Halogenated Carborates

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Carbon Extrusion/Cluster Contraction: Synthesis of the Fluorinated Cyano-*closo*-Undecaborate $K_2[3\text{-NC-}closo\text{-}B_{11}F_{10}]$**

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The first report on the simplest *closo*-undecaborate anion $[B_{11}H_{11}]^{2-}$ was published in 1966,[1] and in recent years improved syntheses have been developed.[2] Salts of the perhalogenated anions $[B_{11}Hal_{11}]^{2-}$ (Hal = Cl, Br, I)[3] as well as partially halogenated anions were prepared.[1,2,4] To date, fluorinated derivatives are unknown,[2] which is not surprising, because $[B_{11}H_{11}]^{2-}$ and its derivatives exhibit a significantly lower chemical stability than $[B_{10}H_{10}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and related species.[2] The fluorination of $[B_{10}H_{10}]^{2-}$ is also difficult; HF is not an appropriate fluorination reagent, because the borate anion is sensitive to acids.[5] Salts of a perfluorinated derivative are only known for the most stable *closo*-borate dianion, $[B_{12}H_{12}]^{2-}$.[6,7]

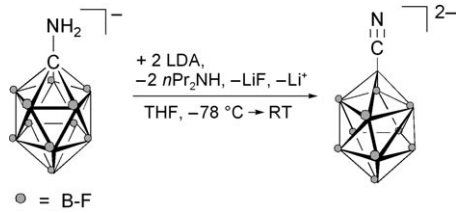
Currently, the chemistry of the monocarba-*closo*-dodecaborate anion is the subject of intensive investigations, because it is of interest for a large number of applications.[8,9] This increasing interest is mainly due to the unique variability of the properties of the anion by variation of the substituents at the C atom and the B atoms.[9] Examples of applications are pharmaceuticals,[10] the stabilization of reactive cations,[9,11–13] and ionic liquids.[9,14] Important derivatives are halogenated monocarba-*closo*-dodecaborate anions, which exhibit high chemical and thermal stabilities; hence, they are attractive weakly coordinating anions.[11–13,15]

Recently, we reported the synthesis of the first functionalized fluorinated monocarba-*closo*-dodecaborate $K[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]$.[16] A comparison of the reactivity of this compound with the related ion $[1\text{-H-}closo\text{-}CB_{11}F_{11}]^-$ revealed similarities (in aqueous KOH solution two fluoro ligands are exchanged for hydroxy groups) as well as different behaviors (the aminocarborate anion is not stable towards aqueous acids).[16]

As a derivatization of the amino group of $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]^-$ is not possible in H_2O under basic conditions, alternate reactions were studied. The deprotonation of the aminocarborate anion was achieved in dimethoxyethane or tetrahydrofuran with stoichiometric amounts of an alkyllithium reagent or lithium diisopropylamide (LDA) [Eq. (1)]. These reactions are reversible: $[1\text{-HN-}closo\text{-}CB_{11}F_{11}]^{2-}$ reacts with water to yield the corresponding amine.

$$[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]^- \underset{+H_2O,\ -OH^-}{\overset{+LDA,\ -nPr_2NH,\ -Li^+}{\rightleftharpoons}} [1\text{-HN-}closo\text{-}CB_{11}F_{11}]^{2-} \quad (1)$$

Addition of two equivalents of LDA or of an alkyllithium reagent results in a second deprotonation reaction. Immediately, an unexpected reaction takes place. The lithiated intermediate, which was not observed, rearranges under loss of F^- (or rather LiF) to produce the cyanoborate dianion $[NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$ (Scheme 1). During this rearrangement,

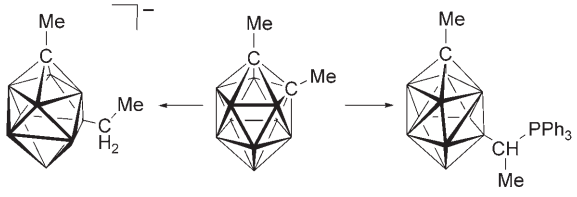


Scheme 1. Carbon extrusion/cluster contraction reaction of $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]^-$ resulting in $[3\text{-NC-}closo\text{-}B_{11}F_{10}]^{2-}$.

the C atom is extruded from the icosahedron, and the 12-vertex *closo*-cluster is converted into a *closo*-undecaborate dianion. To our knowledge, no similar concerted carbon extrusion/cluster contraction reaction has been reported to date. However, this rearrangement reaction may be related to the transformation of $1,2\text{-}Me_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$, which results in either $[1\text{-Me-6-Et-1-}closo\text{-}CB_9H_9]^-$[17] or 2-Me-3-{CHMe($PPh_3$)}-2-*closo*-$CB_{10}H_9$ (Scheme 2),[18] although these two transformations are multistep procedures.

An analogous conversion of primary amines is also unknown in organic chemistry. Though mechanistically different, the carbon extrusion/cluster contraction reaction exhibits parallels to the Favorskii rearrangement, in which α-haloketones are transformed into carboxylic acids or carboxylic acid derivatives (Scheme 3).[19,20]

The anions $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{10}H]^-$ and $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_9H_2]^-$, which are present in the starting material in small



Scheme 2. Multistep reaction of $1,2\text{-}Me_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ to $[1\text{-Me-6-Et-1-}closo\text{-}CB_9H_9]^-$ (left)[17] and 2-Me-3-{CHMe(PPh_3)}-2-*closo*-$CB_{10}H_9$ (right).[18]

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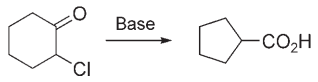
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 3. Example of a Favorskii rearrangement.[19,20]

amounts, react analogously to the fully fluorinated anion. The formation of the resulting anions $[NC\text{-}closo\text{-}B_{11}F_{10-n}H_n]^{2-}$ ($n = 1, 2$) was confirmed by NMR spectroscopy and by mass spectrometry (Figure 1). First attempts to convert other

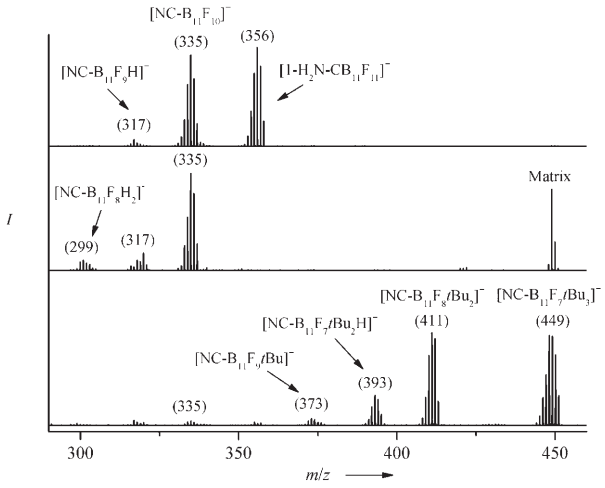


Figure 1. MALDI mass spectra of the products of the reactions of $K[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]$ with 1.5 equiv *t*BuLi (top), with 2.7 equiv LDA (middle) and with 4–5 equiv *t*BuLi (bottom) (impurities with BH groups are due to traces of $K[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11-n}H_n]$ ($n = 1,2$) in the starting material).

aminocarborate anions, such as $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}H_{11}]^-$,[21] $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}I_{11}]^-$,[22] and $[1\text{-}H_2N\text{-}2\text{-}F\text{-}closo\text{-}CB_{11}H_{10}]^-$,[23] into the corresponding cyano-*closo*-undecaborate anions failed. Hence, the carbon extrusion/cluster contraction reaction presented herein might be a unique property of highly fluorinated boron clusters.

The addition of more than two equivalents of an alkyl lithium reagent to a solution of $K[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]$ results in further reaction of the $[NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$ dianion. The fluoro ligands are replaced one after another by alkyl groups. The reaction rate of this ligand exchange decreases with an increasing number of alkyl groups [Eq. (2); R = Me, *n*Bu, *t*Bu; $n = 1$–7].

$$[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]^- \xrightarrow[\text{THF, } -78\,^\circ\text{C}\rightarrow\text{RT}]{+2\,\text{RLi, } -2\,\text{RH, } -\text{LiF, } -\text{Li}^+} [NC\text{-}closo\text{-}B_{11}F_{11}]^{2-} \xrightarrow{+n\text{RLi, } -n\text{LiF}} [NC\text{-}closo\text{-}B_{11}F_{11-n}R_n]^{2-} \quad (2)$$

To date, exchange of a fluoro ligand bonded to a *closo*-boron cluster or a carba-*closo*-boron cluster by reaction with an alkyllithium reagent has not been observed. The only examples of exchange reactions of halogeno substituents at boron clusters by organyl substituents are palladium-catalyzed coupling reactions of iodinated clusters with Grignard reagents and related species.[9,24–27]

When $K[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]$ is treated with an excess of methyllithium, anions containing up to seven methyl groups (i.e. formation of $[NC\text{-}closo\text{-}B_{11}F_3Me_7]^{2-}$) were observed by MALDI mass spectrometry of the reaction mixture. Figure 1 shows an example of a mass spectrum recorded after reaction of *t*BuLi with $K[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]$.

The solid, colorless salt $K_2[3\text{-}NC\text{-}closo\text{-}B_{11}F_{10}]$ is thermally stable up to 137 °C (as determined by differential scanning calorimetry) and can be handled in air. The wavenumber of the C–N stretch (2199 cm^{-1}) is comparable to that found for $Cs_2[1,12\text{-}(NC)_2\text{-}closo\text{-}B_{12}H_{10}]$ (2200 cm^{-1}).[28]

$K_2[3\text{-}NC\text{-}closo\text{-}B_{11}F_{10}]$ crystallizes in the monoclinic space group *C*2/*c*.[29] The cyano substituent is bonded to the B atom in the 3-position of the B_{11} octadecahedron (Figure 2). This finding is in agreement with data derived from DFT

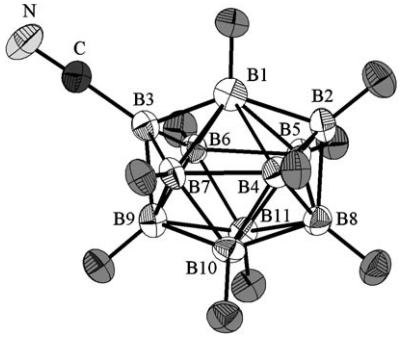


Figure 2. The $[3\text{-}NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$ anion in the crystal structure of $K_2[NC\text{-}closo\text{-}B_{11}F_{10}]$ (thermal ellipsoids are set at the 50% probability level).

calculations,[30] which predict this isomer to be the most stable of the five possible ones (see the Supporting Information). The deviation of the geometry of the anion from C_s symmetry is small in the solid state. The B–C and C–N bond lengths of 1.55(1) and 1.16(1) Å, respectively, are comparable to the corresponding bond lengths in $[NC\text{-}closo\text{-}B_6H_5]^{2-}$ in the Cs^+ salt.[31] The B–B bond lengths are in the range of 1.63(1) to 2.29(1) Å, which can be rationalized by the different numbers of adjacent skeletal atoms (four for B2 and B3, six for B1, and five for B4–B11). The B–F bonds are between 1.34(1) and 1.40(1) Å.

In the ^{19}F NMR spectrum of the $[NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$ ion, only one signal is observed for all ten F atoms, which is due to fast rearrangement of the cluster in solution; such behavior is typical of undecaborate anions.[2,32,33] The signal is split into a quartet because of coupling to the ^{11}B nuclei (Table 1; see also the Supporting Information). Two signals are present in the ^{11}B NMR spectrum of $[NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$ at −5.7 and −38.5 ppm, which was confirmed by a $^{11}B\{^1H\},^{11}B\{^1H\}$-COSY experiment (see the Supporting Information). The signal at −38.5 ppm is assigned to the ^{11}B nucleus of the B–CN group. The signal of the ^{11}B nuclei of the B–F units is detected at −5.7 ppm; $^1J(^{11}B,^{19}F)$ coupling splits it into a doublet. That only one signal is found for the ten ^{11}B nuclei of the B–F units is also due to cluster fluctuation. As an example of a ^{11}B NMR spectrum of cyano-*closo*-undecaborate anions containing alkyl substituents, the spectrum of a mixture of $[NC\text{-}closo\text{-}B_{11}F_{10-n}nBu_n]^{2-}$ ($n = 2$, 3) that shows the assignment of the signals, is depicted in the Supporting Information.

Additional studies on halogenated, especially fluorinated, aminocarba-*closo*-dodecaborates and aminocarba-*closo*-decaborates will reveal the limits of the carbon extrusion/

Table 1: NMR data of the $[NC\text{-}closo\text{-}B_{11}F_{10}]^{2<M->}$ anion and related borate anions.[a]

$\delta(^{11}B)$ [ppm]	$\delta(^{19}F)$ [ppm]	$^1J(^1H,^{11}B)$, $^1J(^{11}B,^{19}F)$[b] [Hz]	assignment
$[NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$			
−5.7	−233.0	63	B-F
−38.5			B-CN
$[NC\text{-}closo\text{-}B_{11}F_9H]^{2-}$			
−4.0	−228.6	≈63	B-F
−25.5		142	B-H
−35.1			B-CN
$[NC\text{-}closo\text{-}B_{11}F_8H_2]^{2-}$			
−2.4	−225.0	≈63	B-F
−24.7		142	B-H
−32.9			B-CN
$[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]^-$			
−18.5	−255.9	44	B2-B6
−17.3	−263.3	42	B7-B11
−10.7	−252.7	59	B12
$[1\text{-}HN\text{-}closo\text{-}CB_{11}F_{11}]^{2-}$[c]			
−17.8	−254.5	n.o.[d]	B2-B6
−17.8	−266.2	n.o.	B7-B11
−13.2	−259.0	n.o.	B12

[a] Solvent: CD_3CN. [b] $^1J(^{11}B,^{19}F)$: ^{19}F NMR spectrum. [c] Solvent: $[D_8]THF$. [d] n.o. = not observed.

cluster contraction reaction presented herein. Furthermore, salts of the $[NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$ anion are promising precursors for the synthesis of fluorinated and alkylated boron clusters.

Experimental Section

$K_2[NC\text{-}closo\text{-}B_{11}F_{10}]$: In a cylindrical reaction vessel (40 mL) equipped with a valve with a PTFE stem (Young, London), $K[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]$ (108 mg, 0.27 mmol) was dissolved in THF (10 mL). The solution was cooled to −78 °C, and a solution of LDA (0.4 mL, 0.72 mmol, 1.8 M) in THF/heptane/ethylbenzene was added while the mixture was stirred. The reaction mixture was warmed to room temperature and stirred for further 12 h. Then a mixture of equal amounts of K_2CO_3 and $KHCO_3$ (250 mg total) was added. The suspension was filtered, and the solid residue was extracted with THF (25 mL). The solvent was removed from the filtrate by rotary evaporation, and the crude product was dried in vacuum to yield solid, colorless $K_2[NC\text{-}closo\text{-}B_{11}F_{10}]$ (102 mg, 0.25 mmol, 90 %).

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[1] E. L. Klanberg, E. L. Muetterties, *Inorg. Chem.* **1966**, *5*, 1955.
[2] O. Volkov, P. Paetzold, *J. Organomet. Chem.* **2003**, *680*, 301.
[3] O. Volkov, P. Paetzold, C. Hu, U. Kölle, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1029.
[4] E. F. Tolpin, W. N. Lipscomb, *J. Am. Chem. Soc.* **1973**, *95*, 2384.
[5] S. V. Ivanov, S. M. Ivanova, S. M. Miller, O. P. Anderson, K. A. Solntsev, S. H. Strauss, *Inorg. Chem.* **1996**, *35*, 6914.
[6] K. A. Solntsev, A. M. Mebel', N. A. Votinova, N. T. Kuznetsov, O. P. Charkin, *Koord. Khim.* **1992**, *18*, 340.
[7] S. V. Ivanov, S. M. Miller, O. P. Anderson, K. A. Solntsev, S. H. Strauss, *J. Am. Chem. Soc.* **2003**, *125*, 4694.
[8] B. Štíbr, *Chem. Rev.* **1992**, *92*, 225.
[9] S. Körbe, P. J. Schreiber, J. Michl, *Chem. Rev.* **2006**, *106*, 5208.
[10] M. F. Hawthorne, A. Maderna, *Chem. Rev.* **1999**, *99*, 3421.
[11] C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 133.
[12] S. H. Strauss, S. V. Ivanov, A. J. Lupinetti, (Colorado State University Research Foundation), WO 98/43983, **1998**.
[13] I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116; *Angew. Chem. Int. Ed.* **2004**, *43*, 2066.
[14] A. S. Larsen, J. D. Holbrey, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2000**, *122*, 7264.
[15] T. Küppers, E. Bernhardt, H. Willner, *Angew. Chem.* **2007**, *119*, 6462; *Angew. Chem. Int. Ed.* **2007**, *46*, 6346.
[16] M. Finze, G. J. Reiss, M. Zähres, *Inorg. Chem.* in press.
[17] A. Laromaine, F. Teixidor, C. Viñas, *Angew. Chem.* **2005**, *117*, 2260; *Angew. Chem. Int. Ed.* **2005**, *44*, 2220.
[18] J. Bould, A. Laromaine, C. Viñas, F. Teixidor, L. Barton, N. P. Rath, R. E. K. Winter, R. Kivekäs, R. Sillanpää, *Organometallics* **2004**, *23*, 3335.
[19] A. A. Akhrem, T. K. Ustynyuk, Y. A. Titov, *Russ. Chem. Rev.* **1970**, *39*, 732.
[20] D. Guijarro, M. Yus, *Curr. Org. Chem.* **2005**, *9*, 1713.
[21] T. Jelínek, J. Plešek, S. Heřmánek, B. Štíbr, *Collect. Czech. Chem. Commun.* **1986**, *51*, 819.
[22] R. R. Srivastava, D. K. Hamlin, D. S. Wilbur, *J. Org. Chem.* **1996**, *61*, 9041.
[23] M. Finze, unpublished results.
[24] L. I. Zakharkin, A. I. Kovredov, V. A. Ol'shevskaya, Z. S. Shaugumbekova, *J. Organomet. Chem.* **1982**, *226*, 217.
[25] T. Peymann, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1998**, *37*, 1544.
[26] P. Kaszynski, *Collect. Czech. Chem. Commun.* **1999**, *64*, 895.
[27] I. B. Sivaev, V. I. Bregadze, S. Sjöberg, *Collect. Czech. Chem. Commun.* **2002**, *67*, 679.
[28] W. R. Hertler, W. H. Knoth, E. L. Muetterties, *J. Am. Chem. Soc.* **1964**, *86*, 5434.
[29] Crystal structure of $K_2[NCB_{11}F_{10}]$: $CB_{11}F_{10}K_2N$, $M_r = 413.13$, STOE-IPDS, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); temperature 120 K. Colorless crystals ($0.30 \times 0.15 \times 0.15$ mm^3), obtained from $CH_3CN/Et_2O/CH_2Cl_2$, monoclinic, space group $C2/c$ (no. 15), $a = 23.935(8)$, $b = 9.903(2)$, $c = 14.367(6)$ Å, $\beta = 126.17(3)°$, $V = 2749.1(16)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.996$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.791$ mm^{-1}, $F(000) = 1568$, 14557 measured reflections ($5.12 < \theta_{max} < 25.00°$), structure solution by direct methods and structure refinement based on F^2 with 2405 independent reflections (1276 independent reflections with $I > 2\sigma(I)$), 231 variables (SHELXS-97).[34,35] All atoms were refined anisotropically. $R_1[F_o^2 > 2\sigma(F_o^2)] = 0.062$, $wR_2 = 0.1178$ (all data), $w = 1/[\sigma^2(F_o^2) + (0.0214P) + 0.5P]$, with $P = (F_o^2 + 2F_c^2)/3$, $S = 1.063$, $\Delta\rho_{max}/\Delta\rho_{min} + 0.58$ and -0.39 e Å^{-3}. CCDC-653913 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[30] Gaussian03 (Revision D.01): M. J. Frisch et al., see the Supporting Information.
[31] W. Preetz, A. Franken, M. Rath, *Z. Naturforsch. B* **1993**, *48*, 598.
[32] D. A. Kleier, D. A. Dixon, W. N. Lipscomb, *Inorg. Chem.* **1978**, *17*, 166.
[33] E. L. Muetterties, E. L. Hoel, C. G. Salentine, M. F. Hawthorne, *Inorg. Chem.* **1975**, *14*, 950.
[34] G. M. Sheldrick, *SHELXS-97*, *Program for Crystal Structure Solution*, Universität Göttingen, **1997**.
[35] G. M. Sheldrick, *SHELXL-97*, *Program for Crystal Structure Refinement*, Universität Göttingen, **1997**.

