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Synthesis and structure of fluorophenyl derivatives of the 10-vertex monocarbaborane anions $[1\text{-}CB_9H_{10}]^-$ and $[2\text{-}CB_9H_{10}]^-$

Vikentii I. Bragin [1], Alexander A. Korlyukov, Pavel V. Petrovskii, Igor B. Sivaev *, Vladimir I. Bregadze

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russia

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ABSTRACT

Reactions of decaborane *nido*-$B_{10}H_{14}$ with a series of fluorobenzaldehydes in alkaline solution followed by treatment with iodine give the *closo*-$[2\text{-}(X\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]^-$ anions (X = 2, 3, 4). Upon heating, these compounds rearrange to more thermodynamically stable *closo*-$[1\text{-}(X\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ anions (X = 2, 3, 4). The compounds synthesized were characterized by multinuclear NMR spectroscopy. The crystal structures of $(Bu_4N)[1\text{-}(2\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$ and $(Bu_4N)_2[2\text{-}(4\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9][1\text{-}(4\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$ were determined by single crystal X-ray diffraction.

1. Introduction

Carborane anions $[1\text{-}R\text{-}1\text{-}CB_{11}H_{11-n}X_n]^-$ and $[1\text{-}R\text{-}1\text{-}CB_9H_{9-n}X_n]^-$ (X = F, Cl, Br, I) have recently received much attention as a new class of robust and weakly coordinating anions [1–3]. The research interest was focused mainly on 12-vertex carboranes whereas their 10-vertex analogues received some less attention [4–7]. Described recently direct synthesis of *C*-aryl derivatives of 1-carba-*closo*-decaborate from decaborane $B_{10}H_{14}$ and aryl aldehydes [8–10] gives possibility to increase total size of carborane anion due to introduction of aryl group. It is known that phenyl groups in the tetraphenylborate anion $[BPh_4]^-$ are able to coordinate to metal ions and to react with electrophilic species [1,11]. The coordinating ability and reactivity of tetraphenylborate could be effectively suppressed by incorporation of electron-withdrawing substituents, such as fluorine atoms or trifluoromethyl groups [1,12]. There are only few examples of coordination of aryl groups in $[B(C_6F_5)_4]^-$ [13] and $[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]^-$ [14] to transition metals. We suppose that combined fluorination of the phenyl ring and the carborane cage could result in new family of bulky weakly coordinating anions. Fluorination of 1-carba-*closo*-decaborate anion $[1\text{-}CB_9H_{10}]^-$ was described earlier [15]. In this study we report synthesis of a series of the fluorophenyl monocarbaborane anions $[1\text{-}(X\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ and $[2\text{-}(X\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]^-$ (X = 2, 3, 4) *via* reaction of decaborane with fluorine-containing aldehydes.

2. Results and discussion

The reaction of decaborane *nido*-$B_{10}H_{14}$ with benzaldehyde PhCHO in alkaline aqueous solution is known to produce the *nido*-$[6\text{-}Ph\text{-}6\text{-}CB_9H_{11}]^-$ anion which undergoes oxidative closure to the *closo*-$[2\text{-}Ph\text{-}6\text{-}CB_9H_9]^-$ anion, and then undergoes rearrangement to more thermodynamically favorable *closo*-$[1\text{-}Ph\text{-}1\text{-}CB_9H_9]^-$ anion [8,9a-c]. This procedure is especially attractive for synthesis of various functional derivatives of the monocarbaborane anions $[1\text{-}CB_9H_{10}]^-$ and $[2\text{-}CB_9H_{10}]^-$ because of the commercial availability of substituted aromatic aldehydes (Scheme 1).

We decided to use the same approach to prepare fluoro derivatives of the 1-carba-*closo*-decaborate anion. At the first step we tried reaction of decaborane with C_6F_5CHO in alkaline aqueous ethanol. Unfortunately, no formation of carborane species was observed, that could be explained by formation of stable pentafluorobenzaldehyde hemiacetal [16]. Similarly, no carborane formation was found in the case of reaction with trifluoroacetaldehyde monohydrate. Nevertheless we have found that the reactions of decaborane with a series of isomeric fluorobenzaldehydes 2-, 3- and 4-FC_6H_4CHO in alkaline solution followed by the treatment with elemental iodine give the corresponding *closo*-$[2\text{-}FC_6H_4\text{-}2\text{-}CB_9H_9]^-$ anions isolated as their tetrabutylammonium salts (Scheme 2).

Dissolution of the 2-isomers in ethanol followed by heating at reflux for 20 h, results in the thermodynamically more stable *closo*-$[1\text{-}FC_6H_4\text{-}1\text{-}CB_9H_9]^-$ anions (Scheme 3). Their tetrabutylammonium

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* Corresponding author. Tel.: +7 499 1359242; fax: +7 499 1355085.
E-mail address: sivaev@ineos.ac.ru (I.B. Sivaev).

[1] Permanent address: State Research Center Institute of Chemistry and Technology of Organoelement Compounds, 38 Enthusiasts Av., 111123 Moscow, Russia.

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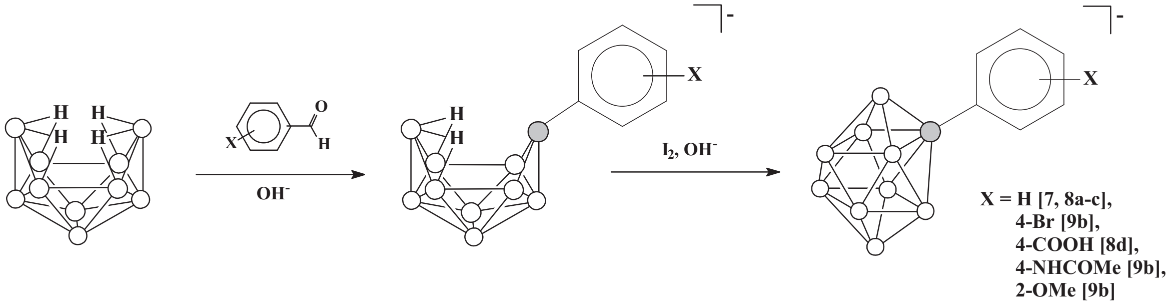
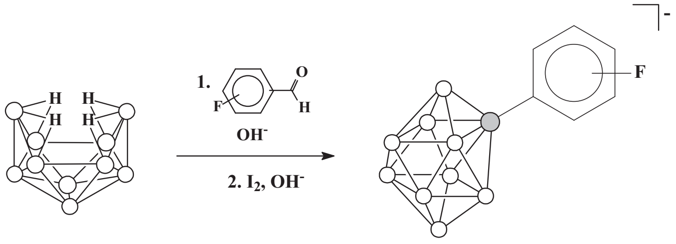


Scheme 1.

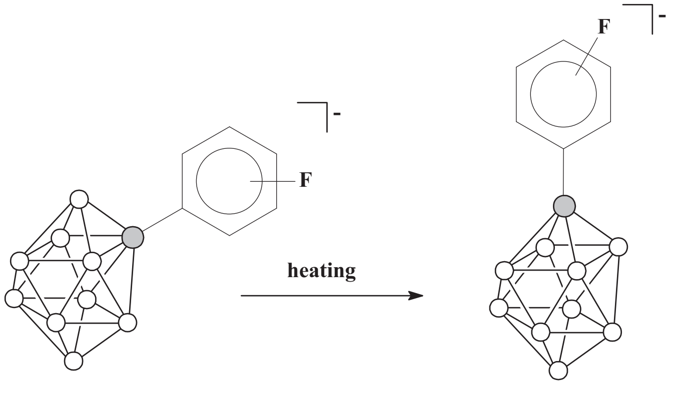
salts crystallize well from hot ethanol giving the crystals suitable for single crystal X-ray diffraction study.

The crystals of $(Bu_4N)[1\text{-}(2\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$ (**1**) and $(Bu_4N)_2[2\text{-}(4\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9][1\text{-}(4\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$ (**2**) were obtained upon cooling of the solutions of the corresponding 2-isomers after refluxing for 20 and 10 h, respectively. The crystal structures of **1** and **2** were studied by single crystal X-ray diffraction (Figs. 1–3). It is noteworthy that **2** is double salt which contains both $[1\text{-}(4\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ and $[2\text{-}(4\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]^-$ anions in 1: 1 ratio. The C–B bonds in the $[1\text{-}FC_6H_4\text{-}1\text{-}CB_9H_9]^-$ anions in the structures of **1** and **2** are somewhat elongated (by 0.02–0.03 Å) in comparison with those in the parent anion $[1\text{-}CB_9H_{10}]^-$ [17]. The C(1)–C(aryl) bonds fall into range for phenyl-substituted derivatives of the 1-carba-*closo*-decaborate anion described in the literature (1.479–1.503 Å) [6,9,10,18] and are some shorter than in icosahedral analogue $[1\text{-}(4\text{-}FC_6H_4)\text{-}1\text{-}CB_{11}H_{11}]^-$ (1.507 Å) [19]. The C–B bonds in the $[2\text{-}(4\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]^-$ anion in the structure of **2** are close to those found in other phenyl-substituted derivatives of the 2-carba-*closo*-decaborate anion [9], except the C(2)–B(1) bond which is some shorter (1.626 Å in comparison with 1.636–1.637 Å).

The fluorophenyl carboranes prepared was found to be stable towards nucleophilic aromatic substitution of fluorine under treatment with phenoxides (phenol, 4-aminophenol) and amines (morpholine, piperidine).



Scheme 2.



Scheme 3.

3. Experimental

Reagents and solvents were obtained commercially and used as supplied. ^1H, ^{11}B, and ^{19}F NMR spectra were collected using Bruker Avance 300, Bruker Avance 400 and Bruker Avance 600 spectrometers.

3.1. General procedure for synthesis of $(Bu_4N)[2\text{-}(FC_6H_4)\text{-}2\text{-}CB_9H_9]$

Decaborane(14) (2.40 g, 20 mmol) was added at 0 °C to 2 M aqueous solution of sodium hydroxide (100 cm^3). After stirring for 20 min, ethanol (70 cm^3) followed by fluorobenzaldehyde (11.17 g, 90 mmol) were added and the reaction mixture was stirred for 4 h. The ethanol was removed under reduced pressure and the residue

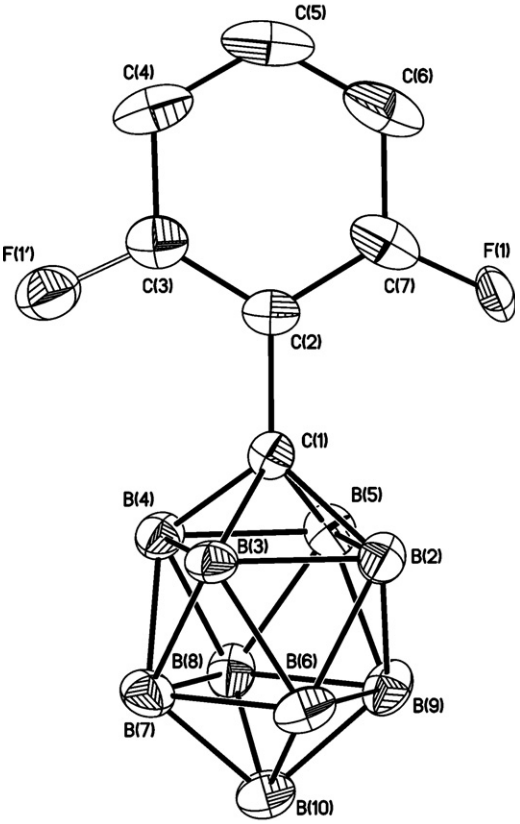


Fig. 1. General view of $[1\text{-}(2\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ anion in crystal structure of **1** presented by thermal ellipsoids at 50% probability. Atom F(1) disordered over two positions.

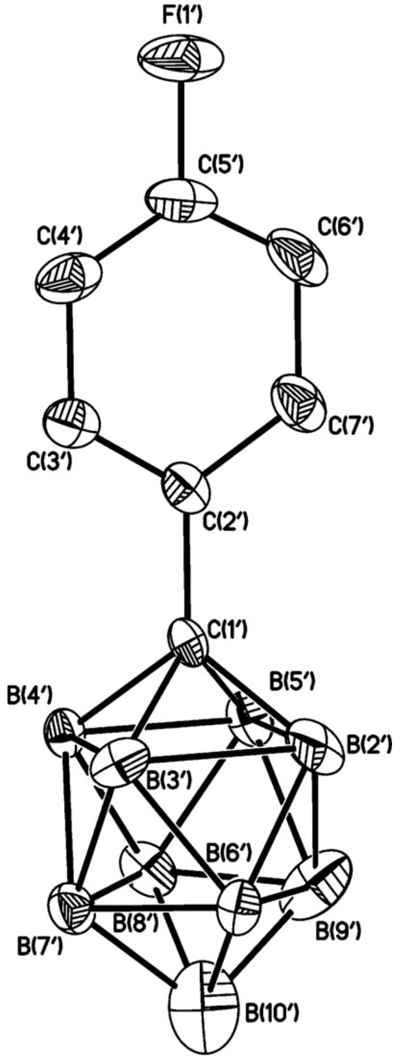


Fig. 2. General view of $[1\text{-}(4\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ anion in crystal structure of **2** presented by thermal ellipsoids at 50% probability.

was extracted with diethyl ether ($3 \times 50\ cm^3$). The diethyl ether was pumped off, the residue was dissolved in 2 M aqueous solution of sodium hydroxide ($120\ cm^3$), treated dropwise with a solution of iodine (20.30 g, 80 mmol) in ethanol ($600\ cm^3$) and stirred for additional 1 h. The solution was neutralized by addition of 1 M aqueous hydrochloric acid. The reaction mixture was evaporated to dryness, the residue was dissolved in water ($60\ cm^3$) and treated with solution of $[Bu_4N]Br$ (12.80 g, 40 mmol) in water ($30\ cm^3$). The precipitate formed was filtered, washed with diethyl ether, dried *in vacuo*, and recrystallized from aqueous ethanol to obtain white crystalline solid.

*3.1.1. Tetrabutylammonium 2-(2-fluorophenyl)-2-carba-*closo-*decaborate* $(Bu_4N)[2\text{-}(2\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]$

Yield 75% (6.84 g). ^1H NMR (400.1 MHz, DMSO-d_6): 6.99 (1H, m, *o*-FC_6H_4), 6.86 (2H, m, *o*-FC_6H_4), 6.74 (1H, m, *o*-FC_6H_4), 3.16 (8H, m, Bu_4N^+), 1.56 (8H, m, Bu_4N^+), 1.30 (8H, m, Bu_4N^+), 0.93 (12H, t, Bu_4N^+). ^{13}C NMR (150.9 MHz, acetone-d_6): 160.5 (d, $J_{C,F}$ = 248 Hz, CF), 132.0 (d, $J_{C,F}$ = 13 Hz, CH), 130.6 (d, $J_{C,F}$ = 18 Hz, CH), 126.4 (d, $J_{C,F}$ = 8 Hz, CH), 123.3, 115.5, 59.3 (C_{carb}), 45.4 (Bu_4N^+), 24.4 (Bu_4N^+), 20.3 (Bu_4N^+), 13.9 (Bu_4N^+). ^{11}B NMR (128.4 MHz, DMSO-d_6): 2.0 (1B, d, $J_{B,H}$ = 154 Hz), -3.1 (1B, d, $J_{B,H}$ = 168 Hz), −20.9 (1B, d, $J_{B,H}$ = 138 Hz), −25.3 (2B, d, $J_{B,H}$ = −147 Hz), −28.5 (4B, d, $J_{B,H}$ = 135 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): −115.2.

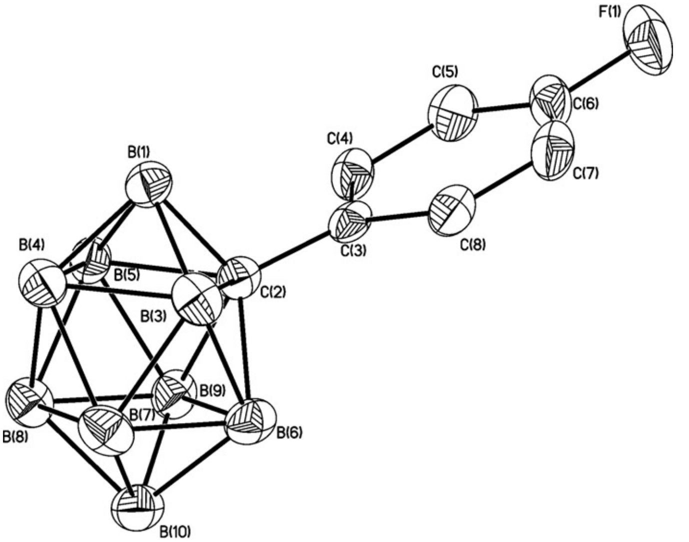


Fig. 3. General view of $[2\text{-}(4\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]^-$ anion in crystal structure of **2** presented by thermal ellipsoids at 50% probability.

*3.1.2. Tetrabutylammonium 2-(3-fluorophenyl)-2-carba-*closo-*decaborate* $(Bu_4N)[2\text{-}(3\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]$

Yield 72% (6.58 g). ^1H NMR (400.1 MHz, DMSO-d_6): 7.06 (1H, m, *m*-FC_6H_4), 6.78 (1H, m, *m*-FC_6H_4), 6.59 (1H, m, *m*-FC_6H_4), 6.45 (1H, m, *m*-FC_6H_4), 3.18 (8H, m, Bu_4N^+), 1.57 (8H, m, Bu_4N^+), 1.31 (8H, m, Bu_4N^+), 0.93 (12H, t, Bu_4N^+). ^{11}B NMR (128.4 MHz, DMSO-d_6): 1.9 (1B, d, $J_{B,H}$ = 156 Hz), −2.8 (1B, d, $J_{B,H}$ = 170 Hz), −21.0 (1B, d, $J_{B,H}$ = 142 Hz), −25.5 (4B, d, $J_{B,H}$ = 152 Hz), −28.4 (4B, d, $J_{B,H}$ = 133 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): −115.1.

*3.1.3. Tetrabutylammonium 2-(4-fluorophenyl)-2-carba-*closo-*decaborate* $(Bu_4N)[2\text{-}(4\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]$

Yield 74% (6.86 g). ^1H NMR (400.1 MHz, DMSO-d_6): 6.86 (2H, m, *p*-FC_6H_4), 6.78 (2H, m, *p*-FC_6H_4), 3.17 (8H, m, Bu_4N^+), 1.57 (8H, m, Bu_4N^+), 1.30 (8H, m, Bu_4N^+), 0.94 (12H, t, Bu_4N^+). ^{11}B NMR (128.4 MHz, DMSO-d_6): 1.7 (1B, d, $J_{B,H}$ = 154 Hz), −2.8 (1B, d, $J_{B,H}$ = 166 Hz), −21.1 (1B, d, $J_{B,H}$ = 135 Hz), -25.6 (2B, d, $J_{B,H}$ = 145 Hz), −28.3 (4B, d, $J_{B,H}$ = 131 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): −119.0.

3.2. General procedure for synthesis of $(Bu_4N)[1\text{-}(FC_6H_4)\text{-}1\text{-}CB_9H_9]$

Solution of $(Bu_4N)[2\text{-}(FC_6H_4)\text{-}2\text{-}CB_9H_9]$ (4.57 g, 10 mmol) in ethanol ($150\ cm^3$) was heated under reflux for 20 h. The solution was allowed to cool to ambient temperature and the ethanol was removed *in vacuo* to obtain white crystalline solid.

*3.2.1. Tetrabutylammonium 1-(2-fluorophenyl)-1-carba-*closo-*decaborate* $(Bu_4N)[1\text{-}(2\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$

Yield 98% (4.48 g). ^1H NMR (400.1 MHz, DMSO-d_6): 7.82 (1H, m, *o*-FC_6H_4), 7.32 (1H, m, *o*-FC_6H_4), 7.23 (2H, m, *o*-FC_6H_4), 3.15 (8H, m, Bu_4N^+), 1.56 (8H, m, Bu_4N^+), 1.30 (8H, m, Bu_4N^+), 0.93 (12H, t, Bu_4N^+). ^{13}C NMR (75.5 MHz, acetone-d_6, Me_4Si): 163.3 (d, $J_{C,F}$ = 249 Hz, CF), 135.0, 132.1 (d, $J_{C,F}$ = 13 Hz, CH), 127.8 (d, $J_{C,F}$ = 8 Hz, CH), 124.1, 115.9 (d, $J_{C,F}$ = 23 Hz, CH), 59.3 (C_{carb}), 47.0 (Bu_4N^+), 24.3 (Bu_4N^+), 20.3 (Bu_4N^+), 13.8 (Bu_4N^+). ^{11}B NMR (128.4 MHz, DMSO-d_6, $BF_3{\cdot}Et_2O$): 30.6 (1B, d, $J_{B,H}$ = 152 Hz), −15.5 (4B, d, $J_{B,H}$ = 149 Hz), −23.9 (4B, d, $J_{B,H}$ = 138 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): −115.5. Anal. Calcd. for $C_{23}H_{49}B_9FN$: C, 60.59; H, 10.83; B, 21.34; N, 3.07. Found: C, 60.35; H, 10.78; B, 21.27; N, 3.00.

Table 1
Details of data collection and structure refinements for $(Bu_4N)[1\text{-}(2\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$ (**1**) and $(Bu_4N)_2[2\text{-}(4\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9][1\text{-}(4\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$ (**2**).

	1	2
Molecular formula	$C_{23}H_{48}B_9FN$	$C_{23}H_{49}B_9FN$
Formula weight	455.92	455.92
Dimension, mm	0.04 × 0.13 × 0.29	0.08 × 0.08 × 0.08
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (No. 14)	$P-1$ (No. 2)
a, Å	11.343(4)	10.7138(9)
b, Å	14.413(6)	15.5663(13)
c, Å	17.666(7)	17.8156(14)
α,°		100.453(2)
β,°	93.889(15)	94.702(2)
γ,°		90.444(2)
V, $Å^3$	2881.7(19)	2911.3(4)
Z	4	4
ρ_{calc}, $g\,cm^{-3}$	1.051	1.040
Temperature, K	100	100
Max. Θ,°	26.00	27.10
Scan type	ω/φ	ω/φ
Radiation, λ(Mo-Kα), Å	0.71073	0.71073
Linear absorption (μ), cm^{-1}	0.59	0.58
T_{min}/T_{max}	0.98/1.00	0.995/0.982
$F(000)$	992	1488
Number of total reflections	27,585	31,051
Number of independent reflections	5634	12839
Number of independent reflections with $I > 2(\sigma(I))$	2742	5940
Parameters	356	421
wR_2	0.1518	0.0804
R_1 [for reflections with $I > 2\sigma(I)$]	0.0683	0.0532
GOF	0.997	0.987
ρ_{max}/ρ_{min}, $eÅ^{-3}$	0.58/−0.021	1.02/−0.488

3.2.2. *Tetrabutylammonium 1-(3-fluorophenyl)-1-carba*-closo-*decaborate* $(Bu_4N)[1\text{-}(3\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$

Yield 98% (4.48 g). ^1H NMR (400.1 MHz, DMSO-d_6): 7.72 (1H, m, *m*-FC_6H_4), 7.58 (1H, m, *m*-FC_6H_4), 7.33 (1H, m, *m*-FC_6H_4), 6.97 (1H, m, *m*-FC_6H_4), 3.31 (8H, m, Bu_4N^+), 1.72 (8H, m, Bu_4N^+), 1.47 (8H, m, Bu_4N^+), 1.05 (12H, t, Bu_4N^+). ^{11}B NMR (128.4 MHz, DMSO-d_6): 30.1 (1B, d, $J_{B,H}$ = 149 Hz), −15.5 (4B, d, $J_{B,H}$ = 147 Hz), −23.7 (4B, d, $J_{B,H}$ = 138 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): −114.9. Anal. Calcd. for $C_{23}H_{49}B_9FN$: 60.59; H, 10.83; B, 21.34; N, 3.07. Found: C, 60.41; H, 10.69; B, 21.38; N, 2.98.

3.2.3. *Tetrabutylammonium 1-(4-fluorophenyl)-1-carba*-closo-*decaborate* $(Bu_4N)[1\text{-}(4\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]$

Yield 97% (4.44 g). ^1H NMR (400.1 MHz, DMSO-d_6): 7.79 (2H, m, *p*-FC_6H_4), 7.17 (2H, t, *p*-FC_6H_4), 3.16 (8H, m, Bu_4N^+), 1.56 (8H, m, Bu_4N^+), 1.31 (8H, m, Bu_4N^+), 0.93 (12H, t, Bu_4N^+). 11B NMR (128.4 MHz, DMSO-d_6): 29.4 (1B, d, $J_{B,H}$ = 152 Hz), −15.6 (4B, d, $J_{B,H}$ = 147 Hz), −23.8 (4B, d, $J_{B,H}$ = 138 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): −117.5. Anal. Calcd. for $C_{23}H_{49}B_9FN$: C, 60.59; H, 10.83; B, 21.34; N, 3.07. Found: C, 60.45; H, 10.67; B, 21.32; N, 2.99.

Table 2
Selected bond distances (Å) and angles (°) for $[1\text{-}(2\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ anion.

C(1)–C(2)	1.491(4)	B(4)–B(7)	1.796(5)
C(1)–B(2)	1.620(4)	B(4)–B(8)	1.798(5)
C(1)–B(3)	1.604(4)	B(5)–B(8)	1.807(5)
C(1)–B(4)	1.603(4)	B(5)–B(9)	1.798(5)
C(1)–B(5)	1.610(4)	B(6)–B(7)	1.835(5)
B(2)–B(3)	1.838(5)	B(6)–B(9)	1.835(5)
B(2)–B(5)	1.827(5)	B(6)–B(10)	1.694(5)
B(2)–B(6)	1.800(5)	B(7)–B(8)	1.838(5)
B(2)–B(9)	1.808(5)	B(7)–B(10)	1.696(5)
B(3)–B(4)	1.841(5)	B(8)–B(9)	1.828(5)
B(3)–B(6)	1.810(5)	B(8)–B(10)	1.690(5)
B(3)–B(7)	1.802(5)	B(9)–B(10)	1.687(5)
B(4)–B(5)	1.831(5)		
C(2)–C(1)–B(4)	125.5(2)	C(2)–C(1)–B(3)	126.0(2)
B(4)–C(1)–B(3)	70.0(2)	C(2)–C(1)–B(5)	126.5(2)
B(4)–C(1)–B(5)	69.4(2)	B(3)–C(1)–B(5)	107.6(2)
C(2)–C(1)–B(2)	127.3(2)		

Table 3
Selected bond distances (Å) and angles (°) for $[1\text{-}(4\text{-}FC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ anion.

C(1′)–C(2′)	1.477(3)	B(4′)–B(7′)	1.798(4)
C(1′)–B(2′)	1.595(3)	B(4′)–B(8′)	1.764(4)
C(1′)–B(3′)	1.615(3)	B(5′)–B(8′)	1.753(4)
C(1′)–B(4′)	1.645(3)	B(5′)–B(9′)	1.771(4)
C(1′)–B(5′)	1.636(3)	B(6′)–B(7′)	1.827(4)
B(2′)–B(3′)	1.936(4)	B(6′)–B(9′)	1.812(4)
B(2′)–B(5′)	1.840(4)	B(6′)–B(10′)	1.751(4)
B(2′)–B(6′)	1.742(4)	B(7′)–B(8′)	1.796(4)
B(2′)–B(9′)	1.764(4)	B(7′)–B(10′)	1.645(5)
B(3′)–B(4′)	1.828(4)	B(8′)–B(9′)	1.814(4)
B(3′)–B(6′)	1.776(4)	B(8′)–B(10′)	1.774(5)
B(3′)–B(7′)	1.784(3)	B(9′)–B(10′)	1.582(5)
B(4′)–B(5′)	1.848(3)		
C(2′)–C(1′)–B(2′)	126.07(19)	B(3′)–C(1′)–B(5′)	108.34(18)
C(2′)–C(1′)–B(3′)	127.13(18)	C(2′)–C(1′)–B(4′)	125.20(18)
B(2′)–C(1′)–B(3′)	74.20(16)	B(2′)–C(1′)–B(4′)	108.56(19)
C(2′)–C(1′)–B(5′)	124.33(18)	B(3′)–C(1′)–B(4′)	68.19(15)
B(2′)–C(1′)–B(5′)	69.40(17)	B(5′)–C(1′)–B(4′)	68.42(14)

3.3. *X-ray crystallography*

X-ray diffraction measurements of **1** and **2** were carried out with a SMART APEX II diffractometer. The frames were integrated and corrected for absorption by APEX2 program suite [20]. The details of crystallographic data and experimental conditions are presented in Table 1. Important structural parameters of structures are shown in captions of Figs. 1–3. The crystals of **1** and **2** were characterized by poor diffraction quality probably due to presence of flexible Bu_4N^+ cations and high intensity of thermal motion of carborane cages.

The structures were solved by the direct method and refined by full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The hydrogen atoms were located from difference electron density syntheses and refined in rigid body model. All calculations were performed using the SHELXTL PLUS 5.10 program package [21]. Fluorine atom in structure **1** is disordered over two positions which are overlapped with position of hydrogen atoms. The correct refinement of coordinates of H and F atoms is impossible. So the C(7)–F(1) and C(3)–F(1′) bonds are shortened in comparison with those standard value. Details concerning the crystal data collection and refinement parameters

Table 4
Selected bond distances (Å) and angles (°) for $[2\text{-}(4\text{-}FC_6H_4)\text{-}2\text{-}CB_9H_9]^-$ anion.

C(2)–C(3)	1.502(3)	B(4)–B(7)	1.825(3)
C(2)–B(1)	1.626(3)	B(4)–B(8)	1.820(3)
C(2)–B(3)	1.763(3)	B(5)–B(8)	1.794(3)
C(2)–B(5)	1.758(3)	B(5)–B(9)	1.800(3)
C(2)–B(6)	1.744(3)	B(6)–B(7)	1.814(4)
C(2)–B(9)	1.750(3)	B(6)–B(9)	1.837(3)
B(1)–B(3)	1.683(3)	B(6)–B(10)	1.684(3)
B(1)–B(4)	1.670(3)	B(7)–B(8)	1.831(3)
B(1)–B(5)	1.685(3)	B(7)–B(10)	1.685(4)
B(3)–B(4)	1.809(3)	B(8)–B(9)	1.819(3)
B(3)–B(6)	1.797(3)	B(8)–B(10)	1.692(3)
B(3)–B(7)	1.792(3)	B(9)–B(10)	1.681(4)
B(4)–B(5)	1.818(3)		
C(3)–C(2)–B(1)	114.19(17)	C(3)–C(2)–B(5)	127.8(2)
C(3)–C(2)–B(6)	117.82(16)	B(1)–C(2)–B(5)	59.6(1)
B(1)–C(2)–B(6)	117.44(16)	B(6)–C(2)–B(5)	107.4(2)
C(3)–C(2)–B(9)	117.2(2)	B(9)–C(2)–B(5)	61.8(1)
B(1)–C(2)–B(9)	117.6(2)	C(3)–C(2)–B(3)	128.9(2)
B(6)–C(2)–B(9)	63.5(1)		

are summarized in Table 1. Selected bond lengths are listed in Tables 2–4. The crystallographic data for **1** and **2** have been deposited to the Cambridge Crystallographic Data Centre (CCDC-662953 and CCDC-662954).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2012.06.019.

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