C-HALOGENATION OF THE *closo*-$[CB_{11}H_{12}]^-$ ANION

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday in recognition of his major contributions to cluster borane chemistry.

A synthesis is described of the four *C*-halogenated 1-X-$CB_{11}H_{11}^-$ anions (X = I, Br, Cl, F) using *N*-halosuccinimides and *N*-fluorobis(benzenesulfonyl)amine as halogenating agents. The procedure yields only the desired product next to unreacted starting material. Regularities in the ^{11}B and ^{13}C NMR chemical shifts of singly halogenated icosahedral carboranes are summarized.

Keywords: Boranes; Boron clusters; Carboranes; Halogenation; Monocarbaboranes; ^{11}B NMR and ^{13}C NMR spectroscopy.

We are interested in 12-vertex *closo*-carboranes $CB_{11}H_{12}^-$ (**1**) with aryl substituents in positions 1 and 12 in connection with the synthesis of rod-like structures for a molecular "Tinkertoy"[1] construction set[2–4]. *C*-Halogenated 1-X-$CB_{11}H_{11}^-$ anions, especially 1-I-$CB_{11}H_{11}^-$ (**2a**) and 1-Br-$CB_{11}H_{11}^-$ (**2b**), seemed to represent possible intermediates for the synthesis of 1-aryl substituted 1-R$CB_{11}H_{11}^-$ anions by Pd-catalyzed carbon–carbon coupling reactions, but no reliable methods appeared to be available for their preparation. Several monohalogenated X-$CB_{11}H_{11}^-$ anions are known: 12-I (**3a**)[5,6], 12-Br (**3b**)[7], 12-Cl (**3c**)[7], 12-F (**3d**)[8], 2-Br (**4b**)[9], 2-Cl (**4c**)[9], 2-F (**4d**)[8,10]; the 12-F-$CB_{11}Me_{11}^-$ anion has also been reported[11]. Here we provide the details of the synthesis of the four *C*-halogenated derivatives of **1** using *N*-halosuccinimides and

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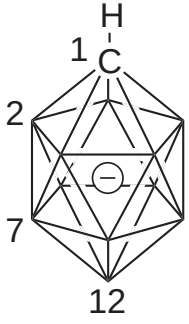
N-fluorobis(benzenesulfonyl)amine [$(PhSO_2)_2NF$] as the halogenating agents[12]. We also note regularities in the NMR spectra of these and some related structures.

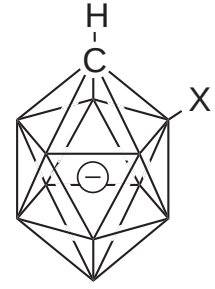


1

	I	Br	Cl	F
x:	**a**	**b**	**c**	**d**

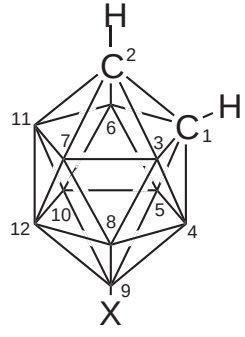
2x

3x

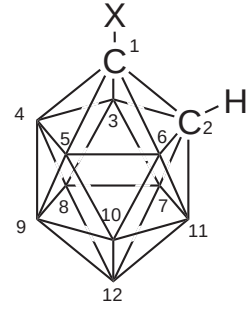


4x

5x



6x



7x

EXPERIMENTAL

General

All reactions were carried out using standard vacuum and inert atmosphere techniques. THF was dried over sodium benzophenone ketyl and distilled before use. All HPLC separations were performed at 14 ml/min on a Waters (reverse phase) C18 μ BondaPak™ preparative column (15–20 μm, 125 Å, 25 × 100 mm) using a buffered water/methanol based solvent system (60% MeOH, 40% H_2O, each containing 0.7% NEt_3 and 1% HOAc). Injection size: 1 ml (50 mg of an Et_3NH^+ salt). Retention times (min): **1**, 14.5; **2a**, 20; **2b** and **2c**, 17; **2d**, 16.5. NMR spectra were measured in acetone-d_6 (to eliminate coincidental signal overlap, **2d** was also measured in CD_2Cl_2). ^1H and ^{11}B NMR spectra were measured with a Varian XL-300 instrument, and the ^{19}F NMR spectrum with a Bruker AM-400 spectrometer. Assignment of the boron signals to individual vertices (shown in parentheses) was established by [^{11}B-^{11}B]-COSY spectra[13] taken with a Varian XL-500 spectrometer at 11.75 tesla, and assignments for individual cluster BH protons were made using ^1H-{^{11}B(selective)}[14] measurements, as described elsewhere[15]. Proton shifts of BH protons were measured with boron decoupling using a Varian XL-500 spectrometer, which was also used to obtain ^{13}C NMR spectra. Chemical shifts are given in ppm (δ-scale) with positive shifts downfield; carbon and proton shifts are referenced to TMS, boron shifts to $BF_3{\cdot}Et_2O$ ($B(OMe)_3$ at 18.1 ppm), and fluorine shifts to $CFCl_3$. Coupling constants (*J*) were obtained from resolution enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in Hz. Electrospray negative ion mass spectra were measured in methanol solutions using a Hewlett–Packard 5989 API/ES/MS instrument (the most intense peak in each spectrum is listed). IR spectra (wavenumbers in cm^{-1}) were measured with a Thermo Nicolet Avatar 360 FTIR. UV-VIS spectra were measured in methanol with a HP 8452 A Diode Array Spectrophotometer. *N*-Fluorobis(benzenesulfonyl)amine was purchased from Oakwood, all other reagents were purchased from Aldrich and were used without further purification.

1-I-$CB_{11}H_{11}^-$ (**2a**)

In a dry 50 ml 3-neck flask, the Cs^+ salt of **1** (0.276 g, 1 mmol) was dissolved in THF (20 ml). At room temperature, butyllithium (1.0 ml, 2 mmol; 2 M in cyclohexane) was added dropwise, and the solution became cloudy white. After 5 min, CuCl (0.098 g, 1 mmol) was added, causing the mixture to turn dark. After 30 min, *N*-iodosuccinimide (0.225 g, 1 mmol) was added and the solution gradually turned pink. After 4 h, reaction was quenched by the addition of methanol and the solution was evaporated to dryness. The residue was dissolved in 4 M HCl and extracted three times with 15 ml portions of diethyl ether. Water was added to the combined ether layers and the ether was evaporated. The aqueous solution was filtered and treated with triethylammonium hydrochloride, yielding a yellowish white solid precipitate (0.401 g after drying) containing **1** and **2a** in a ratio of 1 : 4 as determined by ^{11}B NMR. These salts were then separated by HPLC. After crystallization from a mixture of water and methanol, **2a** (220 mg of Et_3NH salt) was obtained as a white solid (59% yield). ^{11}B NMR: –8.14 (12), –10.92 (2-6), –12.12 (7-11). $^1H\{^{11}B\}$ NMR: 1.98 (12), 2.36 (2-6), 1.55 (7-11). ^1H NMR: 1.39 (t, CH_3); 3.48 (q, CH_2). ^{13}C NMR: 6.3. IR (Cs^+ salt): 2 921, 2 537, 1 429, 1 260, 1 017, 797. UV-VIS, λ_{max}, nm (ε_{max}): 236 (170), 262 (180), 298 (190). MS (ESI), *m/z*: 269.
Exact mass (ES HRMS), found: 271.0954; $CB_{11}H_{11}I$ requires: 271.0929.

1-Br-$CB_{11}H_{11}^-$ (**2b**)

In a dry 50 ml 3-neck flask, the Cs^+ salt of **1** (0.276 g, 1 mmol) was dissolved in THF (20 ml). At room temperature, butyllithium (1.0 ml, 2 mmol; 2 M in cyclohexane) was added dropwise, and the solution became cloudy white. After 5 min, *N*-bromosuccinimide (0.178 g, 1.0 mmol) was added and the solution turned purple. After 4 h, the reaction was quenched by the addition of methanol and evaporated to dryness. The residue was dissolved in 4 M HCl and extracted three times with 15 ml portions of diethyl ether. Water was added to the combined ether layers and the ether was evaporated. The aqueous solution was filtered and treated with triethylammonium hydrochloride, yielding a white solid precipitate (0.200 g after drying) containing only **1** and **2b** in a ratio of 1 : 3 as determined by ^{11}B NMR. These salts were then separated by HPLC. After crystallization from a mixture of water and methanol, **2b** (130 mg of Et_3NH salt) was obtained as a white solid (40% yield). ^{11}B NMR: –10.32 (12), –12.09 (2-6), –12.96 (7-11). $^1H\{^{11}B\}$ NMR: 1.76 (12), 2.16 (2-6), 1.58 (7-11). ^1H NMR: 1.28 (t, CH_3); 3.19 (q, CH_2). ^{13}C NMR: 48.8. IR (Cs^+ salt): 2 922, 2 527, 1 653, 1 558, 1 457, 668. UV-VIS, λ_{max}, nm (ε_{max}): 234 (150). MS (ESI), *m/z*: 222. Exact mass (ES HRMS), found: 225.1052; $CB_{11}H_{11}Br$ requires: 225.1047.

1-Cl-$CB_{11}H_{11}^-$ (**2c**)

In a dry 50 ml 3-neck flask, the Cs^+ salt of **1** (0.276 g, 1 mmol) was dissolved in THF (20 ml). At room temperature, butyllithium (1.0 ml, 2 mmol; 2 M in cyclohexane) was added dropwise, and the solution became cloudy white. After 5 min, CuCl (0.098 g, 1 mmol) was added, causing the mixture to turn dark. *N*-Chlorosuccinimide (0.134 g, 1 mmol) was added and the reaction mixture gradually turned orange. After 3 h the reaction was quenched by the addition of methanol and evaporated to dryness. The residue was dissolved in 4 M HCl and extracted three times with 15 ml portions of diethyl ether. Water was added to the combined ether layers and the ether was evaporated. The aqueous solution was filtered and treated with triethylammonium hydrochloride. A white solid precipitate (0.210 g after drying) was obtained and contained only **1** and **2c** in a ratio of 1 : 2 as determined by ^{11}B NMR. These salts were then separated by HPLC. After crystallization from a mixture of water and methanol, **2c** (120 mg of Et_3NH salt) was obtained as a white solid (43% yield). ^{11}B NMR: –11.37 (12), –12.53 (2-6), –13.1 (7-11). $^1H\{^{11}B\}$ NMR: 1.55 (12), 2.06 (2-6), 1.58 (7-11). ^1H NMR: 1.30 (t, CH_3); 3.41 (q, CH_2). ^{13}C NMR: 69.0. IR (Cs^+ salt): 2 919, 2 517, 1 558, 1 457, 1 003, 873, 720. MS (ESI), *m/z*: 177. Exact mass (ES HRMS), found: 179.1574; $CB_{11}H_{11}Cl$ requires: 179.1573.

1-F-$CB_{11}H_{11}^-$ (**2d**)

To a dry 50 ml 3-neck flask, the Cs^+ salt of anion **1** (0.139 g, 0.50 mmol) was added followed by THF (12 ml). At room temperature, butyllithium (0.25 ml, 0.50 mmol; 2 M in cyclohexane) was added dropwise, and the solution turned cloudy white. After 5 min, *N*-fluorobis(benzenesulfonyl)amine (0.315 g, 1.00 mmol) was added. The solution gradually turned orange. After 30 min, the reaction was quenched by the addition of methanol and evaporated to dryness. The residue was dissolved in 4 M HCl and extracted three times with 15 ml portions of diethyl ether. Water was added to the combined ether layers and the ether was evaporated. The aqueous solution was filtered and treated with triethylammonium hydrochloride to yield a white solid precipitate (0.164 g after drying). ^{11}B NMR spectra

showed **2d** and **1** in a ratio of 4 : 1. These salts were then separated by HPLC. After crystallization from a mixture of water and methanol, **2d** (112 mg of Et_3NH salt) was obtained as a white solid (85% yield). ^{11}B NMR (CD_2Cl_2): –16.8 (12, 7-11), –17.1 (2-6). $^1H\{^{11}B\}$ NMR: 1.98 (7-12), 1.33 (2-6). ^1H NMR: 1.38 (t, CH_3); 3.33 (q, CH_2). ^{13}C NMR: 111.2 (d), J_{CF} = 271. ^{19}F NMR: –157.96. IR (Cs^+ salt): 2 920, 2 851, 2 543, 1 557, 1 456, 1 260, 1 030, 799. MS (ESI), *m/z*: 161. Exact mass (ES HRMS), found: 163.1870; $CB_{11}H_{11}F$ requires: 163.1868.

RESULTS AND DISCUSSION

Synthesis

Under the conditions described, the halogenation reactions give only the *C*-halogenated derivatives of anion **1** and unreacted starting material. Identifying these conditions took a surprising amount of effort since under many conditions tested, the *C*-halogenation fails or yields mixtures of products (Table I). For instance, bromination of $CuCB_{11}H_{11}^-$ with NBS took place with 100% conversion but produced a 1 : 1 mixture of **2b** and **3b**. In the presence of moisture in the THF solvent, **3b** is the dominant product and obviously results from the bromination of **1**.

While NBS reacts readily with $LiCB_{11}H_{11}^-$ to yield only **2b** and unreacted starting material, iodination with *N*-iodosuccinimide (NIS) only occurs in the presence of CuCl, regardless of whether NIS is added before or after CuCl. In the presence of moisture, **3a** is formed. Chlorination also requires the

TABLE I
C-Halogenation of $CB_{11}H_{12}^-$ (**1**)

Reagent	1-Substitution (% yield)	12-Substitution (% yield)	Unreacted **1**
1. CuCl, 2. NIS	80 **2a**	0	20
1. NIS, 2. CuCl	60 **2a**	0	40
NIS	0	0	100
NBS	75 **2b**	0	25
1. CuCl, 2. NBS	50 **2b**	50 **3b**	0
1. CuCl, 2. NCS	65 **2c**	0	35
NCS	0	0	100
$(PhSO_2)_2NF$	75 **2d**	0	25

use of $CuCB_{11}H_{11}^-$. When elemental iodine is used for iodination of $LiCB_{11}H_{11}^-$ in THF, a mixture of **2a** and $R\text{-}CB_{11}H_{11}^-$ results[16], where the substituent R is a polymeric product of THF cleavage.

Our attempts to use the *C*-halogenated anions **2a** and **2b** as reagents in Pd-catalyzed Stille, Suzuki and Negishi[17] coupling reactions have not been successful. This contrasts with the reactivity of the *B*-halogenated anions **3a** which undergo Pd-catalyzed Kumada coupling with alkyl and aryl Grignard reagents smoothly[6]. Fortunately, an inverse Negishi coupling of the 1-ZnCl derivative of **1** with aryl halides proceeds well[12].

NMR Spectra (Table II)

The availability of *C*-halogenated $CB_{11}H_{12}^-$ anions provides an opportunity for a general summary of the effect of monohalogenation on the NMR chemical shifts of the cage atoms in an icosahedral cluster, and particularly, for an additional examination of Heřmánek's[18] antipodal effect[19–22]. This term refers to the observation that upon introduction of a substituent onto an atom in the icosahedral skeleton, the NMR signal of the opposite (para, antipodal) atom is shifted to more negative δ values.

Table II and Fig. 1 summarize all of the shift increments Δδ in the new halo compounds **2x** (**x** stands for **a**–**d**) and compare them with those observed previously in the ipso, ortho, meta, and para positions of several other monohalogenated icosahedral boranes. All of the increments are roughly linearly correlated with Pauling's electronegativities[23] of the halogens.

Two types of response to the nature of the halogen substituent are observed. The shift increment Δδ for the ipso position becomes much more positive as the halogen becomes more electronegative in the series I < Br < Cl < F. This trend is particularly pronounced in the one case when the substituted atom is a carbon, as would be expected in view of the generally higher sensitivity of ^{13}C NMR chemical shifts to substituent effects[24]. In **2x**, these shift increments range over more than 100 ppm, while the ipso ^{11}B NMR shift increments for **3x**–**6x** range only over about 30 ppm. The latter are remarkably similar in these three series of compounds and seem to be the property of the icosahedral cage, little affected by the presence of the heteroatoms.

The chemical shift increments Δδ in the more distant positions ortho, meta, and para are much smaller, and had to be plotted on a different scale in Fig. 1. Unlike the ipso increments, they all become more negative as the halogen becomes more electronegative. This "unnatural" direction of varia-

tion is most pronounced for the antipodal position. In keeping with the long-recognized antipodal effect, all of the para ^{11}B NMR shift increments are negative. Like the ipso shift increments, they seem to be a property of the icosahedron, little dependent on the presence of heteroatoms. They are remarkably similar in the 1-halogenated $CB_{11}H_{12}^-$ monoanions **2x** and the previously studied 1-halogenated $B_{12}H_{12}^{2-}$ dianions **5x** [25,26] and 1-halogenated $C_2B_{10}H_{12}$ carboranes **7x** [24].

The slope of the dependence of shift increments for the ortho and meta positions on halogen electronegativity is smaller than in the para position, but is still quite clear. They show a larger spread of values within the icosahedral families investigated, and most likely will be of reduced diagnostic value.

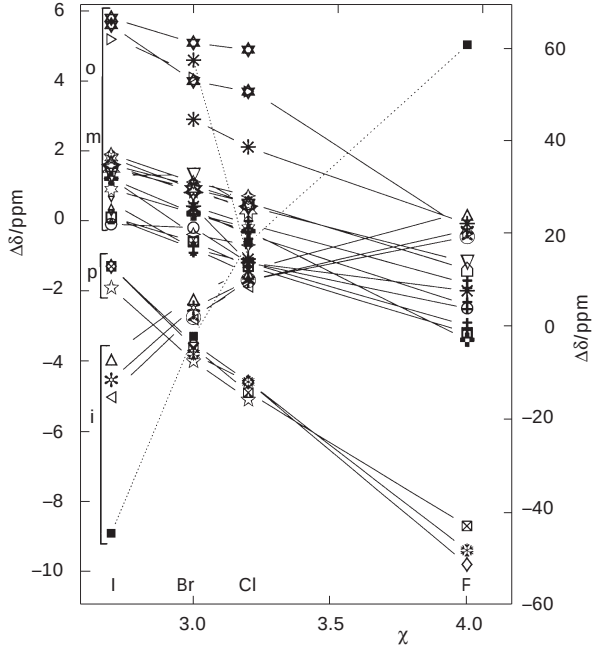


FIG. 1

Trends in halogen induced NMR chemical shift increments Δδ as a function of Pauling electronegativity χ. ^{11}B NMR (full lines) except for **2x** (■) and position 1 in **4x** (✳), which are ^{13}C NMR (dotted lines). Ipso positions (**2x** ■, **3x** ✳, **4x** ✇, **5x** Δ, **6x** ◅, positive slopes) refer to the scale on the right. All other positions (ortho, meta, para, negative slopes) refer to the scale on the left: **2x** (*o*) ▻, **2x** (*m*) ✜, **2x** (*p*) ◇, **3x** (*o*) ∇, **3x** (*m*) ❍, **4x** (*o*) ✳, **4x** (*m*) ‡, **4x** (*p*) ❄, **5x** (*o*) ⌂, **5x** (*m*) ❑, **5x** (*p*) ⊠, **6x** (*o*) ☼, **6x** (*m*) ⧖, **7x** (*o*) ✡, **7x** (*m*) ✧, **7x** (*p*) ★

Although the chemical shifts in icosahedral cages are generally well reproduced by calculations[22], it is not easy to relate the trends observed in Fig. 1 to the underlying physical principles. The qualitative notion[26] that the antipodal shift increments are dominated by π electron donation from the halogen lone pairs, whereas the ipso shift increments are ruled by their σ electron withdrawal, appears to make sense, in that both the π donation and the σ withdrawal abilities increase from iodine to fluorine. The ortho and meta shift increments seem to respond to both kinds of effects to a

TABLE II
^{13}C and ^{11}B NMR chemical shift increments Δδ for halogenated twelve-vertex clusters[a]

Position		**x**:	**a**	**b**	**c**	**d**	Position		**x**:	**a**	**b**	**c**	**d**
rel.	abs.		I	Br	Cl	F	rel.	abs.		I	Br	Cl	F
i	1	**2x**[b]	–44.4	–1.9	18.3	61.1	*m*	7	**2x**[c]	1.2	0.2	–0.3	–3.4
	12	**3x**[c]	–11.2[d]	4.4[e]	10.3[e]	21.0[f]		2	**3x**[c]	–0.1[d]	–0.2[e]	–1.2[e]	–2.5[f]
	2	**4x**[c,g]		2.3	10.3	19.6		4	**4x**[c,g]		0.4	–0.1	–1.8
	1	**5x**[c,h]	–6.0	7.1	12.5	25.1		8	**4x**[c,g]		–0.8	–1.2	–3.0
	9	**6x**[c,h]	–14.2	2.6	9.7			12	**4x**[c,g]		0.3	–0.4	–2.4
o	2	**2x**[c]	5.3	4.2	3.8	–0.3		7	**5x**[c,h]	0.1	–0.6	–1.3	–3.2
	7	**3x**[c]	1.3[d]	1.3[e]	0.4[e]	–1.2[f]		7	**7x**[c,h]	1.9	1.1	0.7	
	1	**4x**[b,g]		4.6	–1.1			8	**7x**[c,h]	1.2	–0.4	–0.7	
	3	**4x**[c,g]		2.9	2.1	–0.1		9	**7x**[c,h]	1.6	0.8	0.4	
	7	**4x**[c,g]		0.4	–1.2	–2.0		3	**6x**[c,h]	0.1	–0.8	–1.5	
	2	**5x**[c,h]	1.6	1.0	0.5	–1.4		7	**6x**[c,h]	0.5	–0.8	–1.5	
	3	**7x**[c,h]	5.8	5.1	4.9		*p*	12	**2x**[c]	–1.3	–3.6	–4.9	–9.8
	4	**7x**[c,h]	5.6[i]	4.0	3.7			9	**4x**[c,g]		–3.8	–4.6	–9.4
	4	**6x**[c,h]	0.9	0.2	–0.2			12	**5x**[c,h]	–1.3	–3.6	–4.9	–8.7
	8	**6x**[c,h]	1.8	0.9	0.5			12	**7x**[c,h]	–1.9	–4.0	–5.1	
	12	**6x**[c,h]	1.5	0.9	0.3								

[a] $\Delta\delta = \delta_{subst} - \delta_{parent}$; *i* = ipso, *o* = ortho, *m* = meta, *p* = para. [b] ^{13}C NMR. [c] ^{11}B NMR. [d] Ref.[6] [e] Ref.[7] [f] Ref.[8] [g] Ref.[9] [h] Ref.[26] [i] This value is listed incorrectly as 1.2 in ref.[26]

comparable degree; a more detailed analysis is not available at the present time.

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REFERENCES AND NOTES

1. Tinkertoy is a trademark of Playskool, Inc., Pawtucket, RI 02862, and designates a children's toy construction set consisting of straight wooden sticks and other simple elements insertable into spool-like connectors.
2. Kaszynski P., Friedli A. C., Michl J.: *J. Am. Chem. Soc.* **1992**, *114*, 601.
3. Müller J., Baše K., Magnera T. F., Michl J.: *J. Am. Chem. Soc.* **1992**, *114*, 9721.
4. Yang X., Jiang W., Knobler C. B., Hawthorne M. F.: *J. Am. Chem. Soc.* **1992**, *114*, 9719.
5. Jelínek T., Plešek J., Heřmánek S., Štíbr B.: *Collect. Czech. Chem. Commun.* **1986**, *51*, 819.
6. Grüner B., Janoušek Z., King B. T., Woodford J. N., Wang C. H., Všetečka V., Michl J.: *J. Am. Chem. Soc.* **1999**, *121*, 3122.
7. Jelínek T., Baldwin P., Scheidt W. R., Reed C. A.: *Inorg. Chem.* **1993**, *32*, 1982.
8. Mair F. S., Morris J. H., Gaines D. F., Powell D. J.: *J. Chem. Soc., Dalton Trans.* **1993**, 135.
9. Franken A., King B. T., Rudolph J., Rao P., Noll B. C., Michl J.: *Collect. Czech. Chem. Commun.* **2001**, *66*, 1238.
10. Ivanov S. V., Lupinetti A. J., Miller S. M., Anderson O. P., Solntsev K. A., Strauss S. H.: *Inorg. Chem.* **1995**, *34*, 6419.
11. King B. T., Noll B. T., McKinley A. J., Michl J.: *J. Am. Chem. Soc.* **1996**, *118*, 10902.
12. For preliminary reports, see: a) Janoušek Z., Craig P. R., Hilton C. L., Lehmann M. U., Michl J.: *BUSA VII, June 2000, Pittsburgh, PA*, Abstr. No. 38; b) Janoušek Z., Craig P. R., Hilton C. L., Michl J.: *EUROBORON 2, September 2001, Dinard, France*, Abstr. No. P18.
13. Hutton W. C., Venable T. L., Grimes R. N.: *J. Am. Chem. Soc.* **1996**, *106*, 29.
14. Fontaine X. L. R., Kennedy J. D.: *J. Chem. Soc., Dalton Trans.* **1987**, 1593.
15. See, for example: Plešek J., Štíbr B., Fontaine X. L. R., Kennedy J. D., Heřmánek S., Jelínek T.: *Collect. Czech. Chem. Commun.* **1991**, *56*, 1618.
16. Clayton J. R.: *M.S. Thesis*. University of Colorado, Boulder 1999.
17. Hegedus L. S.: *Transition Metals in the Synthesis of Complex Organic Molecules*, p. 57. University Science Books, Sausalito (CA) 1999.
18. Heřmánek S., Plešek J., Štíbr B.: *NMR Symposium, November 1974, Prague, Czechoslovakia*, Abstr. No. 11. Prague 1974.
19. Heřmánek S., Gregor V., Štíbr B., Plešek J., Janoušek Z., Antonovich V. V.: *Collect. Czech. Chem. Commun.* **1976**, *41*, 1492.
20. Siedle A. R., Bodner G. M., Garber A. R., Beer D. C., Todd L. J.: *Inorg. Chem.* **1974**, *10*, 2321.
21. Stanko V. I., Babushkina T. A., Klimova T. P., Goltiapin Yu. V., Klimova A. L., Vasilev A. M., Alimov A. M., Khrapov V. V.: *Zh. Obshch. Khim.* **1976**, *46*, 1071.

22. Buehl M., Schleyer P. v. R., Havlas Z., Hnyk D., Heřmánek S.: *Inorg. Chem.* **1991**, *30*, 3107.
23. Allred A. L.: *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.
24. Heřmánek S., Jelínek T., Plešek J., Štíbr B., Fusek J., Mareš F. in: *Boron Chemistry* (S. Heřmánek, Ed.), p. 26. World Scientific, Singapore 1987.
25. Grüner B., Heřmánek S., Plzák Z.: *IMEBORON VII, Torun, Poland, July 30–August 3, 1990*, Poster No. 5.
26. Heřmánek S.: *Chem. Rev.* **1992**, *92*, 325.

Janoušek Z., Hilton C. L., Schreiber P. J., Michl J.: *Collect. Czech. Chem. Commun.* **2002**, *67*, 1025.

The amount of butyllithium to be used in the syntheses af **2a** (p. 1027), **2b** (p. 1028), and **2c** (p. 1028), which is stated to be 1 ml, 2 mmol, should read 0.5 ml, 1 mmol.

The J_{BH} coupling constants deduced from the ^{11}B NMR spectra of **2a**–**2d** were inadvertently omitted. The full text in the Experimental Part should have been:

2a ^{11}B NMR: –8.14 [d, 1B, 143 B(12)], –10.92 [d, 5B, ~138 B(2-6)], –12.12 [d, 5B, ~106 B(7-11)].

2b ^{11}B NMR: –10.32 [d, 1B, ~159 B(12)], –12.09 [d, 5B, 144 B(2-6)], –12.96 [d, 5B, ~110 B(7-11)].

2c ^{11}B NMR: –11.37 [d, 1B, 177 B(12)], –12.53 [d, 5B, 156 B(2-6)], –13.15 [d, 5B, 153 B(7-11)].

2d ^{11}B NMR: –16.8 [d, 11B, ~150 B(2-12)].