CYANOETHYLATION AND (METHOXYCARBONYL)ETHYLATION OF ICOSAHEDRAL *ortho*-CARBORANE DERIVATIVES AT CARBON VERTICES *via* MICHAEL ADDITIONS

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The C-H vertices of *ortho*-carborane and its derivatives can be smoothly cyanoethylated with acrylonitrile in the presence of benzyl(triethyl)ammonium hydroxide in a two-phase system: dichloromethane/water or 1,2-dimethoxyethane/water. The reaction is highly specific and not transferable to its *meta* and *para* isomers. No Michael addition with methyl acrylate takes place under these conditions. However, with NaH as catalyst (methoxycarbonyl)ethylation can be accomplished with *ortho*-carborane; *meta* and *para* isomers react neither with acrylonitrile, nor with methyl acrylate even under such forcing conditions. The syntheses, properties and constitutions of 1-(2-cyanoethyl)-*ortho*-carborane, 1-(2-cyanoethyl)-2-phenyl-*ortho*-carborane, 1,2-bis(2-cyanoethyl)-*ortho*-carborane, 1-[2-(methoxycarbonyl)ethyl]-*ortho*-carborane and 1,2-bis[2-(methoxycarbonyl)ethyl]-*ortho*-carborane, along with their respective acids, are described. Melting points, TLC, "heated-inlet" mass spectrometry, and the ^{1}H and ^{11}B NMR spectra of all compounds, are presented. The scope of cyanoethylations and (methoxycarbonyl)ethylations of other deltahedral carbaboranes and heteroboranes is considered.

Keywords: Boranes; Carboranes; Michael additions; Phase-transfer catalysis; Cyanoethylation; (Methoxycarbonyl)ethylation; ^{1}H and ^{11}B NMR spectroscopy; Heated-inlet mass spectrometry.

Among the many tens of known deltahedral polycarba polyboranes with a general formula $[C_mB_nH_o]^{p(-)}$ the most prominent are the three uncharged icosahedral isomers: 1,2-dicarba-*closo*-dodecaborane (*ortho*-carborane; (**1**)), 1,7-dicarba-*closo*-dodecaborane (*meta*-carborane) and 1,12-dicarba-*closo*-dodecaborane (*para*-carborane). The best accessible and most reactive of them is **1**. Due to uneven charge distribution, the C-H vertices in all carboranes are distinctly positive and, consequently, slightly acidic[1,2]. In the icosahedral family acidity decreases in the series: *ortho* >> *meta*> *para*. However, even with **1** this acidity is hardly comparable with that of, *e.g.*,

cyclopentadiene or dialkyl malonates. Nevertheless, with strong bases, such as RLi, RMgBr, *etc.*, in aprotic solvents, the C-H vertices in all icosahedral isomers are metallated and the resulting C-metallo derivatives react with essentially any electrophile >E–Y (Y = leaving group) under formation of a C-(E)-*o*(*m*,*p*)-carborane derivative. With some electrophiles this sequence can be carried out in liquid ammonia as solvent. In this case, sodium amide (prepared *in situ*) serves as metallating reagent. Using any version of this approach, at least one thousand of C-substituted carborane derivatives have been prepared and reported in hundreds of publications. A majority of them is recorded in the fundamental monography[1] and in the more recent review[2]. Several newer examples are described in ref.[3]. Essential new accomplishments in this area reflect the regularly published *Proceedings of the IMEBORON conferences*[4,5], where also applications of substituted carboranes are considered, *e.g.*, medicinal, precursors to polymerization and hydrogenation catalysts, metallo- and metallaheteroboranes, backbones of temperature resistant polymers, substrates for non-linear optics, *etc.* Potential applications of deltahedral cluster compounds, inclusive carboranes, have been reviewed a decade ago[6]. As we are aware of, none of substituted carboranes is reported to be prepared by a regular Michael addition[7] or by cyanoethylation[8]. Some resemblance to Michael addition is shown only by a stoichiometric addition of *C*-lithiated 1-phenyl-*ortho*-carborane to several chalcones[9]. Mono- and dicyanoethyl *ortho*-carboranes and their respective acids, are known[10] but have been prepared otherwise. Here we show the potential of Michael additions in the carborane series that apparently has not been recognized so far.

RESULTS AND DISCUSSION

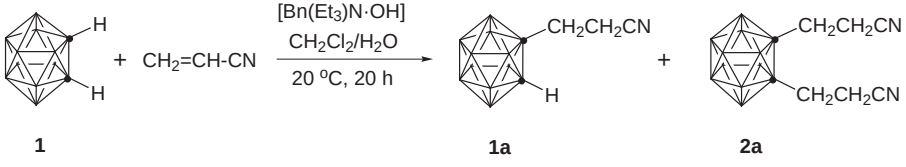
Michael additions[7] belong to the most efficient synthetic reactions of organic chemistry; they are characterized by addition of a slightly acid donor component, *e.g.*, cyclopentadiene, dialkyl malonates, *etc.*; to an α,β-unsaturated acceptor, *e.g.*, –CH=CH–CO–R, –CH=CH–COOR, –CH=CH–CN, *etc.*, under the influence of a basic catalyst. In the specific case of acrylonitrile as acceptor they are called cyanoethylations[8]. With organic donors, aprotic solvents are usually not required and the reactions can also be carried out in two-phase systems. In the latter case the catalyst can be designed to serve also as a phase transfer catalyst. This requirement is fulfilled by a variety of bulky quaternary ammonium hydroxides[8]. It is surprising that the reactions of this kind have not been reported with carborane derivatives as donors, despite that their C–H bonds are distinctly acidic, that the reactions are

easy to carry out in high yields, and that the expected products might be valuable synthons.

Now we have found that **1** is acidic enough to become cyanoethylated in two-phase systems, *e.g.*, dichloromethane/water or 1,2-dimethoxyethane (DME)/water, in the presence of benzyl(triethyl)ammonium hydroxide. The catalyst can be prepared *in situ* on addition of, *e.g.*, 4.0 M KOH to a reaction mixture of both components plus an appropriate amount of benzyl(triethyl)ammonium bromide. It is noteworthy that 1,8-bis(dimethylamino)-naftalene[11], renowned for its strong basicity and low nucleophilicity, is entirely ineffective.

The parent **1** becomes cyanoethylated sequentially at both C-H vertices, with the formation of 1-(2-cyanoethyl)-*ortho*-carborane (**1a**) and 1,2-bis-(2-cyanoethyl)-*ortho*-carborane (**2a**) (Scheme 1). The second C-H vertex probably reacts even faster than the first one.

A major part of the "loss" is apparently due to the general propensity of **1** and its derivatives to degrade by the action of essentially any basic substance and water or ethanol with loss of the $B_{(3)}$-H vertex[1,2,12]. The respective values in Table I indicate that **1** is probably more sensitive to degradation than **1a** and **2a** are because the "loss" decreases with increasing ratios acrylonitrile/**1**. This undesired reaction can be limited by use of the smallest still effective amount of benzyl(triethyl)ammonium hydroxide,



SCHEME 1

TABLE I
Yield dependence on acrylonitrile/**1** ratios (see Experimental)

Ratio	**1a**, %	**2a**, %	**1**, %[a]	Loss, %
1	26.8	31.0	26.7	15.5
2	49.8	28.4	10.7	11.1
3	7.5	85.6	–	6.9

[a] Recovered.

and by use of methylene chloride instead of DME. Under the same conditions 1-phenyl-*ortho*-carborane (**3**) affords 1-(2-cyanoethyl)-2-phenyl-*ortho*-carborane (**3a**) in a nearly quantitative yield. This result along with sequential cyanoethylation of the parent **1** indicates that cyanoethylations of any free C-H vertex in any derivative of **1** should, in principle, be feasible. Under these conditions, the reaction is highly specific for **1**-derivatives and not transferable the *meta* and *para* isomers.

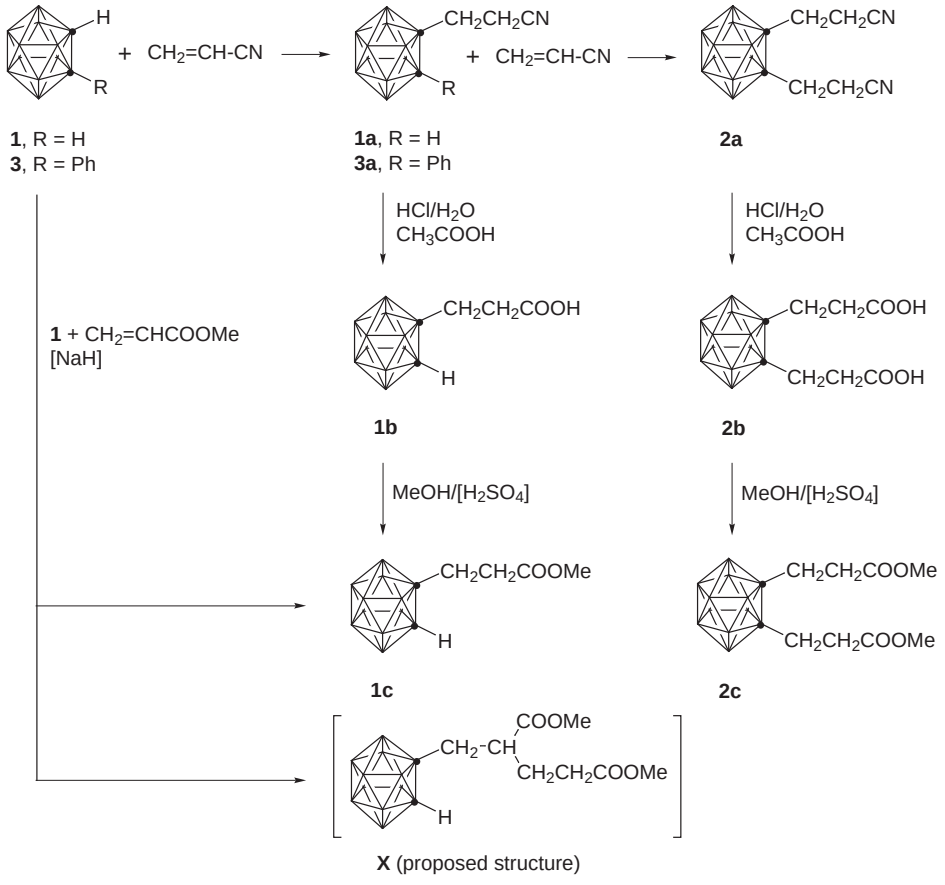
Acid hydrolysis of nitriles **1a** and **2a** affords the respective acids 1-(2-carboxyethyl)-*ortho*-carborane (**1b**) and 1,2-bis(2-carboxyethyl)-*ortho*-carborane (**2b**). Conventional esterification with methanol and some H_2SO_4 converts both acids to the respective methyl esters 1-[2-(methoxycarbonyl)ethyl]-*ortho*-carborane (**1c**) and 1,2-bis[2-(methoxycarbonyl)ethyl]-*ortho*-carborane (**2c**) in high yields. For **2c**, this is the best preparative route whereas **1c** can be obtained more conveniently by a direct Michael addition.

Methyl acrylate (MA) does not react with **1** under conditions of successful cyanoethylations. However, (methoxycarbonyl)ethylation can be accomplished by heating **1** to 70 °C in excess MA over NaH for several hours. The reaction is rather slow, incomplete, and affects only one C-vertex of **1**. After 6 h approximately a half of **1** was recovered and about 30% of solid **1c** could be isolated by column chromatography. About 20% of the well defined (TLC, mass and NMR spectrometry) viscous liquid **X** of a disputable constitution represented the rest of the reaction mixture. Compound **X** is an isomer of **2c** (MS) composed of one **1** and two MA units. Both combined MA units are attached to a single C-H vertex of **1** (^{1}H and ^{11}B NMR). Tentatively, the compound **X** might be dimethyl 2-(l-*o*-carboranylmethyl)-pentanedioate, resulting on addition of a second MA to the $–CH_2–$ group neighboring –COOMe in **1c**, despite there is still another C-H vertex in the *ortho*-carborane moiety of **1c** (Scheme 2). For an unequivocal identification of **X** additional experiments would be desirable. However, this is beyond the scope of this article.

A prolongation of the reaction time to 20 h led just to an appreciable loss of **1** under formation of a complex mixture of acidic by-products (TLC), apparently due to cage degradation of **1** or some derivatives; the yields of **1c** and **X** did not improve and no **2c** could be isolated. Even under these forced conditions neither *meta* nor *para* isomers reacted with MA or acrylonitrile in the same fashion.

In conclusion, we have demonstrated that attachment of some pendant groups to C-H vertices of some deltahedral polycarba(hetero)boranes is feasible *via* Michael additions – without stoichiometric amounts of extreme bases and without aprotic solvents – as is the case of current metallation/

alkylation sequences, which, moreover would hardly be suitable for syntheses of **1a**–**1c**, **2a**–**2c** and **3a**. However, only the cyanoethylations of **1** and its derivatives can be considered as truly preparative procedures so far. For (methoxycarbonyl)ethylations apparently at least a better catalyst should be found. Nevertheless, there are several acceptors more reactive than is methyl acrylate, and there exist dozens of *closo*-, *nido*- and *arachno*-carboranes which might serve as acidic donors. Hundreds of known metallacarboranes and heteroboranes possess the same inherent potential. So it seems that a systematic research in this area might appreciably enlarge the tool-box of chemistry of deltahedral polycarbaboranes.



SCHEME 2

EXPERIMENTAL

Apparatus and Chemicals

TLC was carried out on Silufol Sheets (Kavalier, Votice, Czech Republic) in various solvent mixtures, the spots were made visible by iodine vapour followed by a 1% $AgNO_3$ aqueous spray. The melting points were determined on a Koffler block on an open glass platelet. The NMR spectra (δ, ppm) were taken in deuteroacetone on a Varian UNITY 500 spectrometer (500 MHz for ^1H and 160.4 MHz for ^{11}B). Mass spectrometry was performed on a MAGNUM GC-MS ion-trap system (Finnigan MAT, U.S.A.) equipped with a heated inlet option (Spectronex AG, Basel, Switzerland). The heated inlet was used for direct introduction of samples. The gaseous sample, evaporated in a GC oven environment, was transported into the ion trap by pressure difference between a sample crucible at *ca* 10^{-2} Pa and ion trap manifold at *ca* 10^{-4} Pa. Samples were introduced as solids; typical quantities introduced were at the sub-milligram level. The transfer line was heated at 280 °C. Evaporation curves were obtained with a temperature programme starting at 35 °C followed by a 20 °C/min increase to 280 °C, where it was held to the end of the analysis. A data collection scan rate of 1 s/scan was used.

The compounds *o*-carborane, acrylonitrile and methyl acrylate were of commercial origin. Of these, the liquid reagents were dried over CaH_2 and freshly distilled prior to use. All solvents were of analytical grade and were used without further treatment. Benzyl(triethyl)ammonium bromide was prepared by addition of benzyl bromide to triethylamine in acetone. All reactions were carried out under nitrogen.

Cyanoethylations of *ortho*-Carborane

To a solution of **1** (5.8 g, 40 mmol) in dichloromethane (30 ml), benzyl(triethyl)ammonium bromide (1.4 g, 5 mmol) was added followed by 4 M KOH in water (1 ml). To the stirred turbid mixture, 2.7 ml (40 mmol), 5.4 ml (80 mmol) or 8.1 ml (120 mmol) of acrylonitrile in 30 ml of dichloromethane were added dropwise during 15 min. The colour of the reaction mixture turned deep yellow. After *ca* 3 h, the sparingly soluble **2a** began to separate. The catalyst was rejuvenated after 5 h by addition of another l ml of 4 M KOH and stirring was continued overnight (total time 20 h). Upon acidification by 25 ml of 1.0 M hydrochloric acid the intense yellow-orange colour nearly disappeared. The thick slurry was sucked off (solid A), the filtrate was separated from the water phase and the CH_2Cl_2 stripped off *in vacuo*. The solid A was washed twice with 10 ml of diethyl ether and dried in air before final crystallization. The combined diethyl ether washings were added to the residue after evaporation of the original CH_2Cl_2 filtrate, the solid was filtered off and washed with 5 ml of diethyl ether (solid B). Combined ether extracts were evaporated *in vacuo*, the residue was dissolved in the minimum amount of a chloroform/hexane mixture (l : 2, v/v), transferred onto a column of silica gel (i.d. 20 mm, height 150 mm) and, with the same solvent mixture, recovered **1** was eluted; **1a** was then desorbed by dichloromethane and a small amount of **2a** was eluted with a mixture of acetonitrile/chloroform (1 : 2, v/v). The yields of **1a**, **2a** and of recovered **1** varied with varying ratios of acrylonitrile/**1** (Table I). Crystallizations: A saturated solution of **1a** in dichloromethane was carefully covered with three volumes of hexane and left to stand over three days. Shiny prisms of TLC-pure **1a** separate essentially quantitatively. To a slurry of combined solids A + B + **2a** (from chromatography) in 30 ml of boiling ethanol, as much acetone was added as necessary for a complete dissolution of solid

(about 5 g). After standing overnight to cool, coarse colourless prismatic aggregates of TLC-pure **2a** separated. A second crop of the same quality was obtained after distilling off acetone from the mother liquors and standing overnight; **2a** was only sparingly soluble in ethanol, so crystallization loss was negligible.

1-(2-Cyanoethyl)-ortho-carborane (**1a**): M.p. 140 °C, m/z_{max} = 199, R_F 0.37 (dichloromethane). ^{1}H NMR: 4.74 (s, 1 H; C-H$_{carborane}$); 2.84 (m, 2 H; -CH$_2$-); 2.77 (m, 2 H; -CH$_2$-). ^{11}B NMR: –2.64 (d, 1 B); –5.59 (d, 1 B); –9.45 (d, 2 B); –11.83 (d, 2 + 2 B); –12.89 (d, 2 B).

1,2-Bis(2-cyanoethyl)-ortho-carborane (**2a**): M.p. 227 °C, m/z_{max} = 252, R_F 0.11 (dichloromethane). ^{1}H NMR: 2.92 (m, 4 H; -CH$_2$-); 2.85 (m, 4 H; -CH$_2$-). ^{11}B NMR: –4.51 (d, 2 B); –10.01 (d, 4 B); –10.92 (d, 2 + 2 B).

Bis-cyanoethylation of **1** in 1,2-Dimethoxyethane

To a stirred mixture of **1** (5.8 g, 40 mmol), benzyl(triethyl)ammonium bromide (1.4 g, 5 mmol) and 4 M KOH (1 ml) in DME (30 ml) immersed in a cold water bath, acrylonitrile (8.1 ml, 120 mmol) in DME (20 ml) was added dropwise over 15 min. Almost immediate separation of **2a** began. According to TLC, the reaction was essentially complete after 2 h. Stirring was continued for another 1 h; 20 ml of 5% HCl were added and volatile components were stripped off *in vacuo*. To the remaining slurry diethyl ether (50 ml) was added and after, thorough shaking, the solids were filtered off and washed three times with diethyl ether (10 ml). After crystallization as above, 8.84 g (88.4%) of pure **2a** were obtained. In this case the diethyl ether extracts can be neglected. This is the best way for the rapid preparation of large amounts of **2a**.

Cyanoethylation of 1-Phenyl-*ortho*-carborane

To a stirred mixture of **3** (0.9 g, 4 mmol) and benzyl(triethyl)ammonium bromide (0.28 g, 1 mmol) in dichloromethane (5 ml) 4 M KOH (0.25 ml) was added, followed by acrylonitrile (0.8 ml, 12 mmol) and the mixture was stirred for 20 h; 2 g of citric acid dihydrate in 10 ml water and 20 ml of CH_2Cl_2 were added, the layers were separated, the bottom layer was concentrated *in vacuo* to *ca* 15 ml and filtered through a short column of silica gel to remove traces of immobile impurities. After removal of volatile compounds *in vacuo*, the solid residue was crystallized from 15 ml of boiling hexane to which a few ml of chloroform was gradually added in order to achieve complete dissolution of the solid. After standing overnight, 0.95 g (96.3%) of thin needles separated. The compound was virtually insoluble in hexane.

1-(2-Cyanoethyl)-2-phenyl-ortho-carborane (**3a**): M.p. 182 °C, m/z_{max} = 275, R_F 0.66 (dichloromethane). ^{1}H NMR: 7.79 (d, 2 H; *o*-phenyl); 7.59 (t, 1 H; *p*-phenyl); 7.52 (q, 2 H; *m*-phenyl); 2.79 (t, 2 H; -CH$_2$-); 2.37 (t, 2 H; -CH$_2$-). ^{11}B NMR: –3.62 (d, 2 B); –9.46 (d, 1 B); –10.20 (d, 3 B); –10.92 ppm (d, 4 B).

No reaction of meta- and para-carborane with acrylonitrile was observed under the same conditions, either in CH_2Cl_2 or in DME, even after 20 h; both carboranes were recovered in over 95% yield by sublimation of the evaporation residue at 80 °C/1.3 Pa.

Hydrolysis of Nitriles **1a** and **2a** to Acids **1b** and **2b**

A suspension of 20 mmol of either **1a** or **2a** in 15 ml of concentrated hydrochloric acid and 15 ml of acetic acid was heated to 100 °C for 4 h. After dilution with 50 ml water and stand-

ing overnight, solid acids **1b** or **2b** separated. After filtration and washing with 10 ml of water, the solid products were dried *in vacuo*. Both acids were sparingly soluble in water, but **1b** smoothly dissolved in dichloromethane in which **2b** was virtually insoluble. Thus, crystallization of **1b** was carried out from a saturated dichloromethane solution by slow diffusion of hexane (as above with **1a**); **2b** was crystallized in the same fashion, but with diethyl ether instead of dichloromethane. The yields were essentially quantitative.

1-(2-Carboxyethyl)-ortho-carborane [3-(1-o-carboranyl)propanoic acid] (**1b**): M.p. 140 °C, m/z_{max} = 218, R_F 0.59 (acetonitrile/chloroform 1 : 2, v/v). ^{1}H NMR: 11.51 (v. broad s, 1 H; -COOH); 5.26 (s, 1 H; C-H$_{carborane}$); 3.24 (m, 2 H; -CH$_2$-); 3.17 (m, 2 H; -CH$_2$-). ^{11}B NMR: –0.82 (d, 1 B); –4.06 (d, 1 B); –7.75 (d, 2 B); –9.57 (d, 2 B); –9.96 (d, 2 B); –11.04 (d, 2 B). Titration equivalent (potentiometry in 50% ethanol) found: 4.21 mequivalent/g; calculated: 4.63; pK_a = 4.99.

1,2-Bis(2-carboxyethyl)-ortho-carborane (**2b**): M.p. 246 °C, R_F 0.30 (acetonitrile/chloroform 1 : 2, v/v). ^{1}H NMR: 4.28 (v. broad s, 2 H; 2 -COOH); 2.58 (m, 4 H; 2 -CH$_2$-); 2.21 (m, 4 H; 2 -CH$_2$-). ^{11}B NMR: –5.23 (d, 2 B); –10.70 (d, 4 B); –11.18 (d, 4 B). Titration equivalent (potentiometry in 50% ethanol) found: 7.00 mequivalent/g; calculated: 6.95; p$K_{a1=2}$ = 4.68. In this single case no regular mass spectrum was obtained, possibly due to thermal polycondensation of the diacid.

Esterification of Acids **1b** and **2b** to Dimethyl Esters

To a solution of 10 mmol of **1b** or **2b** in 15 ml methanol, concentrated sulfuric acid (0.5 ml, *ca* 1 mmol) was added. After standing overnight, the mixture was diluted with 20 ml water, neutralized with potassium carbonate, methanol was stripped off *in vacuo* and the products were taken into 15 ml of dichloromethane. According to TLC they were the entirely pure methyl esters **1c** and **2c**; **1c** was crystallized from hot hexane; for **2c**, crystallization from a saturated CH_2Cl_2 solution by slow diffusion of hexane is recommended. Both esters separated as low-melting white needles; the isolated yields were *ca* 90% in both cases.

1-[2-(Methoxycarbonyl)ethyl]-ortho-carborane (**1c**): M.p. 73 °C, m/z_{max} = 232, R_F 0.57 (dichloromethane). ^{1}H NMR: 4.69 (s, 1 H; C-H$_{carborane}$); 3.65 (s, 3 H; -COOCH$_3$); 2.69 (t, 2 H; -CH$_2$-); 2.61 (t, 2 H; -CH$_2$-). ^{11}B NMR: –2.76 (d, 1 B); –5.95 (d, 1 B); –9.67 (d, 2 B); –11.64 (d, 2 + 2 B); –12.96 (d, 2 B).

The identical compound resulted on direct Michael addition of **1** to MA (see below).

1,2-Bis[2-(methoxycarbonyl)ethyl]-ortho-carborane (**2c**): M.p. 75 °C, m/z_{max} = 318, R_F 0.38 (dichloromethane). ^{1}H NMR ($CDCl_3$): 3.79 (s, 6 H; 2 -COOCH$_3$); 2.58 (m, 8 H; 4 -CH$_2$-). ^{11}B NMR: –5.35 (d, 2 B); –11.02 (d, 4 B); –12.00 (d, 4 B).

Direct (Methoxycarbonyl)ethylation of *ortho*-Carborane (**1**)

A slurry of **1** (2.9 g, 20 mmol) and 80% NaH (0.23 g, 7.3 mmol) in MA (5.0 ml, 56 mmol) was stirred at 80 °C for 7 h. The mixture was extracted with 20 ml of boiling hexane, the extraction was repeated with the insoluble residue, the combined hexane extracts were concentrated to 20 ml and left to stand overnight. Part of nearly pure **1** was separated and filtered off; the volatile components of the mother liquors were stripped off *in vacuo*. The semisolid residue from evaporation was dissolved in the minimum amount of a chloroform/hexane mixture (1 : 2, v/v), transferred to a silica gel column (i.d. 15 mm, height 150 mm), and eluted with the same solvent mixture. First, residual **1** was eluted, followed by the **1c** fraction. Final percolation with chloroform afforded a transparent viscous oil **X**.

From the combined **1** fractions the solvents were stripped off, the solids crystallizing out prior to chromatography were added to the evaporation residue and 1.22 g (43.1%) of **1** was recovered by sublimation using an 80 °C bath at 1.3 Pa. The TLC-pure **1c** fraction gives 1.34 g (30.0%) of **1c**, unambiguously identified by m.p. and comparative TLC with an authentic sample.

Compound **X**: Viscous liquid, m/z_{max} = 318, R_F 0.35 (dichloromethane). ^{1}H NMR: 4.61 (s, 1 H; C-$H_{carborane}$); 3.72 (s, 3 H; -$COOCH_3$); 3.03 (s, 3 H; -$COOCH_3$); 2.65 (m, 1 H); 2.47 (d, 2 H); 2.34 (t, 2 H); 1.84 (m, 2 H). ^{11}B NMR: –2.71 (d, 1 B); –5.76 (d, 1 B); –9.62 (d, 2 B); –11.69 (d, 4 B); –12.96 (d, 2 B).

On prolongation of the reaction time to 20 h and work-up as above, 9.5% of **1** were recovered along with 25% of **1c** and 21% of **X**. The remainder consisted of acidic substances, moving in TLC only with acetonitrile/chloroform (1 : 2, v/v) as a string of many reducing spots, indicating cage degradation products.

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