

**PREPARATION OF 7-SUBSTITUTED 7-CARBA-*nido*-UNDECABORANES(12)**

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Reactivity of the ammine group in the 7-H<sub>3</sub>N-7-CB<sub>10</sub>H<sub>12</sub> carbaborane was examined and a series of new 7-L-7-CB<sub>10</sub>H<sub>12</sub> derivatives [L = (CH<sub>3</sub>)<sub>2</sub>C=NH, (CH<sub>2</sub>)<sub>5</sub>C=NH, C<sub>6</sub>H<sub>5</sub>CH=(C<sub>6</sub>H<sub>5</sub>.CH<sub>2</sub>)N, HOOCCH<sub>2</sub>NH<sub>2</sub>, CH<sub>3</sub>CONH<sub>2</sub>, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>, and (CH<sub>3</sub>)<sub>2</sub>S] was characterized. Constitution of all compounds isolated was established on the basis of their mass, IR, <sup>1</sup>H, and <sup>11</sup>B NMR spectra.

7-Ammine-7-carba-*nido*-undecaborane(12) (*I*), 7-H<sub>3</sub>N-7-CB<sub>10</sub>H<sub>12</sub> (Fig. 1), has been employed as an important starting material for obtaining a family of numerous metalloboranes<sup>1-4</sup> and other monocarbaborane compounds<sup>2,5-7</sup>. The species is relatively well available from decaborane(14) (ref.<sup>2</sup>), particularly after improving its preparation<sup>8</sup>. Its N-alkyl derivatives, obtained from decaborane(14) and corresponding alkyl isocyanide<sup>9</sup>, can be methylated to produce N,N-dimethyl-N-alkyl derivatives of *I*. Little attention has been paid so far to other chemical modifications and reactions of the 7-ammine group, the described reactions being restricted to methylation, giving N,N,N-trimethyl derivative<sup>2,5</sup>, and ethylation yielding the N,N-diethyl analogue<sup>10</sup>. In the present investigation we have examined the reactivity of the 7-H<sub>3</sub>N group with the intention of extending the chemistry of this family of compounds.

As we have found, the 7-H<sub>3</sub>N group in compound *I* undergoes reactions resembling those of aliphatic and aromatic amines. The observed reactions, shown in Scheme 1, can be divided into two types. The first type is represented by the reactions in which the nitrogen atom bonded to the CB<sub>10</sub>H<sub>12</sub> cage is retained. To this group belong the reactions of carbonyl compounds (acetone, cyclohexanone) yielding compounds *Ia,b*, while a more reactive benzaldehyde gives benzylimine *Iic*.

Treatment of compound *I* with chloroacetic acid, acetylation with acetanhydride and benzylation with benzoyl chloride result in the formation of the amino acid *III* and amides *IVa,b*, respectively. It is noteworthy that these reactions proceed with difficulties, requiring longer reaction time and elevated temperature.

Interesting is the two-step reaction of *I* with hexamethylenetetramine producing first the *Va* salt which, being dissolved in ethanol and acidified, splits off one hexa-

methylenetetramine nitrogen to incorporate the carborane-bonded nitrogen into the hexamethylenetetramine cage to give derivative *Vb*.

The second type of reactions are those in which the 7-H<sub>3</sub>N group is exchanged for another Lewis base. An attempt has been made to prepare the 7-HO derivative by treatment of *I* with nitrous acid, however, due to a high basicity of the 7-nitrogen, the  $\text{NH}_2 \rightleftharpoons \text{NH}_3^{+}$  equilibrium is shifted to the righthand side and the  $\text{NO}^{+}$  ion cannot react. Nevertheless, in the presence of dimethyl sulphide, the *VI* derivative is smoothly formed in fair yield with a large excess of nitrous acid.

<sup>11</sup>B NMR spectra of all compounds prepared (Table I) consist of 1 : 2 : 2 : 2 : 1 : 2 patterns of doublets corresponding to the B<sub>(5)</sub>, B<sub>(9,10)</sub>, B<sub>(2,3)</sub>, B<sub>(8,11)</sub>, B<sub>(1)</sub> and B<sub>(4,6)</sub> atoms, respectively, the B<sub>(9,10)</sub> and B<sub>(2,3)</sub> signals in compounds *IIa* and *IVb* being incidentally overlapped. The data correspond well to those of hitherto published<sup>2,5,9</sup> substituted species.

In agreement with the proposed structures are also the <sup>1</sup>H NMR spectra (for assignment see Table II) of all isolated derivatives. The spectra of compounds *IIa* and *IIb* exhibit two <sup>1</sup>H signals attributable to two nonequivalent CH<sub>3</sub> and CH<sub>2</sub> groups respectively attached to the N=C carbon. The <sup>1</sup>H NMR spectra of the *IVa* and *IVb* compounds also show the signals assignable to HO groups, as a probable consequence of the  $7\text{-RCNH}_2 \rightleftharpoons 7\text{-RC(OH)=NH}$  equilibrium.

The above discussed derivatives of the *nido*-7-L-7-CB<sub>10</sub>H<sub>12</sub> family of carbaboranes can serve as starting materials for preparing selected types of monocarbaboranes.

## EXPERIMENTAL

<sup>11</sup>B NMR spectra were recorded at 64.18 MHz in hexadeuterioacetone with a Varian XL-200 spectrometer and were externally referenced to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. <sup>1</sup>H NMR spectra were obtained at 60 MHz in hexadeuterioacetone on a Tesla BS-467 equipment and were internally referenced to tetramethylsilane. Chemical shifts are given in δ values, positive values downfield. Mass spectra were collected using a GC/MS HP-5989 device and the IR spectra were measured in Nujol mull on a Perkin-Elmer 684 spectrometer. Purity of individual products was monitored by TLC on Silufol (silica gel on aluminium foil, starch as binder, detection by I<sub>2</sub> vapours followed by

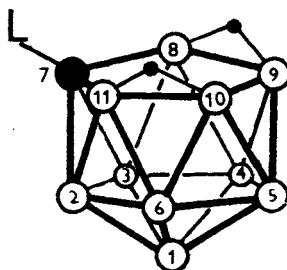
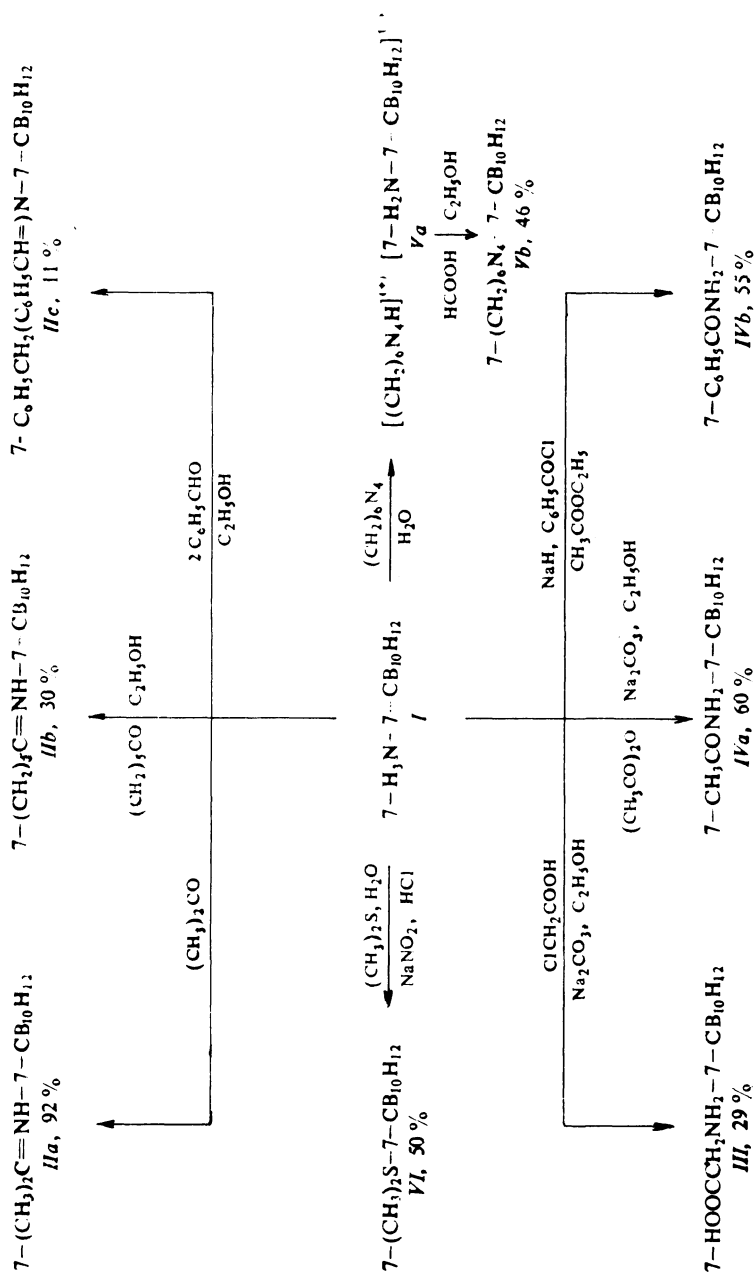


FIG. 1  
Structure of the 7-L-7-CB<sub>10</sub>H<sub>12</sub> derivatives



SCHEME 1

AgNO<sub>3</sub> spray; producer Kavalier, Votice, Czechoslovakia) in acetonitrile–chloroform (1 : 3). Melting points were determined in sealed capillaries and are uncorrected. Solvents for spectral measurements were spectral grade, other solvents and chemicals were reagent grade. Starting 7-H<sub>3</sub>N-7-CB<sub>10</sub>H<sub>12</sub> was prepared according to the previously described<sup>8</sup> method. Properties of all isolated compounds are summarized in Tables I–III.

7-N-2-Propylideneamine-7-carba-*nido*-undecaborane(12) (*I**a*)

A solution of compound *I* (4.5 g; 0.03 mol) in acetone (30 ml) was refluxed for 24 h and after cooling down to room temperature, water (100 ml) was added and the acetone was stripped off *in vacuo*. The separated pale yellow compound was filtered, washed with water and recrystallized from methanol–water to isolate 5.3 g (92%) of compound *I**a*.

TABLE I  
Assignment of the <sup>11</sup>B NMR signals of the 7-L-7-CN<sub>10</sub>H<sub>12</sub> derivatives

Compound	B <sub>(5)</sub>	B <sub>(9,10)</sub>	B <sub>(2,3)</sub>	B <sub>(8,11)</sub>	B <sub>(1)</sub>	B <sub>(4,6)</sub>
<i>I</i>	−1.51 <sup>a</sup> (131) <sup>b</sup>	−9.48 (154)	−11.83 (141)	−22.71 (128)	−26.06 (146)	−32.85 (143)
<i>I</i> <i>a</i>	−0.66 (148)	−9.78 (153)	−10.77 (147)	−22.10 (143)	−25.80 (142)	−32.45 (144)
<i>I</i> <i>b</i>	−0.77 (142)	−10.21 (149)	−10.21	−22.07 (144)	−25.58 (144)	−32.33 (144)
<i>I</i> <i>c</i>	−0.23 (125)	−10.60 (144)	−12.13 (123)	−22.79 (140)	−25.53 (144)	−32.23 (144)
<i>III</i>	0.24 (130)	−9.64 (164)	−12.87 (132)	−22.35 (138)	−25.91 (147)	−32.85 (146)
<i>IV</i> <i>a</i>	−3.43 (141)	−10.20 (140)	−10.20	−23.51 (147)	−26.91 (135)	−32.88 (139)
<i>IV</i> <i>b</i>	−1.29 (134)	−9.92 (151)	−10.61 (142)	−22.59 (141)	−26.17 (142)	−32.80 (142)
<i>V</i> <i>a</i>	−0.72 (140)	−9.82 (161)	−10.88 (142)	−22.22 (142)	−25.91 (142)	−32.57 (146)
<i>V</i> <i>b</i>	1.44 (138)	−11.79 (164)	−14.80 (136)	−22.33 (145)	−26.56 (147)	−33.10 (138)
<i>VI</i>	2.81 (142)	−9.21 (154)	−12.71 (122)	−20.57 (146)	−24.93 (146)	−31.41 (147)

<sup>a</sup> δ<sub>B</sub> in ppm relative to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>; <sup>b</sup> J<sub>11B-1H</sub> in Hz.

7-N-Cyclohexylideneamine-7-carba-*nido*-undecaborane(12) (*I*b)

A solution of compound *I* (1.5 g; 0.01 mol) and cyclohexanone (5.0 g; 0.055 mol) in ethanol (30 ml) was refluxed for 24 h. The ethanol was then removed *in vacuo* and the excess cyclohexanone was distilled off with steam. The separated pasty product was digested with ether (40 ml), filtered, and dried at 25°C/1.3 Pa to give 0.7 g (30%) of *I*b as white crystals.

7-N-Benzal-N-benzylamine-7-carba-*nido*-undecaborane(12) (*I*c)

A mixture of compound *I* (1.5 g; 0.01 mol), benzaldehyde (10.0 g; 0.1 mol) and ethanol (30 ml) was refluxed for 24 h. The ethanol was removed *in vacuo* and the excess benzaldehyde was steam-distilled. The remaining material was shaken with ether (30 ml) to separate crystals which were filtered and dried at 25°C/1.3 Pa to obtain 0.4 g (11%) of compound *I*c.

N-(7-Carba-*nido*-7-undecaboranyl)aminoacetic Acid (*III*)

Sodium carbonate (2.5 g; 0.025 mol) was added to a solution of compound *I* (1.5 g; 0.01 mol) and chloroacetic acid (1.1 g; 0.01 mol) in ethanol (20 ml) and the mixture was heated for 48 h (water bath). The residue leaving after removing the ethanol *in vacuo* was dissolved in diluted (1 : 3) hydrochloric acid (30 ml), the solution was filtered and the filtrate was extracted with two 20 ml portions of ether. The organic extracts were stripped off and the obtained crude product was chromatographed on a column (2.5 × 30 cm) of silica gel in ethyl acetate–chloroform (1 : 1) to obtain 0.6 g (29%) of compound *III* on evaporating the combined fractions of  $R_F$  0.19 (TLC in acetonitrile–chloroform (1 : 3)).

TABLE II  
Properties of the 7-L-7-CB<sub>10</sub>H<sub>12</sub> derivatives

Compound	$R_F$	$m/z$	M.p., °C	$\delta^1\text{H NMR}$			
				NH group		other	
<i>I</i>	0.22	151	280	8.82	—	—	—
<i>IIa</i>	0.60	191	223	7.37	2.65 <sup>a</sup>	2.56 <sup>a</sup>	—
<i>IIb</i>	0.69	231	250	8.06	2.91 <sup>b</sup>	2.80 <sup>b</sup>	1.90 <sup>b</sup>
<i>IIc</i>	0.83	329	264	—	7.84 <sup>c</sup>	4.56 <sup>d</sup>	—
<i>III</i>	0.19	—	280	8.21	3.71 <sup>d</sup>	—	—
<i>IVa</i>	0.10	193	231	7.87	1.95 <sup>e</sup>	5.34 <sup>f</sup>	—
<i>IVb</i>	0.18	255	197	12.30	10.68 <sup>f</sup>	7.73 <sup>c</sup>	—
<i>Va</i>	0.22	—	—	—	4.67 <sup>d</sup>	—	—
<i>Vb</i>	0.33	274	192	—	5.22 <sup>g</sup>	4.71 <sup>g</sup>	—
<i>VI</i>	0.32	196	164 <sup>h</sup>	—	3.03 <sup>e</sup>	—	—

<sup>a</sup> 2-Propylidene CH<sub>3</sub> groups; <sup>b</sup> triplet of the cyclohexylidene CH<sub>2</sub> groups; <sup>c</sup> multiplet of the phenyl group; <sup>d</sup> singlet of the CH<sub>2</sub> group; <sup>e</sup> singlet of the CH<sub>3</sub> group; <sup>f</sup> singlet of the HO group; <sup>g</sup> doublet of the hexamethylenetetramine CH<sub>2</sub> groups; <sup>h</sup> decomposition.

7-Acetamide-7-carba-*nido*-undecaborane(12) (*IVa*)

The mixture of a solution of compound *I* (4.5 g; 0.03 mol) in ethanol (30 ml), acethanhydride (10.8 g; 0.011 mol), and sodium carbonate (3.2 g; 0.03 mol) was heated for 24 h on a water bath. The ethanol was evaporated *in vacuo* and the remaining residue was decomposed by refluxing with water (100 ml) for 3 h. The solution was then neutralized with 10% NaOH and extracted with two 30 ml portions of ether. The organic layer was evaporated *in vacuo* and the residue was dissolved in water (50 ml) and evaporated. The semisolid residue was dried at 90°C/1.3 Pa to give 3.5 g (60%) of compound *IVa*.

7-Benzamide-7-carba-*nido*-undecaborane(12) (*IVb*)

A solution of compound *I* (1.5 g; 0.01 mol) and benzoyl chloride (2.8 g; 0.02 mol) in ethyl acetate (20 ml) was refluxed with sodium hydride (0.3 g; 0.013 mol) for 48 h. The ethyl acetate was then removed *in vacuo* with water (*c.* 1 ml) and the mixture was acidified with diluted (1 : 3) hydrochloric acid. The solution was then extracted with ether (2 × 20 ml) and the organic layer was stripped off *in vacuo* leaving a residue which was dissolved in water (*c.* 30 ml). After shaking with two 30 ml portions of benzene the water phase was filtered with active charcoal, evaporated, and dried at 90°C/1.3 Pa to obtain 1.4 g (55%) of compound *IVb*.

TABLE III

Assignment of some IR absorption bands ( $\text{cm}^{-1}$ ) of the 7-L-7-CB<sub>10</sub>H<sub>12</sub> compounds

<i>Ia</i>	<i>Ib</i>	<i>Ic</i>	<i>III</i>	<i>IVa</i>	<i>IVb</i>	<i>VI</i>	Assignment
--	--	--	3 620	--	--	--	$\nu(\text{O}-\text{H})$
--	--	--	3 580	3 595	3 490	--	$\nu_{\text{sym}}(\text{NH}_2)$
3 270	3 265	3 220	--	--	--	--	$\nu(\text{N}-\text{H})$
--	--	--	3 400	3 405	3 360	--	$\nu_{\text{asym}}(\text{NH}_2)$
2 560	2 550	2 560	2 555	2 545	2 550	2 550	$\nu(\text{B}-\text{H})$
2 505	2 520	2 500	--	--	--	--	$\nu(\text{B}-\text{H})$
--	--	--	1 735	1 650	1 640	--	$\nu(\text{C}=\text{O})$
1 670	1 655	1 660	--	--	--	--	$\nu(\text{C}=\text{N})$
--	--	--	--	1 530	1 525	--	$\delta(\text{NH}_2)$
--	--	1 490	--	--	1 480	--	$\nu(\text{C}-\text{C})$
--	--	--	--	--	--	1 425	$\delta_{\text{asym}}(\text{CH}_3)$ scissoring
--	--	--	--	--	--	1 420	$\delta(\text{CH}_2)$
--	--	--	--	--	--	1 407	$\delta_{\text{sym}}(\text{CH}_3\text{S})$
1 300	1 305	1 305	1 300	1 295	1 300	--	$\nu(\text{C}-\text{N})$
--	--	--	1 255	--	--	--	$\delta(\text{C}-\text{O}-\text{H})$
--	--	--	1 155	--	--	--	$\nu(\text{C}-\text{O})$
--	--	1 040	--	--	1 040	--	$\delta(\text{C}-\text{H})_{\text{arom}}$
--	--	--	--	760	760	--	torsion ( $\text{NH}_2$ )
--	--	700	--	--	695	--	$\delta(\text{C}-\text{H})_{\text{arom}}$
--	--	--	--	--	--	262	$\delta(\text{C}-\text{S}-\text{C})$

7-Hexamethylenetetramine-7-carba-*nido*-undecaborane(12) (*Vb*)

To an aqueous solution (40 ml) of compound *I* (3.0 g; 0.02 mol) a solution of hexamethylenetetramine (3.0 g; 0.025 mol) in water (40 ml) was added to separate a voluminous precipitate of compound *Va*, which was dissolved by adding sufficient amount of ethanol. The solution was filtered, acidified with concentrated formic acid (2 ml) and carefully heated to separate tiny crystals which were filtered off, washed with two 20 ml portions of cold ethanol and dried at 25°C/1.3 Pa to isolate 2.5 g (46%) of compound *Vb*.

7-Dimethyl Sulphide-7-carba-*nido*-undecaborane(12) (*VI*)

Dimethyl sulphide (20 ml) was added to a solution of compound *I* (3.5 g; 0.024 mol) in diluted (1 : 5) hydrochloric acid (45 ml). The mixture was cooled down to 0°C and a solution (10 ml) containing NaNO<sub>2</sub> (5 g; 0.08 mol) was added dropwise under stirring and cooling to 0°C. The mixture developed an intensive red colour under gas evolution and the reaction was continued until the dimethyl sulphide phase decolorized. Ethanol (30 ml) was added and the organic volatiles were removed *in vacuo*. The solid separated was filtered, washed with two 30 ml portions of 2% Na<sub>2</sub>CO<sub>3</sub> and dried at 25°C/1.3 Pa. The crude product was crystallized from hot benzene to give 2.3 g (50%) of compound *VI*.

*Mass spectra were recorded by Dr Z. Weidenhoffer and the <sup>1</sup>H NMR spectra were measured by Dr F. Mareš, all of the Institute of Inorganic Chemistry, Prague. IR spectra were collected by Dr M. Vlček, Pardubice Institute of Chemical Technology. All these colleagues are thanked for their kind assistance.*

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