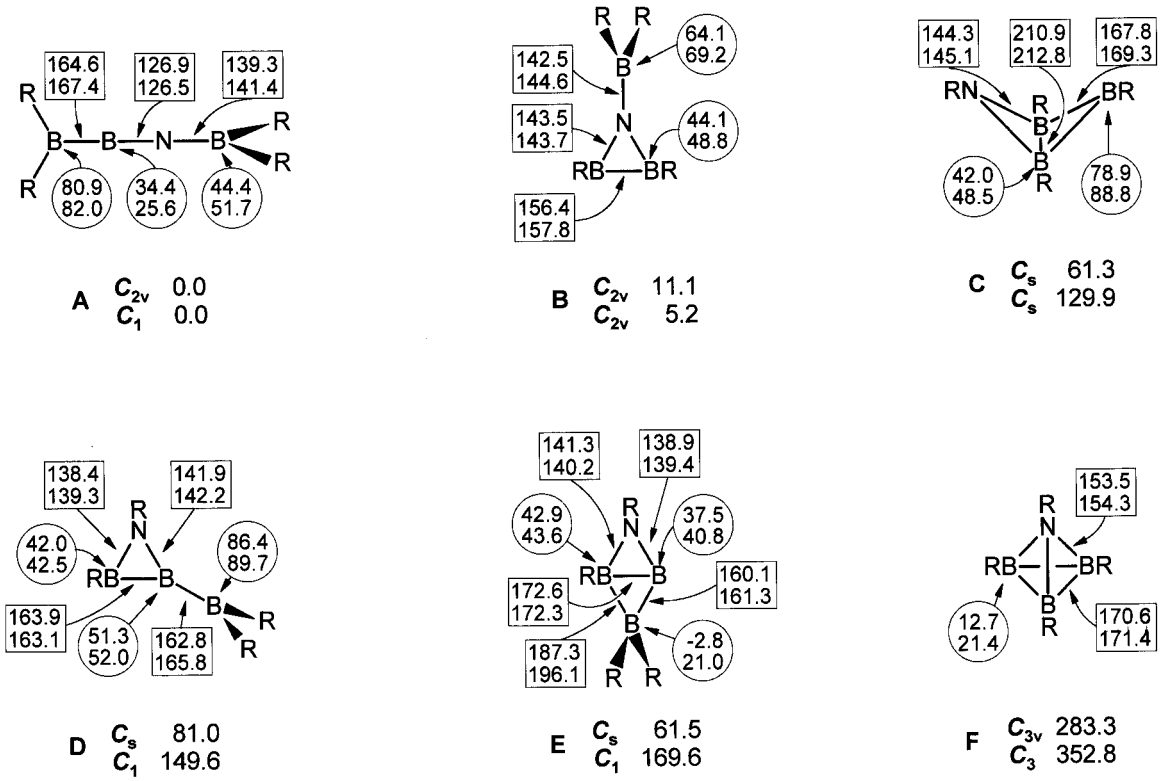


Fig. 3 Calculated minimum structures **A**–**F** of NB_3R_4 (R = H, **9 h**: upper values; R = Me, **9 i**: lower values): symmetry group and relative energies (kJ mol^{-1}; bold); BN and BB distances (pm; in rectangles); ^{11}B NMR shift values (ppm; in circles; GIAO) [B3LYP/6–31++G(d,p) level for geometry and NMR data]

The structure lowest in energy contains an open chain with a very short BN bond (BN "triple bond"). The structure by far worst in energy turns out to be the trigonally distorted tetrahedron with a triplet ground state. With the ligand set R,R,R,R′ (**9 b–g**), only the structures **D** and **E** fit the observed NMR spectra, in particular the non-equivalence of all the three B atoms and groups R. The calculated ^{11}B NMR shifts of **D** agree to the experimental values of **9 b–g**, whereas the ^{11}B NMR shifts of **E** are far away from the experimental values. The calculated values strongly support the structure assumed for **9 b–g**.

Presumably, the rotation of the BRR′ group around the B2–B3 axis goes through the coplanar arrangement of the bond planes around B2 and B3 as the transition state (C_s). Actually, such a coplanar structure is a transition state in the case of **D**, according to our calculations, which is 46.6 kJ mol^{-1} apart from **D** (R = H). The rotational barrier of the molecule H_2B–BH_2, for comparison, had been calculated to be 52.7 kJ mol^{-1} [21]. The calculated geometry of that transition state differs from **D** in three parameters that are noteworthy: Going from **D** to the transition state, the B1–B2 bond is shortened (163.9 → 161.4 pm), the B2–B3 bond is lengthened (162.8 → 171.0 pm), and the bond angle B1–B2–B3 is widened (158.4 → 169.2°). We explain these changes qualitatively by assuming some overlap between the B1–B2 σ-bond and the empty p-orbital of B3, which breaks down, when this p-orbital is twisted out of the plane of optimal overlap. In terms of localized molecular orbitals, the B3 atom obtains an electron octet by constructing an open B1–B2–B3 (3c2e) bond. This (3c2e) bond and the BNB (3c2e) π-bond are the two (3c2e) bonds, which follow necessarily from the orbital/electron balances of a molecule NB_3H_4, obeying the octet rule. [Orbitals: $\Sigma o = 20 = 3t + 2y$; electrons: $\Sigma e = 18 = 2t + 2y$; hence, the number of (3c2e) bonds $t = 2$, the number of (2c2e) bonds $y = 7$.]

Though the structure **E** looks unfamiliar, as compared to conventional molecules, we considered it seriously, having in mind the isoelectronic molecule $C_2B_2H_4$ and its derivatives, for which a bicyclobutane-type unconventional structure, similar to **E**, had been established by theory [22] and experiment [23, 24].

Experimental

General

All reactions were conducted under dry nitrogen. Starting materials were commercially available or were synthesized according to cited procedures. NMR spectra were recorded in solutions of C_6D_6 [$B(CH_2CHEt_2)_3$, $B(CH_2Cy)_3$, $B[CH_2(4\text{-}C_6H_4tBu)]_3$, $BBr_2(CH_2CHEt_2)$, BBr_2Cy, **8 e–g**,

$NB_3tBu_3H_2Cl$, $NB_3tBu_3HCl(CMe_2CHMe_2)$, **9c, e–g]** or [$D_8$]toluene (ca. 0.25 mol/l; **8a–d, h, h′**, **9b, d**) at 499.843 MHz (^1H; tms), 160.364 MHz (^{11}B; $BF_3(OEt_2)$), 125.639 MHz (^{13}C; tms). MS (70 eV): Finnigan MAT-95.

Synthesis of trialkylboranes

Tris(2-ethylbutyl)borane: In analogy to a known procedure [25], a solution of 1-bromo-2-ethylbutane (14.9 g, 90 mmol) in Et_2O (60 ml) is dropped into a mixture of Mg (4 g, 0.17 mol) and $BF_3(OEt_2)$ (4.3 g, 30 mmol) in Et_2O (30 ml) so rapidly that reflux is observed. Further reflux (2 h), stirring overnight at ambient temperature and filtration gives a solution, from which the product (5.3 g, 66%) is obtained by distillation (87 °C/0.1 Pa) as a colourless liquid. ^1H NMR: $\delta = 0.89$ (t, $J = 7.5$ Hz, 2 Me), 1.22 and 1.37 (2 ddq, $J = 13.5$, 7.0, 7.5 Hz, CH^{α} and CH^{β} of 2 CH_2), 1.37 (d, 7.0 Hz, BCH_2), 1.73 (mc, CH). ^{11}B NMR: $\delta = 88.1$. ^{13}C NMR: $\delta = 11.64$ (q), 29.52 (t), 34.6 (br, BC), 38.88 (d). The assignments are in accord with 2 D-$^1H/^1H$ and -$^1H/^{13}C$ NMR spectra.

Tris(cyclohexylmethyl)borane: This product is obtained by an analogous procedure, starting from bromo(cyclohexyl)-methane (25.0 g, 141 mmol), $BF_3(OEt_2)$ (6.7 g, 47 mmol) and Mg (6 g, 0.25 mol). A high vacuo condensation at a bath temperature of 170 °C yields the colourless solid product (8.0 g, 56%). ^1H NMR: $\delta = 0.6$–1.6. ^{11}B NMR: $\delta = 88$. ^{13}C NMR: $\delta = 26.86$, 27.11, 36.98, 38.86 (4 t, 1 : 2 : 2 : 1), 35.66 (d).

Tris[(4-tert-butylphenyl)methyl]borane: A similar procedure is applied with bromo(4-*tert*-butylphenyl)methane (25.0 g, 107 mmol), $BF_3(OEt_2)$ (5.1 g, 36 mmol) and Mg (5 g, 0.21 mol). Before filtering the magnesium salts, ether is removed in vacuo and replaced by hexane (80 ml). Reversely, hexane is then replaced by ether (70 ml). 1,2-Bis(4-*tert*-butylphenyl)ethane crystallizes as a byproduct overnight. After filtration and removal of the solvent, a colourless solid product remains (10 g, 61%). ^1H NMR: $\delta = 1.25$, 2.69 (2 s, 9 : 2), 6.87, 7.23 (2 mc, 1 : 1). ^{11}B NMR: $\delta = 81.7$. ^{13}C NMR: δ 31.56 (q), 34.26 (s), 36.48 (br, BC), 125.45, 129.28 (2 d), 136.76, 147.47 (2 s).

Synthesis of alkyldibromoboranes

Benzyldibromoborane: Analogous to a known procedure [26], a solution of BBr_3 (55 g, 0.22 mol) and $B(CH_2Ph)_3$ [27] (28.4 g, 10.0 mmol) in toluene is stirred for 2 d in the presence of 2 g 9-borabicyclo[3.3.1]nonane. The catalyst is then deactived by the addition of 0.5 g 1-octene. Distillation (106 °C/15 mbar) gives the pure product (60 g, 76%) as a colourless liquid.

Dibromo(2-ethylbutyl)borane: A mixture of $B(CH_2CHEt_2)_3$ (4.82 g, 18.1 mmol), BBr_3 (9.07 g, 36.2 mmol), and $BH_3(SMe_2)$ (0.07 g) in pentane (15 ml) is refluxed (3 h). A distillation (50 °C/4 mbar) yields a colourless liquid (8.0 g, 58%). ^1H NMR: $\delta = 0.70$ (t, $J = 7.5$ Hz, 2 Me), 1.06 and 1.18 (2 ddq, 13.8, 6.5, 7.5 Hz, CH^{α} and CH^{β} of 2 CH_2), 1.28 (d, 7.0 Hz, BCH_2), 1.74 (mc, CH). ^{11}B NMR: $\delta = 64.8$. ^{13}C NMR: $\delta = 11.35$ (q), 28.48 (t), 40.41 (d), 41.44 (br, BC). The assignments are in accord with 2 D-$^1H/^1H$ and -$^1H/^{13}C$ NMR spectra.

Dibromo(cyclohexylmethyl)borane: Starting from $B(CH_2Cy)_3$ (3.79 g, 12.5 mmol), BBr_3 (6.25 g, 25.0 mmol) and $BH_3(SMe_2)$ (3 drops) in hexane (10 ml), the same procedure gives a colourless liquid (5.7 g, 57%) by distillation (53 °C/0.1 Pa). ^1H NMR: $\delta = 0.73$, 0.98, 1.12, 1.51, 1.54, 1.69 [6 m, 2 : 2 : 2 : 2 : 2 : 1; from 2 D-$^1H/^{13}C$ NMR: H2/6, H4 (accidental degenerassy of H_{ax} and H_{eq}), H3/5, H3/5, H2/6, H1 of Cy], 1.24 (d, $J = 7$ Hz, BCH_2). ^{11}B NMR: $\delta = 64.8$. ^{13}C NMR: $\delta = 26.09$, 26.51, 35.34, (3 t, 1 : 2 : 2; C4, C3/5, C2/6 of Cy), 36.68 (d), 45.2 (br, BC).

Dibromo[(4-tert-butylphenyl)methyl]borane: On the addition of BBr_3 (15.0 g, 60 mmol) to a solution of $B[CH_2$-$(4\text{-}C_6H_4tBu)]_3$ (10.0 g, 22 mmol) in hexane (10 ml), a red-brown colour is observed, which disappears, when five drops of $BH_3(SMe_2)$ are added. After refluxing for 2 h, volatile materials are removed in vacuo. Distillation (75 °C/0.1 Pa) gives a colourless liquid (7.6 g, 36%). ^1H NMR: $\delta = 1.16$, 2.71 (2 s, 9 : 2), 6.90, 7.16 (2 mc, 1 : 1). ^{11}B NMR: $\delta = 62.7$. ^{13}C NMR: $\delta = 31.40$ (q), 34.31 (s), 43.6 (br, BC), 125.9, 129.5 (2 d), 132.6, 148.9 (2 s).

Synthesis of [2-alkyl-2-bromo-1-tert-butyldiborane(4)yl]-tert-butyl(tert-butylbromoboryl)amines ***8 a–g***

The bromoborane $R'BBr_2$ is added to pentane or hexane (10–20 ml) at –78 °C (**8a–c**) or *vice versa* (**8d–g**). The solutions are warmed to room temperature within 2 h and then either stirred at this temperature (**8a, b**: 2 h; **8d**: 12 h) or refluxed (**8c, f, g**: 8 h; **8e**: 24 h). The removal of volatile materials in vacuo gives oily products. These are dissolved in hexane and filtered over kieselgur in the case of **3e, f**. The amounts of starting materials, the yields of oily products and the estimated purity (according to NMR spectra) are summarized in Table 8. The products **8a–d** can be brought to purity (as found by microanalysis of the elements C, H, N) either by condensation in vacuo (**8b**; oil bath temperature 120 °C) or by crystallization from hexane at –80 °C (**8a**: m. p. 25 °C; **8c**: m. p. 20 °C; **8d**: dec. at ca. 25 °C).

Reaction of NB_2R_3 with Chloroboranes

Reaction of NB_2R_3 with BCl_3: A solution (0.5 mol/l) of BCl_3 in hexane (3.2 ml) is added to **1** (0.33 g, 1.59 mmol) in pentane (15 ml) at –78 °C. The solution is brought to ambient temperature within 15 min. Volatile materials are removed in high vacuo at –78 °C. The remaining product **8h** can

Table 8 Synthetic data of the products **8a–e**: mass and molar amount of the starting materials **1** (m_1, n_1) and $R'BBr_2$ (m_2, n_2), yield of products (m_3, n_3/n_1)[a] and purity (according to NMR spectra)[a]

Product	8a	8b	8c	8d	8e	8f	8g
m_1 [g]	1.00	0.79	2.76	0.69	0.97	1.45	1.28
n_1 [mmol]	4.80	3.82	13.34	3.34	4.70	7.00	6.18
m_2 [g]	0.90	0.87	3.04	0.88	1.20	1.98	1.96
n_2 [mmol]	4.80	3.82	13.34	3.36	4.70	7.00	6.17
m_3 [g]	1.85	1.51	5.75	1.50	1.98	3.10	3.18
n_3/n_1 [%]	98	91	99	97		93	98
Purity [%]	95	100	95	95	85	95	95

[a] The yields in% are calculated under the assumption that the impurities have the same molar mass as the products.

be characterized by NMR (purity >90%). ^{1}H NMR: δ (24 °C) = 1.05, 11.24 (2 s, 2 : 1); δ (–60 °C) = 1.00, 1.04, 1.15 (3 s, 1 : 1 : 1). ^{11}B NMR: δ (24 °C) = 51.4 ($\omega_{1/2}$ = 640 Hz, 2 B), 71.3 ($\omega_{1/2}$ = 320 Hz, 1 B); δ (–60 °C) = 49.6 ($\omega_{1/2}$ > 1000 Hz, 1 B), 56.6 ($\omega_{1/2}$ > 1000 Hz, 1 B), 71.4 ($\omega_{1/2}$ > 100 Hz, 1 B). ^{13}C NMR: δ (24 °C) = 29.47, 33.59 (2 q, 2 : 1), 56.71 (s); δ (–60 °C) = 29.05, 29.37, 33.30 (3 q), 56.76 (s, NC). – The product **8h** can be stored at –80 °C, but slowly rearranges into **8h′** at room temperature. The rearrangement is complete after 60 min at 60 °C (purity > 90%). ^{1}H NMR: δ = 1.12, 1.13, 1.15 (3 s, 1 : 1 : 1). ^{11}B NMR: δ = 39.1, 64.3, 80.5 (3 s, 1 : 1 : 1). MS: m/z = 266 (27%, M–Bu), 210 (20%, M–Bu–C_4H_8), 57 (100%, $C_4H_9^+$) etc.

Reaction of NB_2R_3 with $BH_2Cl(SMe_2)$: The commercially available sulfane-borane contains 70% $BH_2Cl(SMe_2)$ (^{11}B NMR: δ –6.7, t, J = 131 Hz), 15% $BHCl_2(SMe_2)$ (^{11}B NMR: δ = 2.2, d, J = 157 Hz), and 15% $BH_3(SMe_2)$ (^{11}B NMR: δ –20.0, q, J = 104 Hz), as is known from the literature [28]. This sulfane-borane mixture (0.27 g, 2.5 mmol) was added to a solution of **1** (0.51 g, 2.5 mmol) in pentane (15 ml) at –78 °C. White flocs are precipitated. After 2 h stirring at –78 °C, volatiles are removed in high vacuo. The product is volatile in the high vacuo at an oil bath temperature of 70 °C and is condensed at –78 °C as a glassy solid, which becomes oily at room temperature and undergoes slow decomposition. Besides $NB_3R_3H_2Cl$ as the main product, the product mixture contains ca. 10% $NB_3R_3H_3$ (formed from **1** and $BH_3(SMe_2)$ and identified by the known NMR signals [2]) and ca. 8% of an unknown product [^{11}B NMR: δ = 6.4, 15.4 (2 d, J = 90 and 42 Hz); ^{1}H NMR = 3.27, 1.31 (related by cross-peaks to the ^{11}B NMR peaks)]. The main NMR peaks (82%) belong to $NB_3R_3H_2Cl$. ^{1}H NMR: δ = 1.06, 1.16 (2 s, 1 : 2, *t*Bu), 2.76 (q, ^1J = 85 Hz, 2 H). ^{11}B NMR: δ = –5.6 (t, ^1J = 88 Hz, 1 B), 30.0 (s, 2 B). ^{13}C NMR: δ = 30.10, 31.91 (2 q, 2 : 1), 53.38 (NC).

Reaction of NB_2R_3 with $BHCl_2(SMe_2)$: Commercially available $BHCl_2(SMe_2)$ (0.36 g, 2.46 mmol) is added to **1** (0.51 g, 2.46 mmol) in hexane (8 ml) at –78 °C. Stirring for 2 h gives a clear solution, whose volume is reduced in vacuo (4 ml). The product **8h′** crystallizes at –78 °C within 2 d. The mother liquor is removed with the aid of a syringe. The solid is recrystallized at –78 °C, first from 10 ml, then from 20 ml hexane. The product **8h′** is pure, according to NMR spectra (0.20 g, 25%). Another portion of **8h′** (0.15 g 18%) can be obtained from the united mother liquors by removing volatile materials in vacuo and subliming **8h′** at an oil bath temperature of 40 °C in the high vacuo. The product **8h′** is identified by its NMR spectra. It can be stored at –80 °C, but 4 months storing at –27 °C gives 40% decomposition. The mother liquor contains a considerable amount of $NB_3R_3H_2Cl$ identified by its NMR signals. It is removed from **8h′** in vacuo together with the solvent.

Reaction of NB_2R_3 with $BHCl(CMe_2CHMe_2)(SMe_2)$: This sulfane-borane adduct is synthesized according to a known procedure [29] (^{11}B NMR in CD_2Cl_2: δ = 7.8, ^1J = 128 Hz; ^{1}H NMR from 2 D-^{11}B/^{1}H: δ = 3.1). The azadiboriridine **1** (0.43 g, 2.1 mmol) in hexane (8 ml) is added to the sulfane-borane in CH_2Cl_2 (2.7 ml, 1 mol/l) at –78 °C. Stirring at room temperature (3 h) and subsequent removal of volatiles in vacuo give an oily liquid, whose ^{1}H and ^{11}B NMR spectra in CD_2Cl_2 reveal, that a mixture of four components is present: the starting material $BHCl(CMe_2CHMe_2)$, a mixture of $NB_3H_2R_3(CMe_2CHMe_2)$ of type **3** and type **2** in the known equilibrium ratio of 13 : 1 [3], and $NB_3R_3HCl(CMe_2CHMe_2)$. The oily mixture is dissolved in pentane. A 4 : 1 mixture of $NB_3R_3HCl(CMe_2CHMe_2)$ and $NB_3R_3H_2(CMe_2CHMe_2)$ crystallizes in the course of 14 d at –78 °C. We describe the NMR data of $NB_3R_3HCl(CMe_2CHMe_2)$. ^{1}H NMR: δ = 0.61, 1.33 (2 s, $BCMe_2$), 0.92, 1.04 (2 d, ^3J = 6.7 Hz, $CCMe_2$), 1.21, 1.22, 1.23 (3 s, *t*Bu), 2.28 (sept, ^3J = 6.7 Hz, CH), 2.71 ($\omega_{1/2}$ = 160 Hz, μ-H). ^{11}B NMR: δ = 13.2 (br, B3) 24.0 (B1), 37.5 (B2).

Reaction of NB_2R_3 with BHClR(thf): We first obtained a solution of BHClR(thf) (R = *t*Bu) by adding ethereal HCl (2.5 ml, 0.5 mol/l) to Li[BH_3R] in thf (1.2 ml, 0.96 mol/l) at –78 °C. The solution is brought to room temperature (20 min). Further stirring (3 h) gives NMR spectroscopically pure BHClR(thf). ^{1}H NMR: δ = 0.74 (*t*Bu), 3.10 (2 D-^{11}B/^{1}H HMQC cross-peak). ^{11}B NMR: δ = 13.7 (d, J = 134 Hz). ^{13}C NMR: δ = 28.23 (CH_3). On storing solutions of BHClR(thf) for several hours, decomposition is observed, presumably by the formation of $RBCl_2$ and subsequent cleavage of thf. The dismutation of BHClR′L into $(R'BH_2)_2$ and $R'BCl_2$ had been observed as an equilibrium reaction with different bases L in the case of R′ = CMe_2*i*Pr [29]. An equimolar amount of **1** (1.15 mmol) in thf (1 ml) is added to the solution of BHClR(thf), obtained as described, at –78 °C. After warming to ambient temperature (30 min) and further stirring (2 h), the solvents are removed and [D_8]thf is added. Unreacted **1** and the type **2**/type **3** equilibrium mixture of $NB_3R_4H_2$ are identified by their known NMR signals [3]. The signals of $RBCl_2$ had been detected in the primary reaction mixture; during the removal of the solvents the borane $RBCl_2$ is consumed by ether cleavage.

*Debromination of the boryl(tert-butyl)-diboranylamines **8***

The products **8b–g** (ca. 5 mmol) and tmen (ca. 10 mmol) are dissolved in hexane (10–20 ml). A colourless precipitate is formed. A 15fold excess of lithium powder is added. Ultra sound is applied to the mixture at room temperature as long as starting material is present, which is followed by ^{11}B NMR measurements. Filtration over kieselgur at –30 °C and subsequent removal of volatiles in high vacuo give the oily products **9b–g** in ca. 90% purity, according to ^{11}B NMR signals. Attempts to crystallize the products are not successful, and decomposition is observed on attempts to heat them for distillation. The only product obtained in purity is **9c**, which slowly condenses into a cooled receiver at 24 °C/0.1 Pa (57% yield). The products **9** can be stored at –80 °C for days, but decompose at room temperature, if not dissolved in hydrocarbons. The NMR data of **9b–g** are presented in Table 6, with the exception of the data for R′, which are mentioned here. ^{1}H NMR: δ(**9b**) = 0.89 (t, Me), 0.85–1.50 (C_3H_6); δ(**9c**) = 1.02 (d, Me), 1.46 (br, CH_2), 1.80 (mc, CH); the signals δ = 1.02/1.80 are related by a cross-peak in the 2 D-^{1}H/^{1}H spectrum; irradiation at δ = 1.80 makes ^{1}H-TOCSY signals observable at δ = 1.02 and 1.46, showing that the broad signal at δ = 1.46 represents both of the CH_2 protons; δ(**9d**) = 2.29 (br, CH_2), 6.90, 6.95 (2 mc, Ph); δ(**9e**) = 0.90 (t, Me), 1.0–1.9 ($CH_2CH(CH_2)_2$); δ(**9f**) = 0.9–2.0; δ(**9g**) = 0.92 (s, *t*Bu), 2.85 (br, CH_2), 6.98,

7.13 (2 mc, C_6H_4). ^{13}C NMR: δ(**9b**) = 14.35 (q), 26.96 (t), 31.24 (t); δ(**9c**) = 26.08 (br), 28.91 (d), 41.10 (br, BC); 2 D-$^{13}C/^{1}H$ HETCOR peaks (J = 145 Hz) prove relations within the $^{13}C/^{1}H$ couples δ = 26.08/1.02 and δ = 28.91/1.80, and a relation δ = 41.10/1.46 is established by 2 D-$^{13}C/^{1}H$ HMQC, thus confirming all the assignments given for *t*Bu; δ(**9d**) = 37.40 (t), 124.37, 128.23, 128.55 (3 d), 144.67 (s); δ(**9e**) = 11.93 (q), 29.38 (t), 35.53 (br, BC), 42.32 (d); δ(**9f**) = 26.68, 27.19 (2 t), 36.85 (br, C2/6 of Cy), 38.93 (d), 39,34 (br, BC); δ(**9g**) = 31.55 (q, s; accidental degenerassy of both of the *t*Bu signals), 36.78 (br, BC), 125.10, 128.19 (2 d), 141.51, 146.72 (2 s). MS(**9c**): 275.31270 (obs.), 275.31269 (calc. for M^+). MS(**9d**): 252.22665 (obs.), 252.22661 (calc. for $M–C_4H_9$).

Ab initio calculations

The GAUSSIAN 98 package [13], run on a cluster of workstations (*Rechenzentrum der RWTH Aachen*), was applied for all calculations. The total energies E_h and ZPVE (in parentheses), all calculated on the B3LYP/6–31++G(d,p) level, are as follows (in Hartrees): NB_3H_6: *exo*-**2** –132.953560 (0.071968), *exo*-**3** –132.954643 (0.073227), P_2 (Fig. 1) –132.951477 (0.071646), P_1 (Fig. 1) –132.943151 (0.072384); $NB_3Me_3H_3$: *exo*-**2** –250.933736 (0.155864), *exo*-**3** –250.935373 (0.157371); NB_3H_5Cl: *exo*-**2** –592.590250 (0.065081), *exo*-**3** –592.592394 (0.066407), *endo*-**4** –592.578909 (0.065553), *endo*-**3** –592.584792 (0.066734); $NB_3Me_3H_2Cl$: *exo*-**2** –710.573843 (0.149039), *exo*-**3** –710.575969 (0.150579), *endo*-**3** –710.567150 (0.151032); NB_3H_4: **A** –131.731454 (0.049558), **B** –131.727217 (0.050556), **C** –131.708100 (0.053350), **D** –131.700598 (0.051704), **E** –131.708037 (0.052683), **F** –131.623541 (0.051472); NB_3Me_4: **A** –289.076671 (0.162974), **B** –289.074689 (0.163562), **C** –289.027189 (0.165577), **D** –289.019674 (0.165028), **E** –289.012076 (0.166198), **F** –288.942284 (0.164986). Calculated energies are mentioned in the preceding sections without ZPVE.

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References

[1] M. Müller, P. Paetzold, *Coord. Chem. Rev.* **1998**, *176*, 135.
[2] P. Paetzold, B. Redenz-Stormanns, R. Boese, M. Bühl, P. von Ragué Schleyer, *Angew. Chem.* **1990**, *102*, 1059; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1059.
[3] M. Müller, T. Wagner, U. Englert, P. Paetzold, *Chem. Ber.* **1995**, *128*, 1.
[4] M. Müller, U. Englert, P. Paetzold, *Chem. Ber.* **1995**, *128*, 1105.
[5] S. Luckert, U. Englert, P. Paetzold, *Inorg. Chim. Acta* **1998**, *269*, 43.
[6] R. Boese, B. Kröckert, P. Paetzold, *Chem. Ber.* **1987**, *120*, 1913.
[7] P. Paetzold, B. Redenz-Stormanns, R. Boese, *Chem. Ber.* **1991**, *124*, 2435.
[8] W. Rattay, Dissertation, Universität München, **1987**.
[9] W. Biffar, H. Nöth, H. Pommerening, *Angew. Chem.* **1980**, *92*, 63; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 56.
[10] J. Sandström, *Dynamic NMR Spectroscopy*, Second Printing, Acad. Press, London, **1984**.
[11] C. Brown, R. H. Cragg, T. J. Miller, D. O. Smith, *J. Organomet. Chem.* **1983**, *244*, 209.
[12] A. J. Ashe III, W. Klein, R. Rousseau, *J. Organomet. Chem.* **1994**, *468*, 21.
[13] Gaussian 98, Revision A.6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.
[14] R. Ditchfield, *Mol. Physics* **1974**, *27*, 789.
[15] A. Neu, T. Mennekes, U. Englert, M. Hofmann, P. von Ragué Schleyer, *Inorg. Chim. Acta* **1999**, *289*, 58.
[16] A. Neu, K. Radacki, P. Paetzold, *Angew. Chem.* **1999**, *111*, 1358; *Angew. Chem. Int. Ed.* **1999**, *38*, 1281.
[17] H. Nöth, B. Wrackmeyer in P. Diehl et al. (Eds.) *NMR, Basic Principles and Progress*, Vol. 14, Springer, Berlin **1978**.
[18] B. Wrackmeyer in G. A. Webb (Ed.) *Annual Reports on NMR Spectroscopy*, Vol. 20, Academic Press, London **1988**.
[19] D. F. Gaines, G. M. Edvenson, T. G. Hill, B. R. Adams, *Inorg. Chem.* **1987**, *26*, 1813.
[20] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, 4th ed., Thieme, Stuttgart **1991**.
[21] R. R. Mohr, W. N. Lipscomb, *Inorg. Chem.* **1986**, *25*, 1053.
[22] P. H. M. Budzelaar, K. Krogh-Jespersen, T. Clark, P. von R. Schleyer, *J. Am. Chem. Soc.* **1985**, *107*, 2773.
[23] H. Klusik, A. Berndt, *Angew. Chem.* **1983**, *95*, 895; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 877.
[24] C. Wieczorek, J. Allwohn, G. Schmidt-Lukasch, R. Hunold, W. Massa, A. Berndt, *Angew. Chem.* **1990**, *102*, 435; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 398.
[25] H. C. Brown, U. S. Racherla, *J. Org. Chem.* **1986**, *51*, 427.
[26] H. C. Brown, D. Busavaih, N. G. Bhat, *Organometallics* **1983**, *2*, 1309.
[27] B. G. Ramsay, N. K. Das, *J. Am. Chem. Soc.* **1972**, *94*, 4227.
[28] H. C. Brown, N. Ravindran, *Inorg. Chem.* **1977**, *16*, 2938.
[29] H. C. Brown, J. A. Sikorski, *Organometallics* **1982**, *1*, 28.