Synthesis and Characterization of 3-Chloropropyl-substituted *o*-Carboranes: Crystal Structures of 1,2-(1,3-Propanediyl)-*o*-carborane, 1-(3-Chloropropyl)-*o*-carborane and 1,2-Bis(3-chloropropyl)-*o*-carborane

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The reactions of the lithio-*o*-carborane $Li_2C_2B_{10}H_{10}$ with $ClCH_2CH_2CH_2Br$ were studied under various conditions. While the main product is the known *exo*-polyhedrally cyclized 1,2-(1,3-propanediyl)-*o*-carborane (**2**), the expected 3-chloropropyl-substituted carborane products 1-$(ClCH_2CH_2CH_2)C_2B_{10}H_{11}$ (**3**) and 1,2-$(ClCH_2CH_2CH_2)_2C_2B_{10}H_{10}$ (**4**) can be obtained in a total yield of 22 %. In the presence of CuCl, the same reaction proceeded rather slowly and gave compound **3** and bis(*o*-carborane) (**5**) in small yields, with the recovery of the starting *o*-$C_2B_{10}H_{12}$. Compounds **2** – **4** were characterized by means of IR and NMR spectroscopy and mass spectrometry, as well as by single-crystal X-ray diffraction.

Key words: *o*-Carborane, Chloropropyl, Functionalization, Synthesis, Crystal Structure

Introduction

In the field of boron cluster chemistry, there has been extensive current interest in the functionalized carborane derivatives, especially those of the icosahedral 1,2-dicarba-*closo*-dodecaborane ($C_2B_{10}H_{12}$) or *o*-carborane (**1**) [1, 2]. This is mainly due to the various (potential) applications of these cluster compounds in such areas as biomedical and materials sciences [3 – 7]. Many boron- and carbon-substituted *o*-carborane derivatives have been obtained mainly by electrophilic and nucleophilic substitution reactions of *o*-carborane, respectively, but practically the carbon-substituted ones have been studied more due to the ease of preparation. The C – H ($pK_a \sim 23$) moieties of the *o*-carborane cage can be readily deprotonated using strong bases such as *n*-butyllithium, and the lithio-*o*-carborane species $Li_2C_2B_{10}H_{10}$ or $LiC_2B_{10}H_{11}$ formed can further react with a wide variety of reagents to give the corresponding carborane compounds [1, 2].

The reactions of the lithio-*o*-carborane species with halogenated hydrocarbons usually give the expected carborane products, however, it is documented that such reactions proceed rather sluggish with alkyl halides other than allylic and benzylic ones, therefore elevated temperature and elongated reaction times are needed [1]. Meanwhile, the activity order with different halogen atoms is obvious, *i. e.* the iodinated and brominated rather than chlorinated reaction partners are preferred. However, it may be possible to take advantage of such difference in reactivity with halogen atoms in these reactions. For instance, the reactions of $(LiC)(CMe)B_{10}H_{10}$ with $ClCH_2CH_2CH_2CH_2Br$ [8] / $ClCH_2CH_2CH_2CH_2I$ [9] and $ClCH_2CH_2CH_2Br$ [10] have been reported to selectively generate the corresponding ω-chlorobutyl- or -chloropropyl-*o*-carborane, respectively.

The reactions of $Li_2C_2B_{10}H_{10}$ [11], $LiC_2B_{10}H_{11}$ [12] or $K_2C_2B_{10}H_{10}$ [13] with 1,3-dibromopropane, of 1-iodo-2-(3-bromopropyl)-*o*-carborane with magnesium [14], as well as of 1-(3-

iodopropyl)-*o*-carborane with the lithium salt of imidazolidinone [15], afford the *exo*-polyhedrally cyclized compound 1,2-(1,3-propanediyl)-*o*-carborane (**2**), which is a useful starting material for the synthesis of metallacarboranes [11] and novel 13-vertex carborane clusters [16]. We proposed that by the reaction of $Li_2C_2B_{10}H_{10}$ with 1-bromo-3-chloropropane ($ClCH_2CH_2CH_2Br$) under suitable conditions, it might be possible to obtain in one step the 3-chloropropyl-substitued *o*-carborane derivative(s), which should be useful for further transformations. The known compound 1-$(ClCH_2CH_2CH_2)C_2B_{10}H_{11}$ (**3**) has been previously prepared in two steps, *i. e.* by the reaction of $LiC_2B_{10}H_{11}$ with trimethylene oxide and subsequent chlorination of the resulting *o*-carboranylalcohol [17]. Zakharkin *et al.* [10, 18] obtained compound **3** by the reaction of $B_{10}H_{12}(CH_3CN)_2$ with 3-chloropropylacetylene in toluene. In our study with $ClCH_2CH_2CH_2Br$, it turned out that, apart form compound **2**, the expected *o*-carborane derivatives **3** and 1,2-$(ClCH_2CH_2CH_2)_2C_2B_{10}H_{10}$ (**4**) can be obtained. Herein we report on the spectral characterization and the X-ray crystal structures of compounds **2**–**4**.

Results and Discussion

In order to get the 3-chloropropyl-substituted *o*-carborane derivatives in a one-step reaction starting from *o*-carborane, we tried the reaction of dilithio-*o*-carborane (formed *in situ* by the action of *o*-carborane with two equivalents of *n*-BuLi) with $ClCH_2CH_2CH_2Br$ (Scheme 1) under various conditions. A summary of the amounts of reactants and of the product distribution is given in Table 1.

When the reaction was carried out in diethyl ether with a reactant ratio (*o*-carborane : *n*-BuLi : $ClCH_2CH_2CH_2Br$) of 1 : 2 : 2.2, no expected product was formed, only the known *exo*-polyhedrally cyclized compound **2** was isolated in a yield of 46 % (entry 1). When the ratio was changed to 1 : 2.3 : 4.6, apart from compound **2**, the expected disubstituted product **4** could be obtained by careful chromatographic separation, although in a very low yield (entry 2). By further changing the amount of $ClCH_2CH_2CH_2Br$, the mono-substituted product **3** was obtained after separation, but the total yields of **3** and **4** were still low (entries 3 and 4). When the same reaction (reactant ratio 1 : 2 : 3) was conducted in tetrahydrofuran (THF), compound **4** could be isolated in a yield of 19 %, together with compounds **2** and **3** and some carborane **1** (entry 5).

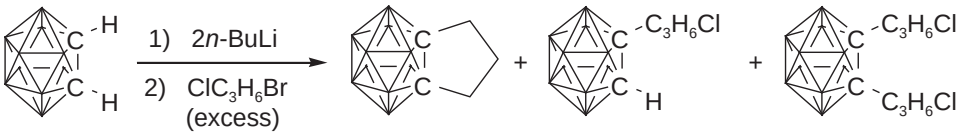
Table 1. The amounts of the reactants and product distribution in the reaction of $Li_2C_2B_{10}H_{10}$ with $ClCH_2CH_2CH_2Br$.

Entry	**1**	*n*-BuLi	ClC_3H_6Br	**2**	**3**	**4**	**5**	**1**
	Amount (mmol)			Isolated yield (%)				
1[a]	1.6	3.3	3.5	46	–	–	–	–
2[a]	2.0	4.6	9.1	77	–	1	–	–
3[a]	2.0	4.4	6.2	68	2	2	–	–
4[a]	3.3	6.6	14.9	58	1	3	–	24
5[b]	3.3	6.6	9.9	67	3	19	–	11
6[c]	2.2	4.4	6.9	–	4	–	19	69

[a] Diethyl ether as the solvent; [b] tetrahydrofuran as the solvent; [c] diethyl ether as the solvent and 4.4 mmol CuCl added.

Compounds **2**–**4** were characterized by IR, NMR, MS methods and X-ray crystallography (see below). The ^1H NMR data (60 MHz in carbon tetrachloride, and 250 MHz in benzene) of compound **2** were first reported by Hawthorne *et al.* [11]. We provide here the more complete NMR data (400 MHz in $CDCl_3$) of this compound. Its ^1H NMR spectrum shows two multiplets at $\delta = 2.51-2.48$ and 2.4–2.3 ppm for the methylene protons, and broad signals at 2.9–1.5 ppm for the boron-bound ones. The $^{11}B\{^1H\}$ NMR spectrum exhibits four signals at -6.4, -7.7, -8.6, and -11.3 ppm with an integral ratio of 1 : 1 : 1 : 2. The ^{13}C NMR spectrum of **2** displays three peaks at 84.0, 34.8, 32.2 ppm, corresponding to the cage and the methylene carbon atoms, respectively.

As to compound **4**, the IR spectrum gives a typical $\nu(B-H)$ absorption band at 2564 cm^{-1}. The



1 **2** **3** **4**

Scheme 1. The reaction of dilithio-*o*-carborane with $ClCH_2CH_2CH_2Br$.

Table 2. Crystal data and details of data collection and structure refinement of **2**, **3** and **4**.

	2	**3**	**4**
Formula	$C_5H_{16}B_{10}$	$C_5H_{17}B_{10}Cl$	$C_8H_{22}B_{10}Cl_2$
M_r	184.28	220.74	297.26
Temperature, K	293 (2)	120 (1)	293 (2)
Crystal size, mm^3	$0.26 \times 0.12 \times 0.03$	$0.38 \times 0.32 \times 0.24$	$0.48 \times 0.46 \times 0.23$
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*C*2*cb*	$P2_1/c$	$P2_1/c$
a, Å	12.0681(13)	11.7944(3)	13.2081(4)
b, Å	9.9786(13)	7.6592(2)	7.8292(3)
c, Å	9.8394(10)	14.5049(5)	15.9410(7)
β, deg	90.00	109.803(4)	90.265(4)
V, Å^3	1184.9(2)	1232.83(7)	1648.42(11)
Z	4	4	4
$D_{calcd.}$, mg mm^{-3}	1.03	1.19	1.20
μ(MoK_α), mm^{-1}	0.0	0.3	0.4
$F(000)$, e	384	456	616
2θ range, deg	3.36 – 26.37	5.86 – 52.74	5.8 – 51.36
hkl range	$-15 \le h \le 11$ $-11 \le k \le 12$ $-12 \le l \le 10$	$-14 \le h \le 14$ $-8 \le k \le 9$ $-15 \le l \le 18$	$-16 \le h \le 16$ $-9 \le k \le 9$ $-16 \le l \le 19$
Refl. total / unique / R_{int}	1714 / 943 / 0.0297	6521 / 2517 / 0.0263	7249 / 3013 / 0.0213
Refl. observed [$I > 2\sigma(I)$]	597	2192	2165
Data / restraints / parameters	943 / 1 / 69	2517 / 0 / 145	3013 / 0 / 181
$R1/wR2$ [$I > 2\sigma(I)$][a]	0.0628 / 0.1557	0.0397 / 0.1020	0.0597 / 0.1562
$R1/wR2$ (all data)[b]	0.1026 / 0.1837	0.0472 / 0.1085	0.0831 / 0.1765
A / B (weighting scheme)[b]	0.1018 / 0.0	0.0514 / 0.5346	0.0811 / 1.0066
GoF (F^2)[c]	1.034	1.070	1.048
Flack parameter	−3(10)	–	–
$\Delta\rho_{max\,/\,min}$, e Å^{-3}	0.136 / −0.204	0.32 / −0.34	0.47 / −0.34

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

^{1}H NMR spectrum shows resonance signals for the 3-chloropropyl group at 3.56 ppm as a triplet, and at 2.4 – 2.3 and 2.1 – 2.0 ppm, each as a multiplet. The ^{11}B{^{1}H} NMR spectrum of **4** displays peaks at −4.5, −10.1 and −10.9 ppm in a ratio of 1 : 3 : 1, and the ^{13}C NMR spectrum exhibits four signals at 78.9, 43.8, 32.4 and 32.2 ppm corresponding to the cage and propyl carbon atoms, respectively. Interestingly, in the EI-MS mass spectra of compounds **3** and **4** the common base peak at $m/z = 183$ is observed, which corresponds to the core of compound **2**, implying the stability of the *exo* five-membered ring.

The afore-mentioned results show that the formation of the cyclized product **2** is preferred under most of the conditions in Table 1, regardless of the addition order of the reactants. In this regard, Viñas *et al.* have reported that the reaction of monolithio-*o*-carborane reacts with dibromopropane to give a 1 : 1 mixture of **2** and **1** [12]. Probably the chelating effect plays an important role in these reactions, leading to **2** as the main product, although the chlorine and bromine functions should have made some difference. Presumably, the halogen exchange of the possible reaction intermediate 1-Li-2-($CH_2CH_2CH_2Cl$)$C_2B_{10}H_{10}$ leading to 1-Li-2-($CH_2CH_2CH_2Br$)$C_2B_{10}H_{10}$ is also involved in the presence of the *in situ*-generated LiBr, which in turn promotes the formation of **2**. The isolation of **3** and **4** proves that the reaction does afford the expected products, although in small yields, and that the yields are better in the more polar solvent THF than in diethyl ether.

Finally, CuCl was added to dilithio-*o*-carborane before adding $ClCH_2CH_2CH_2Br$. The resulting dicopper-*o*-carborane species reacted rather slowly with $ClCH_2CH_2CH_2Br$ to give compound **3** in a very low yield (entry 6, Scheme 2), together with recovered **1** and some bis(*o*-carborane) (**5**) [19] through the homocoupling of the carboranyl copper species. Compounds **2** and **4** were not formed.

Table 3. Selected bond lengths (Å) and angles (deg) for **2**, **3** and **4**.

		2[a]		**3**		**4**
	C1 – C2	1.506(6)	Cl1 – C5	1.8000(17)	Cl1 – C8	1.767(3)
	C1 – B1	1.706(5)	C4 – C5	1.508(2)	Cl2 – C5	1.774(3)
Bond	C1 – C1#	1.628(7)	C4 – C3	1.524(2)	C7 – C6	1.499(4)
lengths	C2 – C5	1.487(7)	C2 – C3	1.524(2)	C7 – C8	1.496(4)
	B1 – B2	1.741(6)	C2 – C1	1.649(2)	C1 – C6	1.528(4)
	B2 – B6	1.773(8)	C2 – B8	1.706(2)	C1 – C2	1.672(3)
	B2 – B4#	1.755(7)			C3 – C2	1.523(4)
	C5 – C2#	1.487(7)			C3 – C4	1.498(4)
	B1 – B3	1.767(6)			C5 – C4	1.504(4)
Angles	C2 – C1 – C1#	106.1(2)	C3 – C2 – C1	115.96(13)	C6 – C1 – C2	117.3(2)
	C5 – C2 – C1	107.9(4)			C3 – C2 – C1	116.3(2)
	C2 – C5 – C2#	112.0(6)			C7 – C6 – C1	114.4(2)

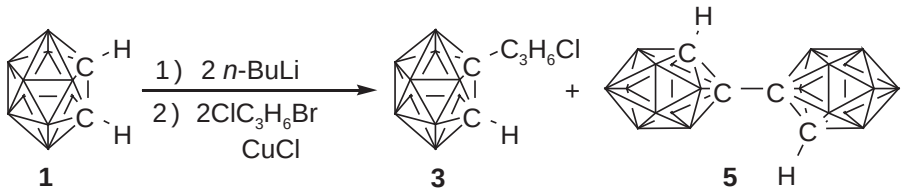
[a] Symmetry transformation used to generate equivalent atoms: # x, $-y+1$, $-z+1$.

Crystal and molecular structures

Colorless crystals of the title carboranes suitable for X-ray analyses were obtained by recrystallization from petroleum ether (b. p. 30 – 60 °C)-methanol (5 : 1, v/v) (compound **2**), *n*-hexane-dichloromethane (1 : 1, v/v) (compound **3**), and petroleum ether (compound **4**) solutions, respectively. The crystal and molecular structures of **2**, **3** and **4** were determined by single-crystal X-ray diffraction (Figs. 1 – 3). Table 2 presents the corresponding crystal data and structure refinement details, and Table 3 lists selected bond lengths and angles for the three molecular structures.

The structures of compounds **2** – **4** all contain an icosahedral C_2B_{10} cluster. In the structure of **2** (Fig. 1) the cage carbon-carbon bond length is 1.628(7) Å, which is nearly the same as that in the parent *o*-carborane (1.629(6)/1.630(6) Å) [20]. The *exo*-polyhedral five-membered ring in the structure of **2** is found to be pseudo-planar with a torsion angle C1-C2-C5-C2# of 0.3(2)°, the planarity representing most probably an average of the conformations present in the crystal. Carborane clusters with a pseudo-planar, saturated *exo*-polyhedral five-membered ring are rather rare, another recently reported example being the 14-vertex C_2B_{12} cluster tethered to a planar five-membered cycle (torsion angle 0.6°) [21]. Interestingly, when the same compound crystallizes with two naphthalene molecules, the five-membered ring was found to be pronouncedly puckered (torsion angle 25.5°) [22]. Yamamoto *et al.* [23] reported the structure of a compound similar to **2** with an *exo*-polyhedral C_{cage}-C(Me)-C-C(OH)-C_{cage} five-membered ring, and the corresponding torsion angles were found to be 22.2/ – 15.4/ – 25.1° (with three independent molecules in the asymmetric unit).

With one 3-chloropyropyl substituent, the cage carbon-carbon bond length in **3** (Fig. 2) is slightly longer (1.649(2) Å) compared to that in **2**, while with two 3-chloropropyl moieties, the corresponding bond length in **4** (Fig. 3) is even longer (1.672(3) Å) for steric reasons. In the structure of **4**, there exists a weak C-H··· Cl hydrogen bond with a C3···Cl2 distance of 3.209(3) Å and a C3-H3B···Cl2 angle of 105°. There are no significant intermolecular interactions in the structures of **2** and **4**. In the case of **3** waek C1-H1···Cl1 (x, $1/2-y$, $-1/2+z$) hydrogen bonds (C1···Cl1 3.571(2) Å, C1-H1···Cl1 159°) link the molecules into a chain.



Scheme 2. The reaction of dilithio-*o*-carborane with $ClCH_2CH_2CH_2Br$ in the presence of CuCl.

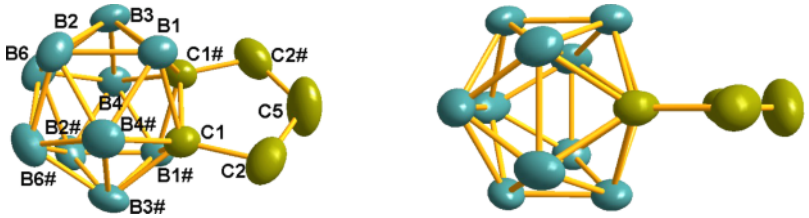


Fig. 1. Molecular structure of **2** in the crystal. Left: side view with atomic numbering scheme; right: another side view showing the pseudo-planarity of the *exo*-ring (hydrogen atoms are omitted for clarity; displacement ellipsoids are drawn at the 30 % probability level).

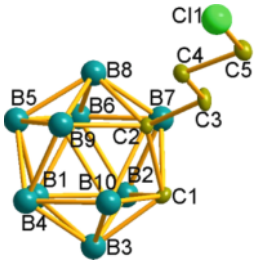


Fig. 2. Molecular structure of **3** in the crystal (hydrogen atoms are omitted for clarity; displacement ellipsoids are drawn at the 30 % probability level).

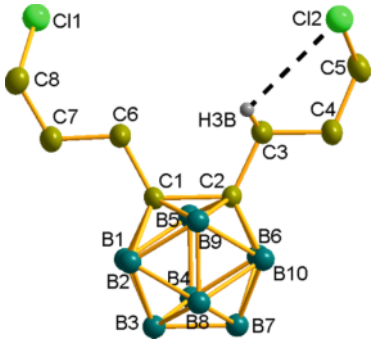


Fig. 3. Molecular structure of **4** in the crystal (only the hydrogen atom involved in hydrogen bonding is shown; displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level).

In summary, we have isolated and structurally characterized two 3-chloropropyl substituted *o*-carborane clusters. Although the one-step synthesis is not selective under the conditions attempted (the *exo*-cyclic compound **2** being the major product), the isolation and characterization of the 3-chloropropyl-substituted carboranes allows for further investigation.

Experimental Section

The solvent diethyl ether was dried over sodium/benzophenone and distilled under nitrogen prior to use. The other reagents were analytically pure and used as received commercially. IR spectra were recorded in the range 400 – 4000 cm^{-1} on a Perkin Elmer Spectrum RX I spectrometer using KBr pellets. NMR analyses were performed on a Bruker Avance III 400 MHz spectrometer with tetramethylsilane (TMS) and the deuterated solvent as internal standard (^{1}H, ^{13}C) and $BF_3 \cdot OEt_2$ as external standard (^{11}B). Melting points were measured with an SGW X-4 apparatus and are not corrected. The mass spectra were recorded on an Agilent 5973N MSD (low resolution) instrument.

*Reaction of dilithio-o-carborane with 1-bromo-3-chloropropane leading to **2***

Under an argon atmosphere, *n*-BuLi (2.2 M in *n*-hexane, 1.5 mL, 3.3 mmol) was added dropwise to a solution of *o*-carborane (**1**, 223 mg, 1.55 mmol) in diethyl ether (25 mL) at 0 °C. The resulting mixture with the colorless precipitate was stirred for 30 min at 0 °C, and for 30 min at room temperature. It was cooled to 0 °C, and 1-bromo-3-chloropropane (542 mg, 3.5 mmol) was added. The reaction mixture was stirred at room temperature for 23 h and quenched with water (10 mL). The organic phase was separated and the water phase extracted with diethyl ether (3 × 30 mL). The organic portions were combined, dried (anhydrous $MgSO_4$) and concentrated *in vacuo*. The resulting yellow oily residue was further purified by column chromatography on silica gel. Elution with *n*-hexane gave **2** as a colorless solid (132 mg, 46 %). – ^{1}H NMR ($CDCl_3$): $\delta = 2.51 - 2.48$ (m, C_{cage}-CH_2-CH_2, 4 H), 2.9 – 1.5 (br, B*H*, 10 H), 2.4 – 2.3 (m, C_{cage}-CH_2-CH_2, 2 H). – ^{11}B{^{1}H} NMR ($CDCl_3$): $\delta = -6.4$ (2 B), −7.7 (2 B), −8.6 (2 B), −11.3 (4 B) ppm. – ^{13}C NMR ($CDCl_3$): $\delta = 84.0$ (C_{cage}), 34.8 (C_{cage}–CH_2-), 32.2 (-$CH_2CH_2CH_2$-) ppm. – MS (EI, 70 eV): $m/z(\%) = 183$ (100) $[M-1]^+$.

*Reaction of dilithio-o-carborane with 1-bromo-3-chloropropane leading to **2**, **3** and **4***

Under an argon atmosphere, *n*-BuLi (2.2 M in hexane, 6.6 mmol) was added dropwise to a solution of *o*-carborane

(**1**, 476 mg, 3.3 mmol) in tetrahydrofuran (20 mL) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C, and for 40 min at room temperature, and transferred to a solution of 1-bromo-3-chloropropane (1550 mg, 9.9 mmol) in tetrahydrofuran (10 mL) at 0 °C during a period of 50 min. The resulting dark-red mixture was stirred at room temperature for 3.5 h and quenched with water (5 mL). The organic phase was separated and the water phase extracted with diethyl ether (3 × 25 mL). The organic portions were combined, dried ($MgSO_4$) and concentrated. Column chromatographic separation of the residue on silica gel (eluent: *n*-hexane) afforded **2** (406 mg, 67 %), **3** (colorless solid, 21 mg, 3 %), **4** (colorless solid, 186 mg, 19 %), and **1** (51 mg, 11 %).

3: IR (KBr): $\nu = 3434$ (m), 3056 (m), 2960 (m), 2928 (m), 2857 (w), 2572 (s, B-H), 1635 (m), 1445 (m), 1321 (m), 1017 (m), 722 (m), 655 (m) cm^{-1}. – ^1H NMR ($CDCl_3$): $\delta = 3.58$ (s, 1 H, $C_{cage}H$), 3.52 (t, 2 H, $J = 6$ Hz, -CH_2 Cl), 2.4 – 2.3 (m, 2 H, C_{cage}–CH_2-), 2.0 – 1.9 (m, 2 H, -CH_2CH_2 CH_2Cl) ppm. – ^{11}B NMR ($CDCl_3$): $\delta = -2.2$ (2 B), −5.6 (2 B), −9.2 (2 B), −11.8 (4 B), −13.0 (2 B) ppm. – MS (EI, 70 eV): $m/z(\%) =$ 219 (27) $[M-2H]^+$, 183 (100) $[M-Cl-2H]^+$.

4: M. p. 60 – 62 °C. – IR (KBr): $\nu = 3435$ (s), 2971 (m), 2930 (m), 2862 (w), 2564 (s, B-H), 1635 (m), 1446 (m), 1286 (m), 1129 (m), 988 (m), 731 (m), 654 (s) cm^{-1}. – ^1H NMR ($CDCl_3$): $\delta = 3.56$ (t, 4 H, $J = 6$ Hz, -CH_2Cl), 2.4 – 2.3 (m, 4 H, C_{cage}–CH_2-), 2.1 – 2.0 (m, 4 H, −CH_2CH_2 CH_2Cl), 2.9 – 1.5 (br, B*H*, 10 H) ppm. – ^{13}C NMR ($CDCl_3$): $\delta =$ 78.9, 43.8, 32.4, 32.2 ppm. – $^{11}B\{^1H\}$ ($CDCl_3$): $\delta = -4.5$ (2 B), −10.1 (6 B), −10.9 (2 B) ppm. – MS (EI, 70 eV): $m/z(\%) = 296$ (20) $[M-1]^+$, 259 (31) $[M-Cl-2H]^+$, 223 (26) $[M-Cl_2-2H]^+$,183 (100) $[M-C_3H_6Cl-Cl-H]^+$.

Copper-mediated reaction of dilithio-o-carborane with 1-bromo-3-chloropropane

Under an argon atmosphere, *n*-BuLi (2.2 M in hexane, 4.4 mmol) was added dropwise to a solution of *o*-carborane (**1**, 317 mg, 2.2 mmol) in diethyl ether (30 mL) at 0 °C. The resulting mixture was stirred for 40 min at 0 °C, and for 30 min at room temperature. It was cooled to 0 °C, and CuCl (440 mg, 4.4 mmol) and 1-bromo-3-chloropropane (1081 mg, 6.87 mmol) were added. The reaction mixture quickly turned to a brown suspension, which was stirred at room temperature for 24 h and quenched with 3 M HCl (10 mL). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 20 mL). The organic portions were combined, dried ($MgSO_4$) and concentrated. Column chromatographic separation of the residue on silica gel (eluent: *n*-hexane) afforded **3** (17 mg, 4 %), **5** (colorless solid, 60 mg, 19 %) and **1** (220 mg, 69 %). The identity of compound **5** was confirmed by comparison of the IR, NMR (^1H and ^{11}B) and analytical TLC data with those of an authentic sample prepared according to the literature [19].

*Crystal structure determination of **2**, **3** and **4***

Suitable single crystals of **2**, **3** and **4** were selected and mounted on an Oxford Gemini E diffractometer for data collection (graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å), ω scan mode). The structures were solved by Direct Methods and expanded using Fourier difference techniques with the SHELXTL-97 program package [24]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were placed in geometric positions and refined isotropically.

CCDC 894813, 911504 and 904884 contain the supplementary crystallographic data of **2**, **3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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