

## CHEMISTRY OF BORANES. XXVII.\*

LEWIS ACIDITY OF SOME SUBSTITUTED  
1,2-DICARBA-CLOSO-DODECABORANES\*\*

J. PLEŠEK, T. HANSLÍK, F. HANOUSEK and S. HEŘMÁNEK

*Institute of Inorganic Syntheses,  
Czechoslovak Academy of Sciences, Prague - Řež*

Received December 6th, 1971

Bromine-substituted 1,2-dicarba-closo-dodecaboranes behave as Lewis acids and with pyridine form compounds to which we assign the structure of 3,6-dipyridine-1,2-dicarba-closo-dodecaboranes, isoelectronic with the  $C_2B_{10}H_{12}^{2-}$  dianion. In unsubstituted 1,2-dicarba-closo-dodecaborane no reaction with Lewis bases has been observed.

The distribution of electronic density in 1,2-dicarba-closo-dodecaborane (*I*) is known from the calculations<sup>1</sup> and from experimental data<sup>2</sup>. The electronic density grows in the following order (sequence) of positions:  $1 < 3 < 4 < 8 < 9$ . This has as a consequence not only a weak C-acidity of compound *I*, but also easy solvolysis, affording 7,8-dicarba-nido-undecaborate anion  $C_2B_9H_{12}^{--}(II)$  which is formed by splitting off of the most positive boron atom in the position<sup>3</sup> 3(6). Solvolysis takes place under the effect of alkali hydroxides in alcoholic solution<sup>3</sup>, or piperidine<sup>4</sup>, or also other bases with a hydrogen on the donor atom<sup>5</sup>. As the solvolysis takes place under the effect of basic reagents, it is probable that the nucleophilic reagent attacks primarily the most positive boron atom in the position 3(6), and after this change the originally stable skeleton undergoes solvolysis<sup>3</sup>. However, up to the present time this primary attack could not be demonstrated; still less the isolation of some compound which would be related to the expected intermediate by its structure. Recently it was observed<sup>6</sup> that C,C-dihalo derivatives of compound *I* undergo an analogous solvolysis under the effect of methanol alone, at room temperature. We met a similar effect during the study of some isomeric C,B- and even B,B-dibromo derivatives of compound *I*. The activating effect of halogen atoms is attributed to the inductive effect and further decrease in electron density in the position 3(6) due to it. The distinct inductive effect of bromine atoms on the skeleton of type *I* is known from the study of dipole moments in this series<sup>6-8</sup>. It was found that the bromine atom in position 1 decreases the dipole moment of compound *I* appreciably, but in contrast to this, that in position 9-substantially increases<sup>6-8</sup>.

We decided to study the behaviour of bromo derivatives of compound *I* in the presence of Lewis bases which do not have any hydrogen atom on the donor atom, expecting that it would be possible to catch their adducts with the activated derivat-

\* Part XXVI: This Journal 37, 3001 (1972).

\*\* The content of this paper was presented as a short communication at the International Conference on the Chemistry of Boron Compounds "Imeboron" in Liblice 21st to 26th June, Czechoslovakia, 1971.

ives of compound *I*, acting as Lewis acids. The following bromocarboranes were investigated: 1-Bromo-1,2-dicarba-closo-dodecaborane (*Ia*), 9,12-dibromo-1,2-dicarba-closo-dodecaborane (*Ib*), and 8,9,12-tribromo-1,2-dicarba-closo-dodecaborane (*Ic*). The following bases were used: Hexamethylenetetramine (*III*), pyridine (*IV*), triphenylphosphine (*V*), triethylamine (*VI*), acetonitrile (*VII*), and dimethylsulfide (*VIII*). Qualitative results of positive interactions are given in Table I.

The reactivity of compounds *Ia-c*, when judged according to their willingness to add Lewis bases, decreases in the following order: *Ic* > *Ia* > *Ib*. The reactivity of bases decreases as follows: *III* > *IV* > *V* > *VI* > *VII* = *VIII*. The last two bases did not react with any carborane from the series *Ia-c*. In contrast to this, base *III* gave crystalline adducts with all three compounds, but also with 9-bromo-1,2-dicarba-closo-dodecaborane (*IX*) and 1,2-dimethoxycarbonyl-1,2-dicarba-closo-dodecaborane (*X*), with which other bases did not react. However, unsubstituted compound *I* does not display any trace of Lewis acidity even with a base of such reactivity as hexamethylenetetramine.

However, all adducts obtained evidently do not belong to the same type. Thus, for example, compound *X/III* is of 1 : 1 type, while all pyridine adducts contained one mol of carborane derivative per two mol of base. Equally, in the IR spectra appreciable differences were observed between the adducts of base *III* and those of pyridine. As the pyridine adducts are well accessible in pure state, they were studied in detail preferentially. The adducts *Ia-c/IV* are not simple solvates formed by weak interaction of the components. During thin-layer chromatography they move as individual compounds, different from the starting compounds and are stable up to 50°C approximately toward methanol, aqueous acetone, dilute methanolic sodium hydroxide or hydrochloric acid. Under such conditions parent carboranes would undergo solvolysis. In contrast to this, on heating above 100°C *in vacuo* adducts *Ia-c/IV* decompose to their components. This was proved by a practically quantitative regeneration of compound *Ia* from the corresponding adduct *Ia/IV* and the thermogram of the adduct *Ib/IV* (Fig. 1). Thermography showed that the

TABLE I  
Review of the Reactions of Lewis Bases *III-VI* with Carboranes *Ia-c*

Substituents	<i>Ia</i>	<i>Ib</i>	<i>Ic</i>
(CH <sub>2</sub> ) <sub>6</sub> N <sub>4</sub> ( <i>III</i> )	140 <sup>a</sup>	165 <sup>a</sup>	130-132 <sup>a</sup>
C <sub>5</sub> H <sub>5</sub> N ( <i>IV</i> )	135-137 <sup>b</sup>	151-152 <sup>b</sup>	122-123 <sup>b</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P ( <i>V</i> )	225 <sup>a</sup>	<sup>c</sup>	<sup>d</sup>
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N ( <i>VI</i> )	<sup>d</sup>	<sup>c</sup>	<sup>d</sup>

<sup>a</sup> Decomposition point in °C; <sup>b</sup> m.p. in °C; <sup>c</sup> do not react, <sup>d</sup> reaction takes place, no defined product was obtained.

splitting off of both pyridine molecules probably takes place gradually, but the difference between the two steps is so small that it was impossible to obtain the adduct of the 1 : 1 composition preparatively.

Very important information was supplied by IR spectrography. The group of B—H stretching vibration bands gives in the case of carboranes *Ia-c* a quite compact contour with the center near to  $2600\text{ cm}^{-1}$ . In adducts *Ia-c/IV* these bands are shifted to higher wave lengths and are both more distinctly split and also display a very distinct anomalous band in the region of about  $2420\text{ cm}^{-1}$  (Fig. 2). This anomalous band may be assigned to the stretching vibration of the B—H bond, the force constant of which is diminished under the effect of the dative bond of the corresponding boron atom with the nitrogen atom of pyridine. The distance of this band from the center of the main bands at  $2500\text{ cm}^{-1}$  should be proportional to the strength of the dative bond B—N, and thus also to the Lewis acidity of parent carboranes. This acidity increases in the following order:  $Ib < Ia < Ic$ . The dative character of the B—N bonds in the adducts *Ia-c/IV* is also corroborated by the  $1430-1630\text{ cm}^{-1}$  region in which four bands are present due to vibrations of the pyridine ligand. The shift of these bands is typical of pyridine bound datively to the boron atom<sup>9</sup> (Table II).

All the facts indicate that adducts *Ia-c/IV* possess the structure of 3,6-dipyridine-1,2-dicarba-closo-dodecaboranes according to Fig. 3. Of course, the hydrogen atom drawn and the ligand *I* may be interchanged on the same boron atom. In an extreme case (when the electrons of the dative bond are shared symmetrically) they would be isoelectronic with the known dianion<sup>10,11</sup>  $\text{C}_2\text{B}_{10}\text{H}_{12}^{2-}$ , the structure of which, however, is still unknown. Definitive corroboration or rejection of this structure may be expected from the results of X-ray diffraction of a monocrystal, which is presently under investigation in another laboratory<sup>12</sup>.

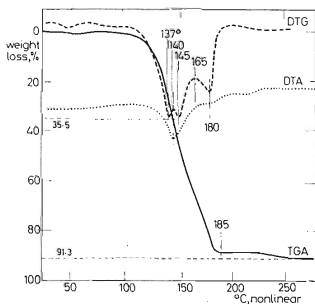


FIG. 1  
Thermogram of Compound *Ib/IV*  
Curves TGA ———, DTG ———, and  
DTA .....

## EXPERIMENTAL

Carboranes *Ia-c* and *IX* were prepared in the conventional manner according to literature. Thin-layer chromatography was carried out on Silufol in tetrachloromethane in the case of free carboranes, and in dichloromethane in the case of their adducts with Lewis bases. The substances were detected with iodine vapours or with silver nitrate<sup>13</sup>. IR spectra were measured on a Zeiss, Jena, UR-10 apparatus and the UV spectra on a Beckman DK 1 spectrophotometer. The thermogram was obtained with a Derivatograph MOM, Hungary. Melting points were determined in sealed capillaries and they are not corrected.

#### Attempts at the Preparation of the Adducts of Substituted Carboranes *Ia-c* with Bases *VI-VIII*

A solution of 0.01 mol of compounds *Ia-c* in 20 ml of base *VI-VII* was allowed to stand for one week, occasionally analysed by thin-layer chromatography for the content of the starting material or a possible product. In the case of bases *VII* and *VIII* in no cases was the formation of an adduct observed (not even by chromatography) and the starting carboranes were isolated unchanged by evaporation of the solvent and vacuum sublimation (*Ia*) or by crystallization from a mixture of chloroform and hexane 1 : 1 (*Ib* and *Ic*). With base *VI* a reaction was observed only with compounds *Ia* and *Ic* which became evident on the basis of distinct spots on the start. However, even after one week's standing the presence of an appreciable amount of *Ia* in the reaction mixture could be observed. Substance *Ic* already disappeared after two days. On evaporation of the excess base in a vacuum an oily residue was obtained in both cases, which was insoluble in hexane, but well soluble in chloroform. It was impossible to isolate from it any well defined substance.

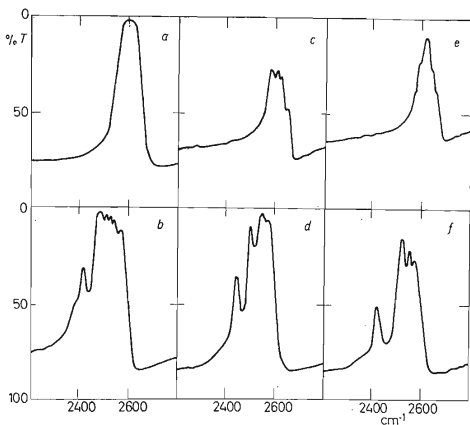


FIG. 2

IR Spectra in the 2220–2800  $\text{cm}^{-1}$  Region (KBr pellet)

*a* = *Ia*; *b* = *Ia/IV*; *c* = *Ib*; *d* = *Ib/IV*; *e* = *Ic*; *f* = *Ic/IV*.

TABLE II

Absorption Bands of Pyridine and Some of its Lewis Adducts with *Ia-c* and  $BX_3$  in the IR Spectrum in the  $1430-1630\text{ cm}^{-1}$  Region

Compound	Absorption band			
<i>IV</i>	1 439	1 482	1 572	1 580
<i>Ia/IV</i>	1 459—	1 486—	1 569—	1 615—
<i>Ib/IV</i>	1 463	1 491	1 577	1 623
<i>Ic/IV</i>	1 462	1 492	—	1 622
$C_5H_5N.BX_3^{\circ}$	1 459	1 488	1 580	1 624
(X = H, Cl, Br)	1 493	1 493	1 610	1 630

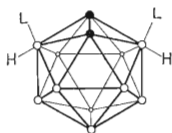


FIG. 3  
Scheme of the Structure of the Adducts

#### Attempts at the Reaction of Compounds *Ia-c* with Triphenylphosphine (*V*)

A solution of compound *Ia* (2.25 g; 0.01 mol) and triphenylphosphine (5.75 g; 0.025 mol) in chloroform (30 ml) was allowed to stand for 3 days. Already after 4 h the presence of a new compound could be detected by thin-layer chromatography in tetrachloromethane which remained on the start; after three days the spot of *Ia* disappeared and a solid substance separated out. The solution was covered with a layer of hexane (30 ml) and allowed to stand overnight. A mixture of crystals and a yellow oil were formed. The crystals were filtered off and recrystallized twice more in the same manner. Yield 2.1 g (32.3%) of adduct *Ia/V* which decomposed at  $225^{\circ}\text{C}$  without previous melting. For  $C_{22}B_{10}H_{11}Br_2(C_6H_5)_3P$  (747.8) calculated: 10.69% Br; found: 11.18% Br. In thin-layer chromatography with dichloromethane its moving rate is 234 if the moving rate of the adduct *Ia/IV* is taken as 100. In the IR spectrum no splitting of the band of terminal B—H vibrations at about  $2600\text{ cm}^{-1}$  was observed. Under the same conditions compound *Ib* was regenerated unchanged. After three days standing of the reaction mixture the presence of a new substance could not be detected even by thin-layer chromatography. Compound *Ic* reacted completely even after one day, but the adduct was oily and nothing definite could be isolated from it.

#### Reactions of Substituted Carboranes with Hexamethylenetetramine (*III*)

To a solution of 0.005 mol of carborane derivative in 20 ml of chloroform substance *III* (2.0 g; 0.11 mol) dissolved in 40 ml of chloroform was added and the mixture allowed to stand at room temperature for one week. The separated crystals were filtered off under suction and washed three times with 10 ml of chloroform in order to wash out the starting components. The melting

or decomposition points of the adducts are listed in Table I. Only the adduct *X/III* has been analysed, m.p. 158–160°C. For  $C_2B_{10}H_{10}(COOCH_3)_2 \cdot N_4(CH_2)_6$  (424.6) calculated: 25.52% B, 13.20% N; found: 25.32% B, 13.55% N. Compound *X/III* is mentioned in the literature<sup>5</sup>; however, there it is considered as an adduct containing 2 mol of hexamethylenetetramine and its structure is not considered at all. Under the same conditions an adduct of compound *IX* was also formed, decomposing at 163–165°C; however, no adduct with the unsubstituted compound *I* was formed even after 2 months standing.

#### Adducts of Carboranes *Ia–c* with Pyridine

Carboranes *Ia–c* (0.02 mol) were dissolved in pyridine (30 ml) and allowed to stand overnight. In the case of substance *Ia* and *Ic* the temperature of the mixture was raised spontaneously up to 60°C. The next day the presence of the free starting carborane in the reaction mixture could in no case be proved by thin-layer chromatography. Hexane (100 ml) was added to the mixture and excess pyridine was extracted from the insoluble adduct by repeated extraction in a vacuum extractor at room temperature. The insoluble residue was extracted with dichloromethane in which the adducts were very weakly soluble. The products were recrystallized from boiling acetone, containing 5% of water. This operation is very lengthy because the adducts are generally poorly soluble. After filtration with suction they were dried at 50°C and  $10^{-2}$  Torr for 4 h; yield about 80%. Relative moving rate in thin-layer chromatography on Silufol, using dichloromethane as solvent, was:  $Ia/IV = 100$ ,  $Ib/IV = 45$ ,  $Ic/IV = 33$ . Adduct *Ia/IV*, m.p. 135–137°C. For  $C_2B_{10}H_{11}Br \cdot 2 C_5H_5N$  (381.4) calculated: 28.45% B, 20.94% Br, 7.35% N; found: 28.46% B, 19.82% Br, 6.82% N. Adduct *Ib/IV*, m.p. 151–152°C. For  $C_2B_{10}H_{10}Br_2 \cdot 2 C_5H_5N$  (460.3) calculated: 23.55% B, 34.68% Br, 6.09% N; found: 23.34% B, 33.79% Br, 5.94% N. Adduct *Ic/IV*, m.p. 122–123°C. For  $C_2B_{10}H_9Br_3 \cdot 2 C_5H_5N$  (539.3) calculated: 20.10% B, 44.50% Br, 5.22% N; found: 18.74% B, 40.88% Br, 4.61% N. This analysis is not satisfactory, the substance was only about 93% pure, but the ratio of B : Br : N was 10.01 : 3.00 : 1.93, which is in good agreement with the expected value.

*Stability of the adducts:* A suspension of 0.5 of adduct *Ia/IV* in 50 ml of methanol containing either 2.0 g NaOH or 10 ml of conc. HCl was heated at 50°C for 3 h. The mixture was then cooled, diluted with 50 ml of water, and the product was filtered off under suction, washed with 10 ml of water, methanol and ether, and dried *in vacuo* ( $10^{-2}$  Torr) at 50°C for 3 h. In both cases only about 0.45 g of unchanged and chromatographically pure starting adduct were isolated. From the suspension of 1.0 g of adduct *Ib/IV* in 50 ml of methanol and 10 ml of conc. HCl the starting adduct could be isolated unchanged and practically quantitatively even after two months standing at room temperature.

*Regeneration of carborane Ia from adduct Ia/IV:* Adduct *Ia/IV* (3.8 g; 0.01 mol) was heated (water in the condenser was 12°C) at  $10^{-2}$  Torr and 110°C until all substance sublimed off (approx. 3 h). The sublimate in the condenser was rinsed with 5 ml of pentane. According to thin-layer chromatography the solution obtained contained only pure compound *Ia*. After evaporation of pentane in a vacuum the product was resublimed at  $10^{-2}$  Torr and 45°C. Yield 2.1 g (94.6%) of compound *Ia*, m.p. 180°C.

#### Solvolysis of Carboranes *Ib* and *Ic*

A suspension of *Ib* or *Ic* (0.01 mol) in 50 ml of methanol was stirred at room temperature. The starting substances dissolved gradually under liberation of a gas. Every 5 min the mixture was neutralized by addition of 3% NaOH in methanol. The reaction lasted for 10 hours in the case

of substance *Ib*, and 2 h in the case of *Ic*. As soon as the liberation of gas ceased and the mixture did not contain any starting material the mixture was diluted with 100 ml of water, methanol was evaporated *in vacuo* and on the addition of one equivalent of  $\text{Cs}_2\text{SO}_4$ , cesium salt was precipitated. The latter was crystallized from hot water and dried at  $50^\circ\text{C}$  and  $10^{-2}$  Torr for 4 hours. In both cases the yield was 90%. For  $\text{C}_2\text{B}_9\text{H}_{10}\text{Br}_2\text{Cs}$  (414.1) calculated: 23.50% B, 38.59% Br, 32.08% Cs; found: 22.30% B, 37.95% Br, 29.14% Cs. For  $\text{C}_2\text{B}_9\text{H}_9\text{Br}_3\text{Cs}$  (493.0) calculated: 19.71% B, 48.55% Br, 26.92% Cs, found: 19.21% B, 47.01% Br, 26.87% Cs.

## REFERENCES

1. Potenza J. A., Lipscomb W. N.: *J. Inorg. Chem.* 3, 1673 (1964).
2. Potenza J. A., Lipscomb W. N., Vickers G. D., Schroeder H. A.: *J. Am. Chem. Soc.* 88, 628 (1966).
3. Wiesboeck R. A., Hawthorne M. F.: *J. Am. Chem. Soc.* 86, 1642 (1964).
4. Zakharkin L. I., Kalinin V. N.: *Tetrahedron Letters* 1965, 407.
5. Grafstein D., Bobinski J., Dvorak J., Smith H. F., Schwartz N. N., Cohen M. S., Fein M. M.: *J. Inorg. Chem.* 2, 1120 (1963).
6. Stanko V. I., Anorova G. A., Klimova T. P.: *Ž. Obšč. Chim.* 39, 1073 (1969).
7. Maruca R., Schroeder H. A., Laubengayer A. N.: *J. Inorg. Chem.* 6, 572 (1967).
8. Jehlička V., Gregor V., Stuchlík J.: *This Journal*, in press.
9. Katritzky A. R.: *J. Chem. Soc.* 1959, 2049.
10. Grafstein D., Dvorak J.: *J. Inorg. Chem.* 2, 1128 (1963).
11. Zakharkin L. I., Kalinin V. N., Podvisotskaja L. S.: *Izv. Akad. Nauk SSSR, Ser. Chim.* 1966, 1495.
12. Beall H.: *Thesis*. Worcester Institute of Technology, Mass, USA.
13. Plešek J., Gregor V., Heřmánek S.: *This Journal*, in press.

Translated by Ž. Procházka.