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SPECIFIC CARBORANE-12 ISOMERIZATION THROUGH DIANIONS

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Summary

The behaviour of the dianions from *o*-, *m*- and *p*-carboranes and of their *C*-methyl derivatives was studied by means of ^{11}B NMR spectroscopy. The specificity of carborane "redox" isomerization through the dianions is discussed.

One of the most interesting features of the $C_2B_nH_{n+2}$ series is the mutual isomerization of their polyhedral structures. The most extensively studied structural conversion is that through the dianions formed on addition of two electrons to molecules of *o*-, *m*- or *p*-carboranes-12. Such conversions have been accounted for in different ways [1—5].

The first to describe theoretically the isomerization mechanism of these carboranes was Lipscomb et al. [6, 7] whereas Fein et al. [8] showed from a study of the interaction of sodium and lithium with isopropyl- and isopropenylcarboranes in liquid ammonia, that the *o*-carborane molecule could add two alkali metal equivalents. Grafstein and Dvorak [9] treated the dianion from *m*-carborane with hydrochloric acid and isolated *o*-carborane in a 16% yield. Later Zakharkin et al. [3, 4] reported that the oxidation of the dianions from *o*- and *m*-carboranes resulted in *o*-carborane only and suggested that the dianion from *m*-carborane underwent spontaneous isomerization to an *ortho*-dianion, oxidation of which involved only the removal of two electrons.

We have reported that oxidation of the dianion from *p*-carborane gives *m*-carborane rather then *o*-carborane [1, 2]. It was then shown [10] that the dianions prepared from *B*- and *C*-halogeno derivatives of *o*-, *m*- and *p*-carboranes gave unsubstituted carboranes with unchanged structures at rates dependent on the nature of the solvent and the reaction conditions. The resulting carborane is capable of adding two more alkali metal equivalents. Thus, 2-chloro-*p*-carborane in THF and ammonia with excess sodium leads to a dianion whose ^{11}B NMR spectrum is identical to that of the unsubstituted *p*-carborane. Oxidation of the dianions from 2-halogen-*p*-carboranes gives a mixture of all possible *B*-halogen isomers of *m*-carboranes together with *m*- and *p*-carboranes, whereas the dianions from 9-halogeno-*m*-carborane give rise essentially to 10-halogeno-and 3-amino-*o*-carboranes together with *o*- and *m*-carborane [10]. "Redox" isomerization of 1-halogenomethyl-*o*-carboranes results in the formation of 1-methyl-*m*-carborane [11], as well as 1-methyl-*o*-carborane and *o*-carborane resulting from the cleavage of the C—C bond. Under these conditions, isomerization of 1-chloro-(bromo)-12-methyl-*p*-carborane and 1-iodo-*p*-carborane is rather specific [12, 13]. Oxidation of the dianions obtained from the above compounds and sodium in liquid ammonia leads to a mixture of *ortho*- and *meta*-carboranes in a practically quantitative yield. If these dianions are, however, kept for some time in liquid ammonia without oxidation they result in the unrearranged carboranes, 1-methyl-*p*-carborane and *p*-carborane, respectively.

$$p\text{-RCB}_{10}\text{H}_{10}\text{C—X} + 2e \rightarrow [\text{RCB}_{10}\text{H}_{10}\text{C—X}]^{2-} \xrightarrow{\text{NH}_3} p\text{-RCB}_{10}\text{H}_{10}\text{CH} + \text{X}^- + \text{NH}_2^-$$

$(R = H, CH_3;\ X = Cl, Br, I)$

Of interest is also the fact that the three carborane isomers are formed in different ratios on separate oxidations of the cobalt and nickel complexes of the dianions from *o*-, *m*- and *p*-carboranes [14, 15]. From the complexes from *o*-carborane, the yield of carborane isomers is 80 to 85%. The yield of *o*-, *m*- and *p*-carboranes from complexes of the dianions of *m*- and *p*-carboranes with an excess of oxidant does not exceed 25-30%. Such a difference in the overall yields of the carborane might be due to parallel oxidation reactions of complex fragmentation leading to a number of structures unstable to the oxidants. If the dianions from *m*- and *p*-carboranes had not quantitavively formed complexes, the oxidation products of the reaction mixture in THF would have involved only carboranes rather then destruction products.

The interaction of sodium in liquid ammonia with bis(*o*-carboranyl)- and bis(*p*-carboranyl)-mercury followed by oxidation gives rise to *o*- and *m*-carboranes, respectively. The mercury atom does not therefore seem to affect the change in the carborane structure. It might be presumed that the formation of the dianions is accompanied by solvolysis of bis(carboranyl)mercury. This process does take place, but it proceeds in liquid ammonia rather slowly to leave in the reaction mass a considerable amount of bis(carboranyl)mercury even after the oxidation of dianions. The bis(carboranyl)mercury is decomposed by KOH in ethanol solution to mercuric oxide and a single isomerised carborane, (*o* → *o* and *p* → *m*).

Our experimental evidence on the isomerization peculiarities of the anions from *o*-, *m*- and *p*-carboranes-12, *C*- and *B*-derivatives and their metallic complexes has suggested a possible route of the "redox" isomerization of carboranes-12 occurs via these anions.

The number of bonding orbitals in the carborane molecule is known to be $N = n/2$, with n being the number of electrons participating in the formation of the carborane skeleton [7]. Addition of two electrons leads to a considerable rearrangement of the electronic shell and geometrical structure of the molecule to result in a new system of bonding orbitals, in number $N + 1$. If addition of electrons to *o*-, *m*- or *p*-carboranes had not structurally affected the icosahedron,

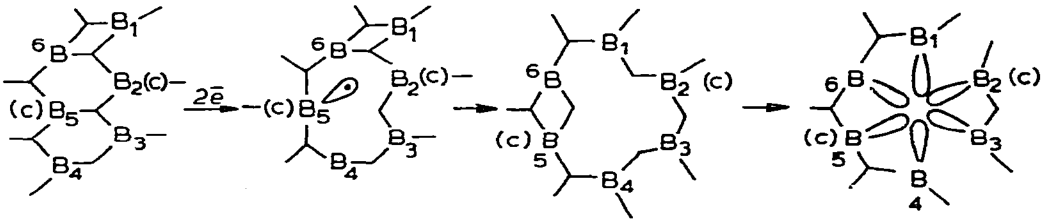


Fig. 1. The simplified scheme of two electron addition to three-centre bonds.

the ^{11}B NMR spectra of the *o*-dianions would have been similar to those of the carboranes for the chemical shift of some boron atoms [15].

Setting aside the actual distribution of the electron density in the molecule, it is possible to visualise the addition process of two electrons to proceed as shown in Fig. 1, in terms of a localised three-centre orbital, one of the bonding units in carborane. Addition of two electrons results in a system involving one two-centre orbital and an unshared pair on the atomic orbital of the third atom. This pair of electrons interacts then with another three-centre orbital to form a system of three two-centre orbitals. Thus the system of two three-centre orbitals rearranges to a system of three two-centre orbitals with two electrons in the additional orbital. This system of three bonding orbitals can involve six adjacent atoms of the icosahedron to form a distorted face containing both boron and carbon atoms. This face is rather mobile and participates in exchange processes with other atoms of the polyhedron [15]. The exchange processes, due partly to purely electronic redistribution, are known to proceed at a rate up to 10^{18}/sec and may therefore not affect the geometry of the icosahedron. On the other hand, when proceeding at a rate of 10^{11} and 10^{12}/sec or lower (characteristic of the movement of atoms) these processes can lead to dynamic redistributions involving the cooperative action of all atoms in the polyhedron. It has also to be borne in mind that, depending on the nature of the substituent and its position in the icosahedron, a different dianion structure from that of the unsubstituted carborane can be obtained (e.g. in the case of electron addition at the boron—halogen or carbon—halogen bond before the electron delocalization in several three-centre units). This can be exemplified by carborane formation from the dianions from *C*- and *B*-halogeno-*m*- and -*p*-carboranes having the same structure as the starting compounds. Depending on the structure of the starting carborane and the properties of the substituent on the carbon and boron atoms the structures formed can also include those with one or two carbon atoms in the distorted pentagonal or hexagonal faces. In contrast to the starting carboranes the

TABLE 1

SPECTRAL DATA

Dianions from carboranes	λ (nm)	ν (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})
ortho	298 ± 10	33560	8000
meta	295 ± 10	33400	7500
para	335	29850	5000

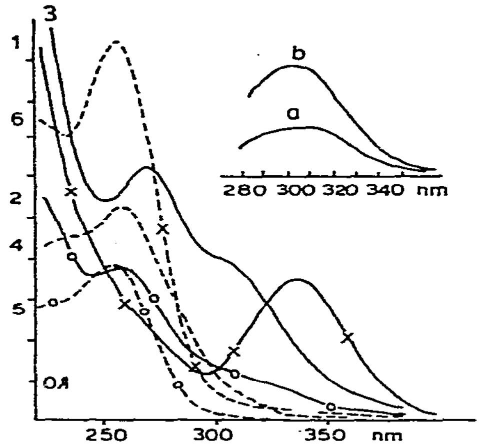


Fig. 2. UV Spectra of dianions in THF solutions from *o*-(1), *m*-(2), *p*-(3) carboranes, and solutions of monoanions from compound I (4) II (5) and III (6). Above are also shown the spectra of the dianions from *m*-(a) and *o*-(b) carboranes, obtained by subtraction of monoanion spectra from those of mixtures of mono- and dianions.

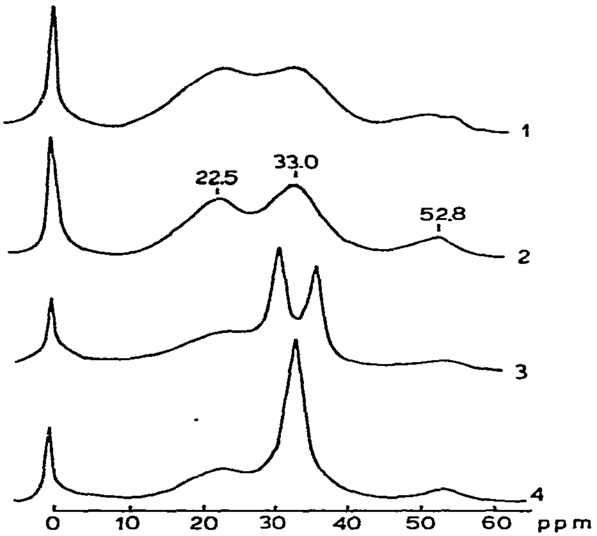


Fig. 3. NMR spectra: 1, ^{11}B of the dianions from *p*-carborane; 2, $^{11}B\{H\}$ of the dianions from *p*-carborane; 3, ^{11}B of the dianions from *p*-carborane + 10% of *p*-carborane; 4, $^{11}B\{H\}$ of the dianions from *p*-carborane + 10% of *p*-carborane.

anions $C_2B_{10}H_{12}^{2-}$ have intense absorption bands (Table 1). Absorption bands of the dianions (Fig. 2) from *o*- and *m*-carboranes are rather broad ($\Delta\nu$ 1/2 = 8000 cm^{-1}). The half-width of the absorption band for the dianions from *p*-carboranes ($\Delta\nu_{1/2}$ = 5000 cm^{-1}) is less than that for the dianions from *o*- and *m*-carboranes, which apparently accounts for the predominant existence of energeticully equivalent structures in the dianions from *p*-carboranes and the presence of dynamic structures with different energy levels in the dianions from *o*- and *m*-carboranes.

If the carbon atom is regarded as a source of perturbation affecting the even electron density distribution, the increased number of carbon atoms in the system of three two-centre orbitals must considerably affect the energy levels. It is, therefore, possible that the absorption-band-shifts to shorter wavelengths on passing from the dianions from *p*-carboranes to those from *m*- and *o*-carboranes account for the decreased delocalization of the electron density of the latter compounds.

Depending on the position and nature of the substituent in the icosahedron the cleavage of three-centre bonds can take place on addition of two electrons in different places to give a set of structures different from those formed from unsubstituted carboranes. The substituents in the dianions must thereby substantially affect the rate of exchange processes as well. We have shown [12, 13] that oxidation of the dianions from 1-chloro-(bromo)-12-methyl-*p*-carborane gives a mixture of neutral products consisting of 1-methyl *o*- and *m*-carboranes, whereas oxidation of the freshly prepared dianion from 1-methyl-*p*-carborane in ammonia results exclusively in 1-methyl-*m*-carborane.

Proceeding with the NMR study of the dianions from *o*-, *m*- and *p*-carboranes [15] we have analysed the spectral changes of these carboranes and their *C*-methyl derivatives with time. Figs. 3—7. The dianion spectrum from *p*-carborane is found to be practically unchanged after one month and consists of three lines with a 4/5/1 intensity (Fig. 3). Oxidation of the dianion from *p*-carborane in THF, kept for a month or heated in boiling THF for six hours, gives quantitatively *m*-carborane.

It is to be noted concerning the work of Hawthorne et al. [5] that in the dianion spectrum from *p*-carborane, the signal with an intensity of 5 at 33 ppm is masked by the intense *p*-carborane signal at 33.1 ppm (Fig. 3). This explains why the authors report only two signals for the anions from *p*-carborane [5]. A similar case is to be found for 1-methyl-*p*-carborane in THF (Fig. 4). We have already noted that due to the poor solubility of *p*-carborane in liquid ammonia, a quantitative yield of dianions is only obtained by adding a *p*-carborane solution in THF rather than a solid powder to liquid amonia. ^{11}B NMR spectra of the dianions from *o*- and *m*-carboranes differ from those from *p*-carboranes in that changes occur during the first hours and then the spectra remain stable for 30 days. The spectra resemble each other except for the intensity of several lines in the 30-33 ppm region.

The change in properties of the dianions from 1-methyl-*o*-, *m*- and *p*-carboranes with time has also been studied by ^{11}B NMR spectroscopy in terms of the "redox" isomerization of 1-(halogenomethyl)-*o*-carborane and 1-halogen-12-methyl-*p*-carborane to order to elucidate the effect of substituents on the state and the rate of dynamic changes in the dianion. It is thereby found that ^{11}B NMR spectra of the dianions from 1-methyl *o*- and *m*-carboranes remain

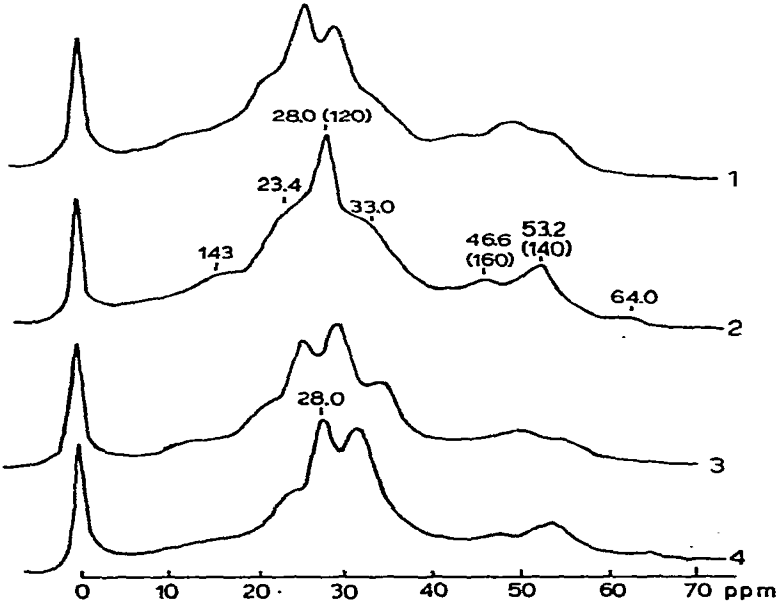
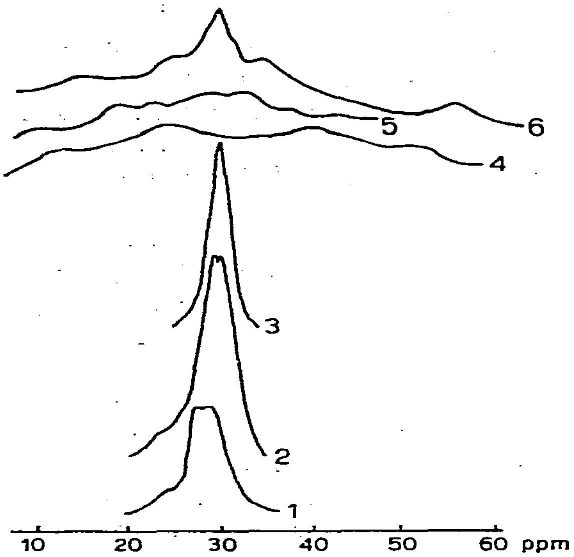


Fig. 4. NMR spectra: 1, ^{11}B of the dianions from 1-methyl-*p*-carborane; 2, ^{11}B{H} of the dianions from 1-methyl-*p*-carborane; 3, ^{11}B of the dianions from 1-methyl-*p*-carborane + 15% 1-methyl-*p*-carborane; 4, ^{11}B{H} of the dianions from 1-methyl-*p*-carborane + 15% 1-methyl-*p*-carborane.



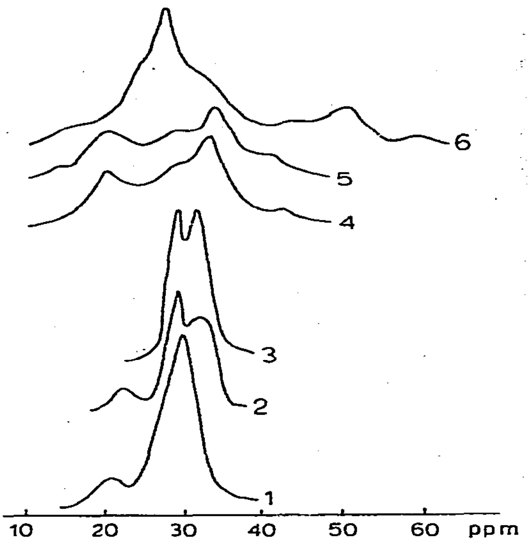


Fig. 5. $^{11}B\{H\}$ NMR spectra of *C*-methyl-*C*^{1}-chloro-*o*- (1); *m*- (2), *p*- (3) -carboranes and the dianions from *o*- (4), *m*- (5), *p*- (6).

Fig. 6. $^{11}B\{H\}$ NMR spectra of 1-methyl-*o*- (1), *m*- (2), *p*- (3)- carboranes and the dianions from these compounds *o*- (4), *m*- (5), *p*- (6).

unaffected for a month and are similar but for the intensity of lines at 19.6 and 33.4 ppm (Figs. 5 and 6). The spectrum of the freshly prepared dianion from 1-methyl-*p*-carborane is in principle different from those of 1-methyl-*o*- and *m*-carboranes. In addition it has three high-field lines (Fig. 7) at 46.6, 53.2 and 64 ppm that can be assigned, as in the case of the dianion from *p*-carborane, to the boron atom whose bonds with carbon are broken. This fact is considered to explain the formation of at least three isomeric structures with different statistical weights and dynamic stabilities. The dianion spectrum from 1-methyl-*p*-carborane changes in 30 days to those of the dianions from 1-methyl-*o*- and *m*-carboranes except for the well-defined high-field region.

It is to be noted although the two central signals at 27.9 and 33.0 ppm change their position only a little with time, the intensity of the latter peak rises sharply. The low-field spectral region is most markedly affected at 19.7 ppm. The three lines in the high-field region are slightly shifted to low field.

The changing dianion spectrum from 1-methyl-*p*-carborane confirms our suggestion [15] that dianions are not individual compounds but a set of labile structures whose composition and structure depend on the properties of the substituent at the carbon atom.

The dynamic effects are manifested over a wide width of ^{11}B NMR lines. At concentrations of 10 to 25% and at room temperature the spectra are not readily resolved, the optimum concentrations being 5-7% in THF at 35-40°.

Thus, the nature of the sustituent is found to affect the nature of the rupture of C—C and B—C bonds on addition of two electrons the type of resulting structures, the readiness of mutual interconversion and the rate of dynamic processes.

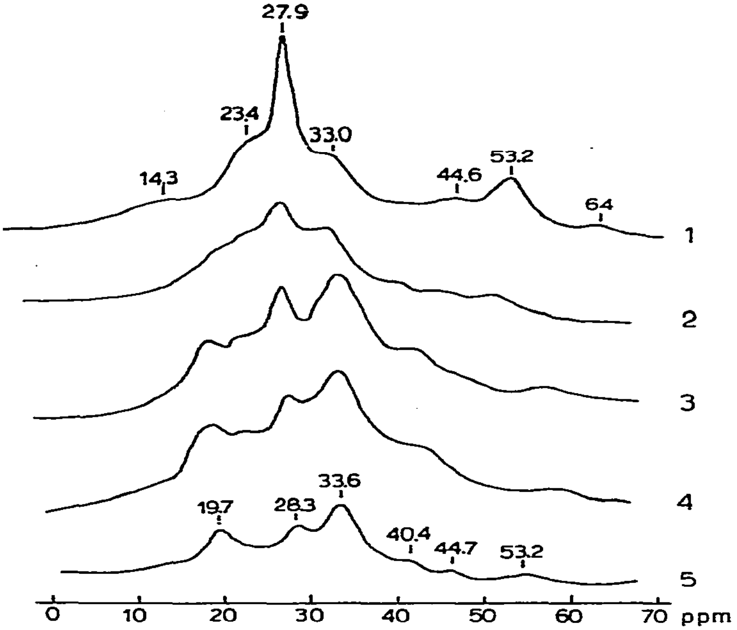


Fig. 7. The change of $^{11}B\{H\}$ NMR spectra of the dianions from 1-methyl-*p*-carborane with time. 1, 1st day; 2, 10th day; 3, 15th day; 4, 18th day; 5, 28th day.

As a result, oxidation of the dianions from 2-halogeno-*p*-carborane gives a mixture of *B*-halogeno-*m*-carboranes and oxidation of the dianions from 1-halogeno-*p*-carborane leads to compounds with *o*- and *m*-structures [10, 12, 13].

The formation of the icosahedral backbone of the carboranes is determined at the oxidation stage during which several structures may give rise to one and the same compound to form firstly a bond between the carbon atoms independent of their position in the deformed face. However, if there is only one carbon atom in this plane a bond is formed between the carbon and boron atom bonded to the carbon at the lower part of the polyhedron to give *m*-carborane, whereas the formation of *p*-carborane necessitates the introduction of the thirteenth atom.

The ^{11}B NMR spectra of the monoanions obtained by addition of water to the dianions in THF alone or with ammonia are clear resolved spectra which differ, in principle, from those of the starting carboranes and their dianions [15]. Depending on the conditions used in preparing and isolating the dianion and the amount of water added the spectra differ both in the intensity and the chemical shift of their lines and reveal lines characteristic of isomers of dicarbadodecarborate monoanions [5] as well as lines of further degradation products up to boric acid (1 to 65 ppm).

Oxidation of the monoanions $C_2B_{10}H_{13}^-$ with $KMnO_4$ in liquid ammonia gives only traces of neutral carboranes. However, when treated with sodium amide these monoanions are oxidized to yield 20-25% of carboranes, e.g. 3-amino-*o*-carborane in the case of monoanions from *o*- and *m*-carboranes. It is thus seen that hydrolysis of dianions $C_2B_{10}H_{12}^{2-}$ gives a mixture of isomeric monoanions $C_2B_{10}H_{13}^-$, some of which fail to donate a proton and convert to the dianion even under the action of such strong bases as the amide-ion, which is in accord with the data reported by Hawthorne et al. [5]. However, some monoanions are comparatively readily deprotonated to give dianions that on amination [16] are reconverted to neutral carboranes under the action of an oxidant:

$$C_2B_{10}H_{13}^- \xrightarrow[NH_3]{NH_2^-} [C_2B_{10}H_{12}]^{2-} \xrightarrow[NH_3]{NH_2^-} [C_2B_{10}H_{11}NH_2]^{2-} \xrightarrow[NH_3]{KMnO_4} o\text{-}C_2B_{10}H_{11}NH_2$$

It is to be noted that X-ray structural data must be regarded with caution because of atom migration on irradiation in these labile systems [17].

We have suggested [15] that the action of electrophilic reagents, including protonation, results in the opening of a part of the structure to form structures differing from those of the dianions, and depending on the nature of the electrophilic species and the properties of the substituents at the carbon or boron atoms*.

It has also to be borne in mind that the structure of the carbon fragments resulting from the decomposition of the monoanions by $PdCl_2$ in propionic acid [5] cannot account for the structure of the monoanion, let alone for that of the dianion. We have shown [19, 20] that oxidation of *o*-, *m*-diphenylcarbaundecarborates leads in both cases to compounds with either one or two carbons of the carborane nucleus in the carbon fragment.

Experimental

^{11}B NMR spectra were taken on an Varian HA-100D spectrometer at 32.01 MHz (8 mm ampoules) using heteronuclear resonance and with field sweep, the external standard being $B(OCH_3)_3$. UV spectra of dianions from *o*-, *m*- and *p*-carboranes in THF solution (Fig. 1) were taken on an SP-1800 spectrometer in the region 220-370 nm in a 0.01 cm cuvette, with the dianion concentration from 0.0092 to 0.0046 mmol/l. The results are listed in Table 1 and Fig. 2.

Preparation of $Na_2C_2B_{10}H_{12}$ solution in THF from o-carborane

To a solution of 2.00 g (13.9 mmol) of *o*-carborane in 10 ml of absolute THF in a 100 ml round-bottom flask fitted with a ground joint with a stopcock (kept open) was added 60 ml of liquid ammonia and then 0.65 g (28.3 mmol) of sodium (before the appearance of a constant weak blue colouring). Excess sodium was removed by adding several drops of a diluted solution of *o*-carborane in THF and ammonia was allowed to evaporate. The remaining solvents were evaporated in vacuo to dryness, the flask was filled with argon and the dry residue of $Na_2C_2B_{10}H_{12}$ dissolved in 27 ml of THF. This solution, carefully protected from oxygen and moisture, was poured into two ampoules and the

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* When this report was being prepared Lipscomb et al. expressed similar views on the structure of the dianions and monoanions [18].

^{11}B NMR spectra taken, with one ampoule being immediately sealed. Solutions of $Na_2C_2B_{10}H_{12}$ from *m*- and *p*-carboranes and the respective salts from *C*-methyl-*o*-, *C*-methyl-*m*- and *C*-methyl-*p*-carboranes were obtained under identical conditions with ampoules filled and sealed as above. The concentration of solutions was 0.46 mol/l.

Attempted proton abstraction from monoanion (ortho) and reestablishment of the carborane structure

To dry $Na_2C_2B_{10}H_{12}$ prepared from 1.44 g (10 mmol) of *o*-carborane in liquid ammonia was added 20 ml of hexane. The mixture was cooled to 0° and treated with 20 ml of alcohol. The solution was poured into 200 ml of water, extracted with benzene (3 × 30 ml) and then with ethyl acetate (3 × 50 ml). Ethyl acetate was evaporated to leave 1.00 g of a viscous mass that was then dissolved in 20 ml of liquid ammonia and poured into a solution of 25 mmol of sodium amide in 50 ml of liquid ammonia. The solution was oxidized by $KMnO_4$ over a period of 20 min. (until excess $KMnO_4$ resulted in a pink colouring), and the reaction mixture was decomposed with 300 ml water and extracted with ether (3 × 50 ml). The ether was evaporated and the residue sublimed in vacuo, to yield 0.19 g of a crystalline material consisting of 95% of 3-amino-*o*-carborane and 5% of *o*-carborane.

Similar treatment of the monoanion from 1.44 g of *m*-carborane gave 0.13 g of sublimed crystalline mixture of the same composition.

"Redox" isomerization of p-carborane

A solution of $Na_2C_2B_{10}H_{12}$ in 20 ml of THF prepared from 1.44 g (10 mmol) of *p*-carborane and 0.5 g (22 mmol) sodium under conditions described above was refluxed under argon for 6 h. The reaction mixture was poured into a 20 ml solution of 2.5 g (23 mmol) of benzoquinone in THF. The mixture was kept for 1 h at room temperature, 40 ml of benzene were then added and the solution was chromatographed using an alumina column (benzene as eluant). The solvent was evaporated in vacuo to yield 1.2 g of white crystalline substance that was found by GLC to be pure *m*-carborane(12).

"Redox" isomerization of 1-methyl-p-carborane

2.5 ml of 0.47 *M* solution of $Na_2CH_3C_2B_{10}H_{11}$ in THF, prepared by the reaction of 1-methyl-*p*-carborane with sodium in liquid ammonia and kept in a sealed ampoule for a month, was poured onto 5 ml of 0.5 g of benzoquinone solution in THF. The solution was kept for an hour, 5 g of alumina was added and the mixture was eluted on Al_2O_3. The solvent was evaporated to yield 0.12 g (70%) of a mixture of 95% of 1-methyl-*o*-carborane and 5% of 1-methyl-*m*-carborane. Boiling this dianion in THF solution under argon for 4 h resulted in a similar mixture of 1-methyl-*o*- and *m*-carboranes.

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