

## CHEMISTRY OF COMPOUNDS WITH THE 1-CARBA-*closo*-DODECABORANE(12) FRAMEWORK

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Synthesis of various compounds containing the 1-carba-*closo*-dodecaborane cage is reported. The isolated derivatives include zwitterionic 1-L-1-CB<sub>11</sub>H<sub>11</sub> (L = H<sub>3</sub>N and (CH<sub>3</sub>)<sub>2</sub>S) and 12-L-1-CB<sub>11</sub>H<sub>11</sub> (L = (CH<sub>3</sub>)<sub>2</sub>S and CH<sub>3</sub>SCH<sub>2</sub>SCH<sub>3</sub>) compounds along with C-substituted derivatives of the general formula [1-X-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (X = HOOC, HO, CH<sub>3</sub>O, HS and CH<sub>3</sub>S). Direct halogenation of [1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> produces [7,8,9,10,12-Cl<sub>5</sub>-1-CB<sub>11</sub>H<sub>7</sub>]<sup>-</sup>, [7,8,9,10,11,12-X<sub>6</sub>-1-CB<sub>11</sub>H<sub>6</sub>]<sup>-</sup> (X = Cl, Br), [12-I-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> and [7,12-I<sub>2</sub>-1-CB<sub>11</sub>H<sub>10</sub>]<sup>-</sup> substituted species. Constitution of all products was established by <sup>1</sup>H, <sup>11</sup>B, IR and mass spectrometry and is supported by some chemical reactions of the compounds.

The [1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anion (*I*) was first isolated in 1967 by Knoth<sup>1</sup>, who later<sup>2</sup> improved the synthesis and made initial attempts at substitution, impure samples of B-bromo and 1-(CH<sub>3</sub>)<sub>3</sub>Si-derivatives being the only products. We have recently found a more convenient route<sup>3,4</sup> to the parent anion *I* and to some of its uncharged 1-L-1-CB<sub>11</sub>H<sub>11</sub> (*II*) (L = CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH and (CH<sub>3</sub>)<sub>3</sub>N) congeners. We wish to report in this paper some other possibilities of synthesizing a series of new substituted derivatives in this area of borane chemistry.

Several new derivatives of the anion *I* and its zwitterionic analogues *II* can be obtained either from the relevant 7-substituted 7-carba-*nido*-undecaboranes, 7-L-7-CB<sub>10</sub>H<sub>12</sub> (*III*), by inserting the missing boron vertex or by modifying the present exoskeletal functional group in the compounds of the type *II*.

If 7-H<sub>3</sub>N-7-CB<sub>10</sub>H<sub>12</sub> (*IIIa*) is treated with sodium tetrahydroborate followed by prolonged heating with triethylamine borane at 200°C and the intermediate product is then hydrolyzed with hydrochloric acid, 1-amine-1-carba-*closo*-dodecaborane(*II*), 1-H<sub>3</sub>N-1-CB<sub>11</sub>H<sub>11</sub> (*IIa*), can be obtained in good yield as the parent compound of the 1-N-substituted species. Its N-monomethyl derivative *Iib* is available from the N,N-dimethyl derivative<sup>3</sup> *Iic* by a curious demethylation with iodine<sup>4</sup> and the N,N,N-trimethyl derivative *Iid* results from successive methylation of any of compounds *IIa-c*. Derivatives *IIa-c* behave as weak N-acids with pK<sub>a</sub> values 6.0, 6.5, and 5.7, respectively (50% ethanol), giving rise to anions [1-H<sub>2</sub>N-1-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (*Ia*), [1-CH<sub>3</sub>NH-1-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (*Ib*)<sup>4</sup> and [1-(CH<sub>3</sub>)<sub>2</sub>N-1-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (*Ic*)<sup>3</sup>.

Successive methylation of *Ia* affords its trimethyl derivative *IId* and, obviously, other alkylations would give rise to a whole family of such zwitterionic compounds. The amine group can therefore act as a linkage to any organic compound designed for coupling to the carbaborane cage.

Deamination of *Ia* with nitrous acid is surprisingly difficult, possibly due to the strong basicity of the *Ia* anion in which the reacting  $\text{NO}^+$  particle cannot find a free electron pair to attack it. Only a mixture of the  $[\text{1-HO-1-CB}_{11}\text{H}_{11}]^-$  anion (*Id*), which can be isolated as tetramethylammonium salt, with much starting compound is obtained in water using a large excess of nitrous acid. On successive methylation of the mixture the starting compound separates as insoluble *IId* and the  $[\text{1-CH}_3\text{O-1-CB}_{11}\text{H}_{11}]^-$  (*Ie*) anion, isolated as tetramethylammonium salt, remains in the solution.

Treatment of *Ia* with nitrous acid in the presence of excess dimethyl sulphide results in the formation of uncharged  $\text{1-(CH}_3)_2\text{S-1-CB}_{11}\text{H}_{11}$  (*IIf*) in good yield, which is apparently due to the reaction taking place in the dimethyl sulphide phase rather than in water. The same course of a reaction was also observed in the deamination of *nido*-compound *IIIa* in dimethyl sulphide<sup>5</sup> giving good yield of  $\text{7-(CH}_3)_2\text{S-7-CB}_{10}\text{H}_{12}$  (*IIIb*).

The latter species reacts smoothly with triethylamine-borane at  $200^\circ\text{C}$  giving fair yield of  $[\text{1-CH}_3\text{S-1-CB}_{11}\text{H}_{11}]^-$  (*If*), the second methyl group being probably split off as methane. Methylation of *If* is unexpectedly difficult, nevertheless, compound *IIf* is eventually obtained in low yield. One of the reasons might be a low basicity of the  $\text{CH}_3\text{S}$  group as a result of its attachment to the most positive vertex of the cage.

Analogously to other carboranes<sup>6</sup>, two types of substitution reactions of the parent anion *I* can be observed: Those performed under electrophilic conditions, leading to B-substituted derivatives, and the second type, comprising the reactions performed via C-lithiation followed by the addition of a suitable electrophilic reagent to obtain C-substituted anions.

Under electrophilic conditions, the most negative  $\text{B}_{(12)}$  vertex is attacked first. Thus with iodine at ambient temperature in a very slow reaction, the  $[\text{12-I-1-CB}_{11}\text{H}_{11}]^-$  (*Ig*) anion is formed, accompanied by small amount (*c* 5%, identified by its  $^{11}\text{B}$  NMR spectrum) of the 7-isomer. Similarly, dimethyl sulphoxide in strongly acidic medium reacts with *I* to obtain uncharged  $\text{12-(CH}_3)_2\text{S-1-CB}_{11}\text{H}_{11}$  (*IIf*) along with  $\text{12-CH}_3\text{SCH}_2\text{SCH}_3\text{-1-CB}_{11}\text{H}_{11}$  (*Ilg*) as the only products.

Chlorination of *I* in acetic acid at ambient temperature with excess chlorine leads to  $[\text{7,8,9,10,12-Cl}_5\text{-1-CB}_{11}\text{H}_7]^-$  (*Ii*) whereas at  $100^\circ\text{C}$  the hexachloro derivative  $[\text{7,8,9,10,11,12-Cl}_6\text{-1-CB}_{11}\text{H}_6]^-$  (*Ij*) is obtained. With excess bromine in acetic acid at  $80^\circ\text{C}$ , only the hexabromo derivative  $[\text{7,8,9,10,11,12-Br}_6\text{-1-CB}_{11}\text{H}_6]^-$  (*Ik*) is formed and with excess iodine under the same conditions diiodo derivative  $[\text{7,12-I}_2\text{-1-CB}_{11}\text{H}_{10}]^-$  is produced (*Ih*).

Lithiation of *I* with excess butyllithium in tetrahydrofuran followed by the reaction of the resulting solution either with carbon dioxide or with elemental sulphur produces C-carboxylic acid [1-HOOC-1-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (*II*) and the C-thiol [1-HS-1-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (*Im*), respectively. Successive methylation of *Im* yielded uncharged compound *IIe*; here again, as in the case of *If*, the reaction is very difficult for the same reason.

Unambiguous evidence for the constitution of all above discussed compounds is based on spectral measurements (see Tables I–III) and is supported by the described interconversions of the relevant derivatives shown in Schemes 1 and 2.

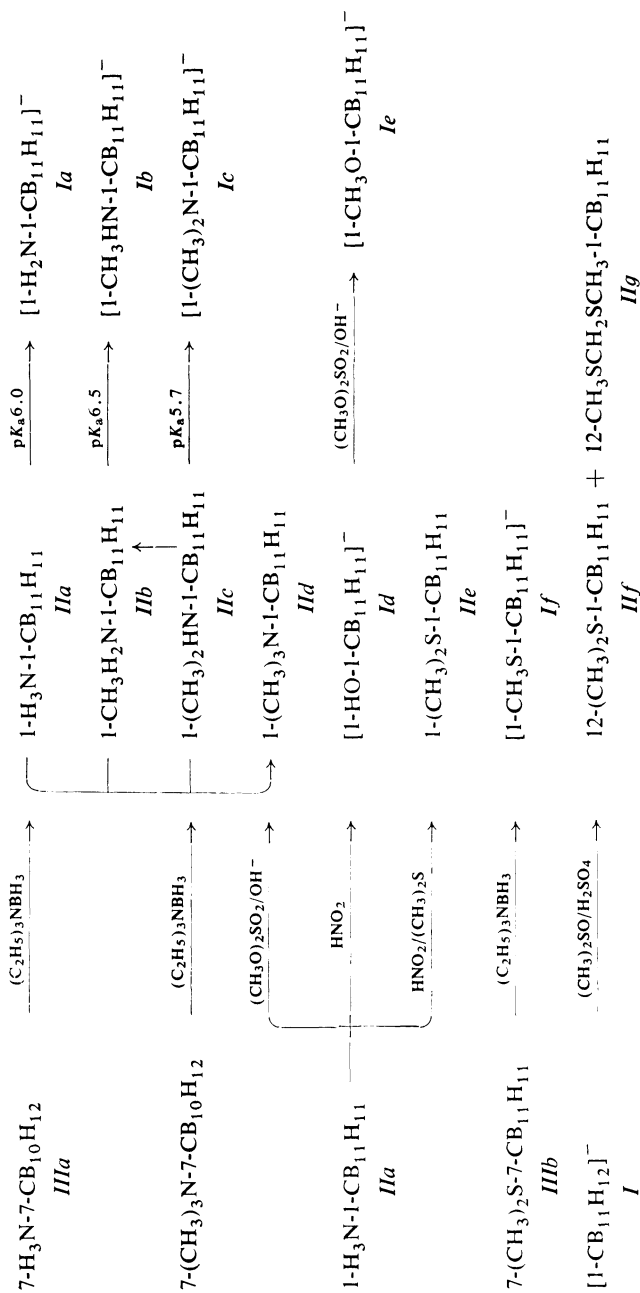
Compounds with the 1-carba-*closo*-dodecaborane skeleton are nearly ideal for studying long-range effects of substituents on the <sup>11</sup>B NMR chemical shifts of individual boron atoms<sup>7</sup>. The assignment of individual signals and an analysis of changes in NMR characteristics will be discussed elsewhere.

TABLE I

Some properties of the [1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> derivatives

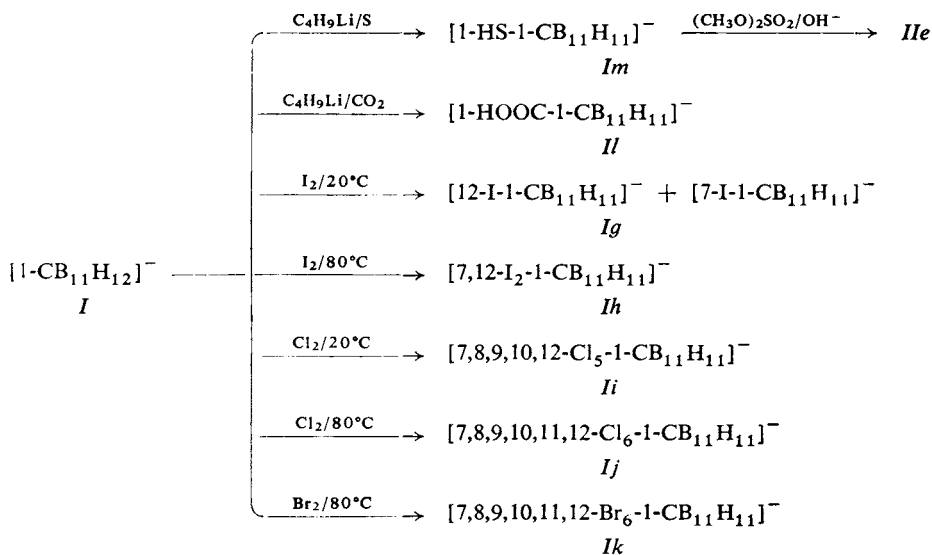
Compound	R <sub>F</sub>	<i>m/z</i>	δ <sup>1</sup> H NMR	
<i>Ia</i>	0.22	—	3.44 <sup>a</sup>	—
<i>Ib</i>	0.35	—	3.43 <sup>a</sup>	2.22 <sup>b</sup>
<i>Ic</i>	0.55	—	3.46	2.25 <sup>b</sup> , 2.80 <sup>c</sup>
<i>Id</i>	0.20	—	3.44 <sup>a</sup>	9.16 <sup>d</sup>
<i>Ie</i>	0.36	—	3.44 <sup>a</sup>	3.14 <sup>b</sup>
<i>If</i>	0.22	—	3.45 <sup>a</sup>	2.11 <sup>b</sup>
<i>Ig</i>	0.24	—	3.45 <sup>a</sup>	2.61 <sup>e</sup>
<i>Ih</i>	0.38	—	3.42 <sup>a</sup>	2.73 <sup>e</sup>
<i>Ii</i>	0.30	—	3.43 <sup>a</sup>	2.51 <sup>e</sup>
<i>Ij</i>	0.35	—	3.46 <sup>a</sup>	2.56 <sup>e</sup>
<i>Ik</i>	0.35	—	3.46 <sup>a</sup>	2.92 <sup>e</sup>
<i>Il</i>	0.18	—	3.41 <sup>a</sup>	8.64 <sup>f</sup>
<i>Im</i>	0.30	—	3.43 <sup>a</sup>	3.31 <sup>g</sup>
<i>IIa</i>	0.25	161	8.98 <sup>h</sup>	—
<i>IIb</i>	0.35	175	2.87 <sup>b</sup>	8.99 <sup>i</sup>
<i>IIc</i>	0.57	189	3.14 <sup>b</sup>	8.34 <sup>c</sup>
<i>IId</i>	0.60	203	3.47 <sup>b</sup>	—
<i>IIe</i>	0.54 <sup>j</sup>	206	3.15 <sup>b</sup>	—
<i>IIf</i>	0.46	206	2.61 <sup>b</sup>	2.67 <sup>b</sup>
<i>IIg<sup>k</sup></i>	—	—	2.48 <sup>b</sup>	2.75 <sup>e</sup>
<i>IIg</i>	0.61	252	2.32 <sup>b</sup>	2.78 <sup>e</sup>
			2.67 <sup>b</sup>	4.22 <sup>l</sup>

<sup>a</sup> (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> singlet; <sup>b</sup> CH<sub>3</sub> singlet; <sup>c</sup> NH signal; <sup>d</sup> HO signal; <sup>e</sup> CH<sub>ske1</sub> singlet; <sup>f</sup> HOOC signal; <sup>g</sup> HS singlet; <sup>h</sup> H<sub>3</sub>N signal; <sup>i</sup> H<sub>2</sub>N signal; <sup>j</sup> in benzene; <sup>k</sup> in trideuterioacetonitrile; <sup>l</sup> CH<sub>2</sub> signal.

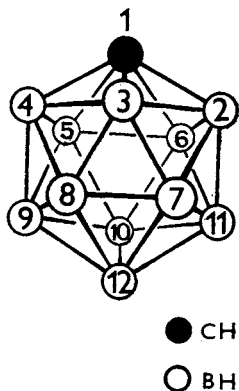


SCHEME 1

Synthesis and reactions of uncharged derivatives of [1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup>



SCHEME 2

Substitution reactions of the  $[\text{1-CB}_{11}\text{H}_{12}]^{-}$  anionSimplified structure of the  $[\text{1-CB}_{11}\text{H}_{12}]^{-}$  anion

## EXPERIMENTAL

$^1\text{H}$  (200 MHz) and  $^{11}\text{B}$  (64.18 MHz) NMR spectra were recorded in hexadeuterioacetone on a Varian XL-200 spectrometer, chemical shifts are given in  $\delta$  (ppm referenced to tetramethylsilane and  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ , positive values downfield). IR spectra were obtained in Nujol mulls using a Perkin-Elmer 684 equipment. Mass spectra were collected at 70 eV on a GC/MS HP-5989 device. TLC was performed on Silufol sheets (silica gel on aluminium foil, producer Kavalier, Czechoslovakia) in acetonitrile-chloroform (1 : 3). The  $\text{p}K_{\text{a}}$  values were determined by potentiometric titration in 50% ethanol. Tetrahydrofuran was distilled with  $\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OCH}_3)_2$

prior to use and other solvents were purified by standard distillation procedures. Starting 7-H<sub>3</sub>N-7-CB<sub>10</sub>H<sub>12</sub> and the [1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anion were prepared according to our previously described method<sup>3</sup>. Other commercially available chemicals were reagent grade and were used as received. All evaporations of solvents were performed *in vacuo* on a standard rotary evaporator, unless otherwise stated. Properties of all compounds isolated are summarized in Tables I—III.

#### 1-Amine-1-carba-*closo*-dodecaborane(11) (IIa)

Sodium tetrahydroborate (2.5 g; 0.066 mol) was added to a solution of 7-H<sub>3</sub>N-7-CB<sub>10</sub>H<sub>12</sub> (6 g; 0.04 mol) in tetrahydrofuran (25 ml). After the initial hydrogen evolution had ceased, triethylamine borane (10 ml; 0.07 mol) was added and the mixture was heated at 190—200°C

TABLE II  
δ<sup>11</sup>B NMR chemical shifts (±0.05 ppm) of the [1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> derivatives in hexadeuterioacetone

Compound	B <sub>(12)</sub>	Signals of intensity 5	
		B <sub>(2-6)</sub>	or B <sub>(7-11)</sub>
<i>I</i> <sup>3</sup>	-6.90	-13.30	-16.30
<i>Ia</i>	-14.40	-12.88	-14.40
<i>Ib</i> <sup>4</sup>	-12.95	-14.40	-14.40
<i>Ic</i> <sup>3</sup>	-11.68	-14.86	-14.86
<i>Id</i>	-15.69	-14.03	-15.69
<i>Ie</i>	-13.30	-15.52	-15.52
<i>If</i>	-8.95	-12.98	-12.98
<i>Ig</i>	-17.92 <sup>a</sup>	-11.90	-16.35
<i>Ih</i>	-16.26 <sup>a</sup>	-21.99 <sup>a</sup>	-15.16
		-9.92	-11.66
		-15.92	-17.59
<i>Ii</i>	1.42 <sup>a</sup>	-4.95 <sup>a</sup>	-22.33
		-5.76 <sup>a</sup>	-20.37
		-13.88	-23.81
<i>Ij</i>	0.74 <sup>a</sup>	-5.95 <sup>a</sup>	-23.51
<i>Ik</i>	-2.02 <sup>a</sup>	-9.84 <sup>a</sup>	-20.34
<i>Il</i>	-6.37	-13.40	-13.40
<i>Im</i>	-10.21	-11.95	-12.63
<i>IIa</i>	-9.20	-15.02	-13.42
<i>IIb</i>	-9.53	-15.77	-13.70
<i>IIc</i>	-8.37	-13.65	-15.07
<i>IId</i>	-7.43	-13.65	-15.02
<i>IIe</i>	-4.33	-14.88	-11.88
<i>IIf</i>	-3.50	-14.30	-15.80
<i>IIg</i>	-3.77	-14.27	-15.80

<sup>a</sup> Singlet of the substituted boron atom.

for 5 h. The resulting melt was then cooled down to ambient temperature, decomposed with methanol (40 ml) and the solution formed was hydrolysed at 80°C (bath) with a mixture of concentrated hydrochloric acid (40 ml) and glycerol (15 ml) for 12 h. The methanol was then removed and the residue was extracted with two 50 ml portions of ether. The material obtained after removing the ether was extracted with several 50 ml portions of chloroform and the solid residue was dissolved in (1 : 5) hydrochloric acid (50 ml) and extracted with two 50 ml portions of ether. The solid remaining after evaporation of the ether was dissolved in a minimum amount of water which was then stripped off and the solid residue was dried at 120°C/1.3 Pa to yield 4.2 g (65%) of *Ila* as a solid not melting up to 280°C and very soluble in water and alcohols.

**Tetramethylammonium salt:** 1 mol l<sup>-1</sup> tetramethylammonium chloride (15 ml) was added to a solution of compound *Ila* (1.6 g; 0.01 mol) in 2% potassium hydroxide (30 ml), the resulting suspension was heated and ethanol was added to obtain clear solution from which 2.0 g (86%) of [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> [1-H<sub>2</sub>N-1-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (*Ia*) crystallized on standing at room temperature.

TABLE III  
Assignment of some IR absorption bands (cm<sup>-1</sup>) of sulphur containing compounds

<i>I</i>	<i>If</i>	<i>Im</i>	<i>Ile</i>	<i>Ilf</i>	<i>Ilg</i>	Assignment
3 040	—	—	—	3 075	3 075	$\nu(\text{C—H})$
2 530	2 550	2 535	2 550	2 570	2 570	$\nu(\text{B—H})$
1 485	1 486	1 483	—	—	—	$\delta_{\text{asym}} \text{CH}_3^a$
—	—	—	1 425	1 425	1 425	$\delta_{\text{asym}} \text{CH}_3^b$
1 418	1 418	1 416	—	—	—	$\delta_{\text{sym}} \text{CH}_3^a$
—	—	—	1 412	1 412	—	—
—	—	—	1 330	1 330	1 325	$\delta_{\text{sym}} \text{CH}_3^b$
—	—	—	—	—	1 262	—
—	—	—	—	—	1 140	—
1 090	1 092	1 095	1 093	1 095	1 092	skeletal [CB <sub>11</sub> H <sub>12</sub> ] <sup>-</sup>
1 062	1 050	1 050	1 046	1 040	—	skeletal [CB <sub>11</sub> H <sub>12</sub> ] <sup>-</sup>
1 020	1 009	1 010	—	1 010	1 010	skeletal [CB <sub>11</sub> H <sub>12</sub> ] <sup>-</sup>
—	—	—	995	993	995	$\nu_{\text{asym}} \text{skel. CSC}^b$
—	983	970	—	—	—	—
952	950	950	—	—	—	rocking [(CH <sub>3</sub> ) <sub>4</sub> N] <sup>+</sup>
—	—	880	—	—	—	$\delta \text{CSH}$
—	—	—	—	860	860	—
—	800	—	800	—	815	$\nu(\text{C—S})$
—	—	—	—	680	682	$\nu_{\text{sym}} \text{CSC}$
—	—	—	—	—	565	—
—	—	—	475	475	475	$\delta_{\text{asym}} \text{CSC}$
—	372	366	364	325	315	—
—	275	—	275	235	242	$\delta_{\text{sym}} \text{CSC}$
—	—	—	260	—	—	—

<sup>a</sup> From [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup>; <sup>b</sup> from (CH<sub>3</sub>)<sub>2</sub>S.

1-Trimethylamine-1-carba-*closo*-dodecaborane(11) (*IId*)

To a solution of *IId* (1.6 g; 0.01 mol) in 5% sodium hydroxide (50 ml) was added dimethyl sulphate (8.2 g; 0.065 mol) and the mixture was stirred for 2 h at room temperature. The separated product was filtered off, washed with water (50 ml), methanol (20 ml) and dried at 25°C/1.3 Pa to give 1.9 g (93%) of *IId* (ref.<sup>3</sup>).

Tetramethylammonium 1-Hydroxy-1-carba-*closo*-dodecaborate(1-) (*Id*)

Under stirring and cooling to 0°C, an aqueous solution (8 ml) of sodium nitrite (3.0 g; 0.043 mol) was added dropwise to a solution of compound *IId* (1.0 g; 6.0 mmol) in water (50 ml). Stirring was continued until the starting compound *IId* was present in the mixture (identified by TLC). Concentrated hydrochloric acid (20 ml) and zinc dust (5.0 g; 0.08 mol) were then carefully added and the mixture was heated for 3 h (water bath), filtered and extracted with two 30 ml portions of ether. The ether was stripped off and the solid residue was dissolved in water (50 ml) which was acidified with several drops of concentrated hydrochloric acid. The mixture was then treated with 1 mol l<sup>-1</sup> tetramethylammonium chloride (20 ml), the resulting precipitate was filtered off, washed with water and crystallized from ethanol to obtain 0.5 g (36%) of *Id*.

Tetramethylammonium 1-Methoxy-1-carba-*closo*-dodecaborate(1-) (*Ie*)

The mixture obtained after reduction with zinc dust as in the preceding experiment was filtered and extracted with two 30 ml portion of ether. The ethereal extract was evaporated, the solid residue was dissolved in 5% potassium hydroxide (50 ml) and the resulting solution was treated with dimethyl sulphate (2.0 g; 0.016 mol). After stirring for 3 h at room temperature, the solution was filtered with activated charcoal and treated with 1 mol l<sup>-1</sup> tetramethylammonium chloride (20 ml). The precipitate was filtered, washed twice with hot water (50 ml) and crystallized from aqueous ethanol to give 0.85 g (57%) of *Ie*.

1-Dimethyl Sulphide-1-carba-*closo*-dodecaborane(11) (*IIf*)

Dimethyl sulphide (10 ml) and concentrated hydrochloric acid (10 ml) were added to a solution of compound *IId* (1.0 g; 6 mmol) in water (50 ml). The mixture was cooled down to 0°C and solid sodium nitrite (1.0 g; 0.015 mol) was added under continuous stirring (gas evolution). After the mixture had decolorized, the dimethyl sulphide was removed and the separated precipitate was filtered off, washed with water (50 ml) and dissolved in acetone which was then evaporated with water (100 ml). The formed precipitate was washed with 5% sodium carbonate (50 ml) and water (50 ml). The crude product was dried at 25°C/1.3 Pa and crystallized from dichloromethane to isolate 0.7 g (57%) of *IIf*, well soluble in chloroform and dichloromethane.

Tetramethylammonium 1-Methylsulphido-1-carba-*closo*-dodecaborate(1-) (*If*)

Trimethylamine borane (6 ml; 0.04 mol) was added to 7-(CH<sub>3</sub>)<sub>2</sub>S-7-CB<sub>10</sub>H<sub>12</sub> (*IIIb*)<sup>5</sup> and the mixture was heated at 190–200°C for 4 h (hydrogen evolution). The mixture was then cooled to room temperature and carefully decomposed with a mixture of methanol (30 ml) and concentrated hydrochloric acid (30 ml). The solution was heated for 8 h (water bath) and the methanol was removed after cooling to room temperature. The formed precipitate was shaken with concentrated hydrochloric acid (100 ml) and ether (100 ml). The suspension was filtered, the ether layer was evaporated and the solid residue was dissolved in 5% potassium hydroxide (100 ml). The mixture was then filtered and the filtrate treated with 1 mol l<sup>-1</sup> tetramethylammo-



nium chloride (25 ml). The precipitate was filtered off, washed with water and crystallized from aqueous acetone to obtain 2.0 g (61%) of *If*.

#### Tetramethylammonium 1-Mercapto-1-carba-*closo*-dodecaborate(1-) (*Im*)

Butyllithium (20 ml of a 20% solution in hexane) was added dropwise to a suspension of  $[(\text{CH}_3)_3\text{.NH}]^+ [1\text{-CB}_{11}\text{H}_{12}]^-$  in tetrahydrofuran (40 ml) under stirring for 30 min at room temperature (nitrogen atmosphere). Sulphur (0.6 g; 0.019 g) was then added to develop red colour. After the initial exothermic reaction had ceased, the mixture was stirred at 50°C (bath) for 1 h. The tetrahydrofuran was removed and the solid residue was dissolved in water (100 ml). After filtration, the filtrate was acidified with diluted (1 : 3) hydrochloric acid (20 ml), refiltered and the filtrate was extracted with two 30 ml portions of ether. The organic layer was evaporated and the solid residue was treated with 5% potassium hydroxide (50 ml). The mixture was filtered and the filtrate was precipitated with  $1 \text{ mol l}^{-1}$  tetramethylammonium chloride (15 ml). The precipitate was filtered off, washed with water and crystallized from aqueous acetone to give 1.8 g (72%) of *Im*, yellow crystals.

#### Methylation of the $[1\text{-HS-1-CB}_{11}\text{H}_{11}]^-$ (*Im*) Anion

Compound *Im* (0.8 g; 3 mmol) was suspended in diluted (1 : 3) hydrochloric acid (50 ml) and the mixture was shaken with ether (50 ml) and the organic layer was evaporated. The residue was dissolved in acetone (15 ml), 5% potassium hydroxide (15 ml) and dimethyl sulphate (2.0 g; 0.016 mol) were added and the mixture was refluxed for 48 h. After removing the acetone, the mixture was diluted with water (50 ml) and filtered. The obtained solid was washed with water, dried at 25°C/1.3 Pa and extracted with benzene (Soxhlet extractor). The benzene extract was evaporated and the solid residue was chromatographed in ethyl acetate using a column (2.5 × 30 cm) of silica gel. Evaporation of the combined fractions of  $R_F$  0.54 yielded 0.3 g (45%) of *Ie*.

#### Tetramethylammonium 1-Carboxy-1-carba-*closo*-dodecaborate(1-) (*Il*)

Butyllithium (20 ml of a 20% solution in hexane) was added dropwise to a suspension of  $[(\text{CH}_3)_3\text{.NH}]^+ [1\text{-CB}_{11}\text{H}_{12}]^-$  (*I*) (2.0 g; 0.01 mol) in tetrahydrofuran (40 ml) (nitrogen atmosphere) and the mixture was stirred at room temperature for 30 min. The solution was then poured to a powdered solid carbon dioxide and the tetrahydrofuran was removed. The solution was filtered with activated charcoal and the filtrate was extracted with two 50 ml portions of ether. The organic layer was evaporated and the solid residue was dissolved in water (100 ml). The solution was treated with  $1 \text{ mol l}^{-1}$  tetramethylammonium chloride (5 ml; 0.05 mol, 50% of the theoretical amount) to precipitate unreacted *I* along with a small amount of the *Il* anion (identified by its  $^{11}\text{B}$  NMR spectrum). The precipitate was then filtered off and the second portion of  $1 \text{ mol l}^{-1}$  tetramethylammonium chloride (5 ml; 0.05 mol) was added to the filtrate. The separated voluminous product was filtered, washed with water and crystallized from aqueous acetone to obtain 1.2 g (46%) of *Il*, well soluble in alcohols and acetone.

#### Tetramethylammonium 12-Iodo-1-carba-*closo*-dodecaborate(1-) (*Ig*)

Compound *I* (trimethylammonium salt) (0.7 g; 3.45 mmol) was dissolved in 5% potassium hydroxide (40 ml) and the trimethylamine evolved was removed *in vacuo*. Iodine (0.9 g; 6 mmol) was then added and the solution was stirred for 1 h. After adding diluted (1 : 3) hydrochloric acid (10 ml) and  $\text{Na}_2\text{SO}_3 \cdot 7 \text{H}_2\text{O}$  (0.5 g), the solution was filtered and extracted with ether (30 ml).

The organic layer was evaporated, the solid residue was dissolved in water (50 ml) and the solution was treated with  $1 \text{ mol l}^{-1}$  tetramethylammonium chloride (10 ml). The precipitate was filtered off, washed with water and dried at  $25^\circ\text{C}/1.3 \text{ Pa}$  to give 1.0 g (85%) of as yellow crystals containing less than 5% of the 7-I isomer, which was identified by the  $^{11}\text{B}$  NMR spectrum.

Tetramethylammonium 7,12-Diiodo-1-carba-*closo*-dodecaborate(1-) (*Ih*)

Compound *I* (trimethylammonium salt) (0.75 g; 3.65 mmol) was dissolved in 5% potassium hydroxide (50 ml). The evolved trimethylamine was removed *in vacuo*, the solution was acidified with concentrated hydrochloric acid to pH 1 and extracted with two 25 ml portions of ether. The ether extracts were evaporated leaving free acid of the anion *I* as a viscous material which was dissolved in glacial acetic acid (25 ml). Iodine (2.5 g; 0.02 mol) was added and the mixture was heated (water bath) for 48 h. The acetic acid was then distilled off and the residue was diluted with water (40 ml). The unreacted iodine was removed with solid sodium sulphite, the mixture was then neutralized with 5% potassium hydroxide and precipitated with  $1 \text{ mol l}^{-1}$  tetramethylammonium chloride (15 ml). The separated crude product was filtered, washed with water and crystallized from acetone-methanol to give 1.2 g (70%) *Ih* as large needles.

Tetramethylammonium 7,8,9,10,11,12-Hexachloro-1-carba-*closo*-dodecaborate(1-) (*Ij*)

Free acid of the anion *I* prepared from its trimethylammonium salt (1.0 g; 4.9 mmol) as in the preceding experiment was dissolved in glacial acetic acid (25 ml). Chlorine was introduced into the solution at  $80^\circ\text{C}$  for c. 1 h. Further work up of the reaction mixture as in the preceding experiment resulted in the isolation of *Ij* (1.6 g; 77%).

Tetramethylammonium 7,8,9,10,11,12-Hexabromo-1-carba-*closo*-dodecaborate(1-) (*Ik*)

Free acid of the anion *I*, obtained from its trimethylammonium salt as in preceding experiments (1.0 g; 4.9 mmol), was dissolved in glacial acetic acid (25 ml) and bromine (10.0 g; 0.125 mol) was added dropwise to the solution which was heated at  $80^\circ\text{C}$  for 48 h. The acetic acid along with excess bromine were removed, the residue was dissolved in water (40 ml) and the residual bromine was removed by adding sodium sulphite. The solution was filtered, neutralized with 5% potassium hydroxide and precipitated with  $1 \text{ mol l}^{-1}$  tetramethylammonium chloride (15 ml). The crude product was sucked off, washed with water and crystallized from hot acetone to give 2.6 g (77%) of *Ik*.

12-Dimethyl Sulphide-1-carba-*closo*-dodecaborane(11) (*IIf*) and

12-(2,4-Dithiapentane)-1-carba-*closo*-dodecaborane(11) (*IIG*)

Free acid of the anion *I*, prepared from its trimethylammonium salt (2.0 g; 0.01 mol) as in the preceding experiment, was dissolved in acetonitrile (15 ml) and dimethyl sulphoxide (3.0 g; 0.038 mol) followed by concentrated sulphuric acid (1 ml, dropwise) were added to the solution. After the initial exothermic reaction had ceased, the mixture was heated at  $90-100^\circ\text{C}$  for 4 h. The acetonitrile was then removed *in vacuo* and the residue was treated with 10% potassium hydroxide (40 ml). The mixture was extracted with two 50 ml portions of benzene and the benzene layer was evaporated leaving a mixture of both *IIf* and *IIG*. The mixture was separated by chromatography on a column ( $2.5 \times 30 \text{ cm}$ ) of silica gel in benzene-hexane (1 : 3) and purity of the fractions was checked by TLC in benzene. Concentration of the combined fractions containing pure products caused separation of crystalline *IIf* (0.9 g; 44%) and *IIG* (0.5 g; 23%).

*Mass spectra were measured by Dr Z. Weidenhoffer, the  $pK_a$  values were determined by Mr M. Skalický, both of the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague. The IR spectra were recorded by Dr M. Vlček of the Institute of Chemical Technology, Pardubice. We wish to thank these colleagues for their kind assistance.*

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