Journal of Organometallic Chemistry, 149 (1978) 9—21

SYNTHESIS AND CRYSTAL STRUCTURE OF *B*-ARYL-*o*-CARBORANES AND ELECTRONIC EFFECTS OF *B*-*o*-CARBORANYL GROUPS *

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(Received September 27th, 1977)

Summary

Dicarbadodecaborate(14) dianions interact with aryl magnesium halides and aryl lithiums forming *B*-aryldianions of dicarbadodecaborate(14), the oxidation of which with $CuCl_2$ yields 3-, 4-, 8- and 9-aryl-*o*-carboranes. Molecular structures of 1,2-dimethyl-9-aryl-*o*-carborane and 4-(*p*-tolyl)-*o*-carborane were determined. On the basis of the ionization constants of *B*-(*p*- and *m*-carboxyphenyl)-*o*-carboranes and of ^{19}F chemical shifts in the NMR spectra of *B*-(*p*- and *m*-fluorophenyl)-*o*-carboranes, it is established that 4-*o*- and 9-*o*-carboranyl groups are electron-releasing substituents.

Introduction

The high stability of carborane derivatives containing a B—C bond is in sharp contrast to derivatives of three-coordinated boron [2—5]. The chemical behavior of carboranes with functional groups bonded to boron is similar to that of substituted polyhedral ions $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ [6]. A considerable number of methods for preparing boron-substituted carboranes have been developed. However, aryl-substituted carboranes may be synthesized only by the method proposed by Hawthorne and Wegner [7,8] that involves completion of the 1,2-dicarbollide ion with boron dihalides. The method was subsequently extended to the preparation of 2-aryl-*m*-carboranes [9].

Results and discussion

Synthesis of B-aryl-o-carboranes

Dicarbadodecaborate(14) dianions, easily formed on addition of two electrons to carboranes [10] exhibit a reactivity that differentiales them from neutral carboranes. They readily react with ammonia forming *B*-aminated dianions

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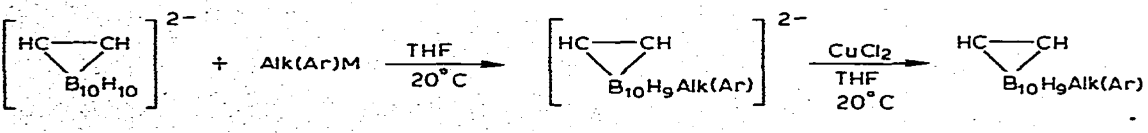
* Preliminary communication, see Ref. 1.

[11,12], are added to the carbonyl group of aromatic aldehydes [13,14] and form complexes with transition metals in which the carborane acts as a π-ligand [15,16]. Bilevich, Zakharkin and Oklobystin reported the interaction of dicarbadodecaborate(14) dianion with CH_3MgI to form a *B*-methylated dianion, hydtolysis of which gave a salt of *B*-methyldicarbadodecaborate(14) [17].

Dicarbadodecaborate(14) dianions interact with various organomagnesium and lithium compounds and this reaction may be used to introduce aliphatic and aromatic radicals of organometallic compounds into the polyhedral nucleus. Oxidation of the formed *B*-aryl(alkyl)dianions with cupric chloride produces *B*-alkyl-(aryl)-*o*-carboranes. Therefore, the reaction of dicarbadodecaborate(14) dianions with organometallic compounds and subsequent oxidation of the formed products, can be used to synthesize *B*-substituted *o*-carboranes containing a B—C bond (Scheme 1).

SCHEME 1



(M = Li, MgX)

The general features of these reactions have been described previously [18]. The reaction of dicarbadodecaborate(14) dianions with ArMgX or ArLi is nonselective and oxidation rendere a mixture of *B*-arylcarboranes with the aryl group at different positions on the *o*-carborane nucleus: 3-, 4-, 8- and 9-aryl-*o*-carboranes. On the basis of the dependence of the time of retention in a chromatographic column on the dipole moment in a series of isomeric carboranes [19] it may be as assumed that *B*-aryl-*o*-carboranes will be ordered according to the retention time as follows: 3- < 4- < 8- < 9-substituted *o*-carboranes. X-ray structural analysis of one of the isomeric 1,2-dimethyl-*B*-phenyl-*o*-carboranes and of *B*-(*p*-tolyl)*o*-carborane unequivocally confirmed this assumption and enabled assignment of the isomers under the given chromatographic conditions.

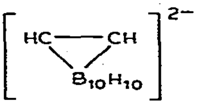
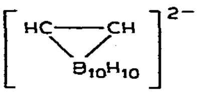
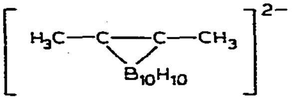
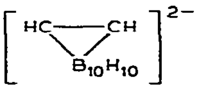
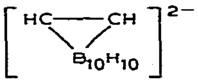
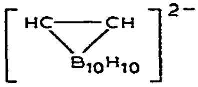
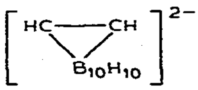
The reaction of dicarbadodecaborate(14) dianions with arylmagnesium halides and aryllithiums is nonselective. Thus, interaction of equimolar quantities of dicarbadodecaborate(14)dianion and of phenyllithium yields 20—25% of mono-(B-aryl)-*o*-carboranes, up to 30% of *o*-carborane and up to 30% of di- and tri-(*B*-aryl)-*o*-carboranes. An increase in the molar ratio dicarbadodecaborate(14) anion: organometallic compound 1 : 4 does not significantly increase the yield of mono-(*B*-aryl)-*o*-carboranes, since this leads to higher yields of polyarylated carboranes.

In the mass spectra of the *B*-phenyl-substituted products, peaks corresponding to di-, tri-, tetra- and penta-substituted *o*-carboranes are observed with *m/e* 296, 372, 448 and 524, respectively. The relative content of isomeric *B*-aryl-*o*-carboranes for a 1 : 1 molar ratio dicarbadodecaborate(14) dianion: organometallic compound is given in Table 1.

After oxidation, identical compositions of *B*-phenyl-*o*-carboranes are obtained when interacting dicarbadodecaborate(14) dianions, prepared from *m*- and *c*-car-

TABLE 1

THE RELATIVE CONTENT OF *B*-ARYL-*o*-CARBORANES FORMED BY OXIDATION OF THE PRODUCTS OF DICARBADODECABORATE(14) DIANION INTERACTION WITH ORGANOMETALLIC COMPOUNDS (1 : 1 MOLAR RATIO)

Reagents	Total yield of *B*-monoaryl-o-carboranes in relation to the initial o-carborane (%)	Relative content of isomeric *B*-aryl-*o*-carboranes		
		3-	4-	8- + 9-[a]
 + C_6H_5Li	15	25	51	24
 + C_6H_5MgBr	15	29	47	24
 + C_6H_5MgBr	23	13	36	51
 + p-$CH_3C_6H_4MgBr$	20	30	45	25
 + m-$CH_3C_6H_4MgBr$	12	27	49	24
 + p-FC_6H_4MgBr	5	33	42	25
 + m-FC_6H_4MgBr	5	26	47	27

[a] On account of the close GLC retention times of 8- and 9-aryl-*o*-carboranes their total relative content is given.

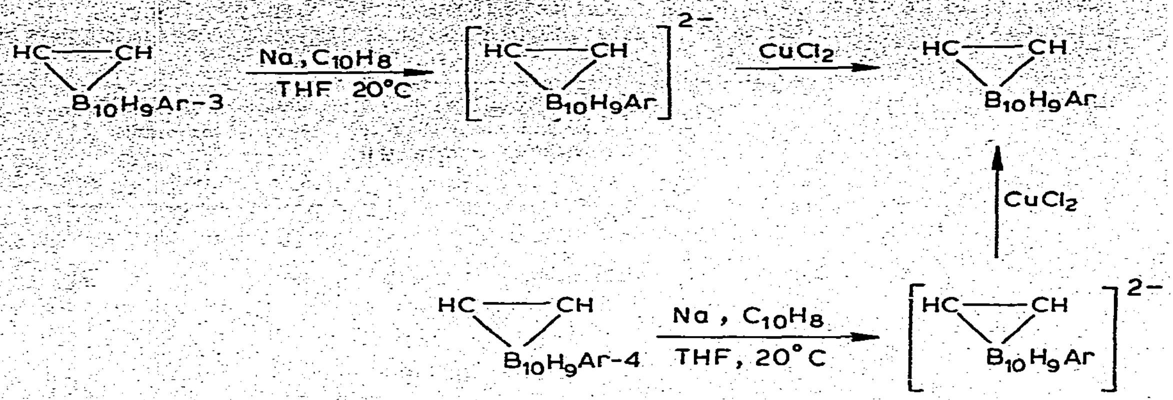
boranes, with phenylmagnesium bromide. This is explained by the identical structure of the dianions [20].

Dicarbadodecaborate(14) dianions prepared from 3- and 4-aryl-*o*-carboranes exhibit an interesting property. Similar to other *o*-carboranes [10], 3- and 4-aryl-*o*-carboranes readily attract two electrons when interacting with naphthalene-sodium in THF solution forming *B*-aryldicarbadodecaborate(14) dianions.

B-Aryl-*o*-carboranes with aryl groups in 3-, 4-, 8- and 9-positions are formed on oxidation of these dianions with $CuCl_2$. Oxidation of dianions prepared from 3- and from 4-aryl-*o*-carboranes renders a mixture of B-aryl-o-carboranes of the same composition (Scheme 2). In this respect the behavior of dianions of *B*-aryl-*o*-carboranes differs from the dianion prepared from 3-alkoxy-*o*-carborane oxidation which leads to the initial carborane [20].

Complexation of the dianion prepared from 3-aryl-*o*-carborane with transition

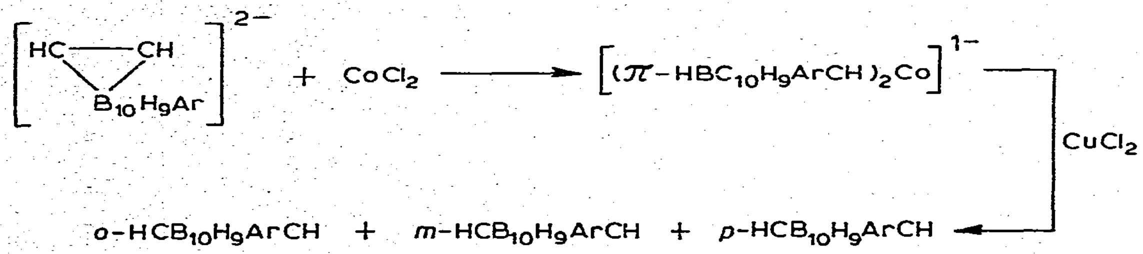
SCHEME 2



(Ar = C_6H_5 , p- and m-$C_6H_4CH_3$)

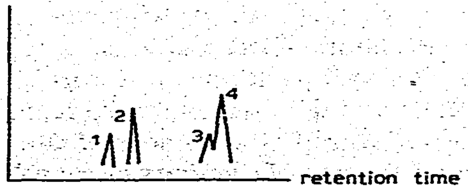
metals (for instance, Co^{3+}) leads to metallocarboranes which are oxidized with $CuCl_2$ in THF to *B*-aryl-*o*-, *m*- and *p*-carboranes (Scheme 3). Oxidation of dianions prepared from *B*-aryl-*o*- and *m*-carboranes and of their complexes with transition metals will be discussed in our next communication.

SCHEME 3



Crystal structure of 1,2-dimethyl-9-phenyl-o-carborane (I) and of 4-(p-tolyl)-o-carborane (II)

Interaction of the dianion prepared from 1,2-dimethyl-*o*-carborane with phenylmagnesium bromide, and subsequent oxidation, gives a mixture of 1,2-dimethyl-*B*-phenyl-*o*-carboranes. The chromotogram of this mixture is given in Fig. 1. We carried out an X-ray analysis of the compound I (number 4 in Fig. 1).



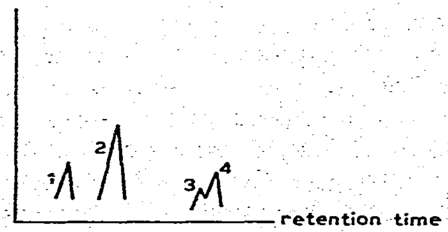


Fig. 1. Chromatogram of a mixture of 1,2 dimethyl-*B*-phenyl-*o*-carboranes.

Fig. 2. Chromatogram of a mixture of *B*-(p-tolyl)-*o*-carboranes.

TABLE 2

1,2-DIMETHYL-9-PHENYL-o-CARBORANE. ATOM COORDINATES AND TEMPERATURE FACTORS[a]

Atom	*X*	*Y*	*Z*	B_j
C(1)	0.3800(12)	0.1378(8)	0.8794(21)	5.1(4)
C(2)	0.4609(12)	0.0948(8)	0.8200(22)	4.9(4)
B(3)	0.3639(13)	0.0629(9)	0.8548(25)	4.5(5)
B(4)	0.2925(13)	0.1170(9)	0.7775(24)	4.8(5)
B(5)	0.3475(14)	0.1787(9)	0.7198(24)	4.4(5)
B(6)	0.4534(13)	0.1649(9)	0.7518(25)	4.6(4)
B(7)	0.4283(14)	0.0451(10)	0.6962(27)	4.9(5)
B(8)	0.3212(14)	0.0580(10)	0.6566(27)	4.9(5)
B(9)	0.3089(12)	0.1296(8)	0.5736(24)	4.0(4)
B(10)	0.4116(14)	0.1595(10)	0.5636(27)	5.0(5)
B(11)	0.4888(16)	0.1065(11)	0.6360(29)	6.6(6)
B(12)	0.3969(15)	0.0871(10)	0.5157(26)	5.5(5)
C(13)	0.3782(14)	0.1596(10)	1.0491(29)	6.6(5)
C(14)	0.5257(13)	0.0813(9)	0.9495(26)	5.9(5)
C(15)	0.2365(11)	0.1448(8)	0.4578(22)	3.9(4)
C(16)	0.1971(13)	0.2007(9)	0.4687(24)	6.3(5)
C(17)	0.1355(14)	0.2160(9)	0.3557(25)	6.0(5)
C(18)	0.1128(15)	0.1800(9)	0.2343(27)	6.1(5)
C(19)	0.1542(14)	0.1260(9)	0.2176(26)	6.9(5)
C(20)	0.2151(11)	0.1101(8)	0.3315(22)	4.5(4)

[a] Errors of parameter determination are given in parentheses.

TABLE 3

BOND LENGTHS OF 1,2-DIMETHYL-9-PHENYL-o-CARBORANE, *d* (Å) (ERRORS IN DETERMINING THE LAST DIGIT ARE GIVEN IN PARENTHESES)

Bond	*d*	Bond	*d*
C—C		B—B	
1—2	1.70(3)	3—4	1.80(3)
1—13	1.51(3)	3—7	1.73(3)
2—14	1.53(3)	3—8	1.80(3)
15—16	1.43(3)	4—5	1.80(3)
16—17	1.41(3)	4—8	1.75(3)
17—18	1.36(3)	4—9	1.75(3)
18—19	1.41(3)	5—6	1.74(3)
19—20	1.41(3)	5—9	1.77(3)
20—15	1.36(3)	5—10	1.72(3)
		6—10	1.71(3)
C—B		6—11	1.72(3)
1—3	1.74(3)	7—8	1.76(3)
1—4	1.71(3)	7—11	1.73(3)
1—5	1.70(3)	7—12	1.86(3)
1—6	1.70(3)	8—9	1.79(3)
2—3	1.73(3)	8—12	1.81(3)
2—6	1.71(3)	9—10	1.78(3)
2—7	1.62(3)	9—12	1.78(3)
2—11	1.60(3)	10—11	1.77(3)
15—9	1.55	10—12	1.72(3)
		11—12	1.76(3)

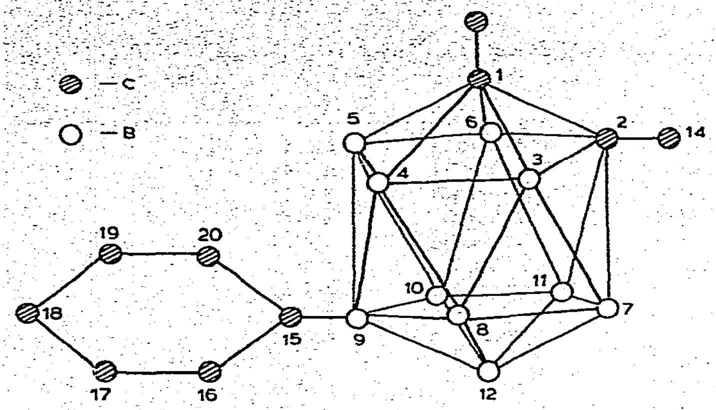


Fig. 3. Stereochemistry of 1,2-dimethyl-9-phenyl-*o*-carborane.

Compound I (1,2-dimethyl-9-phenyl-*o*-carborane), m.p. 121°C, forms prismatic crystals. Lattice parameters were determined in a "Weissenberg" chamber and refined on a Hilger-Watts difractometer: $a = 15.955(4)$, $b = 22.885(6)$, $c = 8.372(2)$ Å; space group *Pbca*; $D_{cal} = 1.11$ g cm^{-3} at $X = 8$. Intensities of 674 reflections with $I \geqslant 2\,\sigma(I)$ were measured on the same diffractometer. The structure was solved by the direct method. All 20 B and C atoms were located in the E series. The structure was refined by the isotropic least-square method to R 0.18. Atom coordinates are given in Table 2, bond lengths in Table 3 and the stereochemistry of the molecule and atom numbers are shown in Fig. 3. The length of the B—phenyl-carbon bond is 1.55 Å.

To establish the structure of B-(p-tolyl)-*o*-carboranes formed by oxidation of the products of dicarbadodecaborate(14) dianion interaction with *p*-tolylmagnesium bromide, we carried out an X-ray analysis of compound II (Compound 2 in Fig. 2).

Compound II, 4-(*p*-tolyl)-*o*-carborane: m.p. 90—91°C; $a = 18.114 \pm 0.004$; $b = 6.777 \pm 0.002$; $c = 11.826 \pm 0.003$ A; $D_{cal} = 1.076$ g cm^{-3} at $Z = 4$; space group $P\,2_12_12_1$. 849 independent reflections with $7 \geqslant 3\,\sigma(7)$ were used for solution and refinement.

The structure was solved by the direct method. The structure was refined by the isotropic least-squares method to R 0.16. Location of carbon atoms in the carborane nucleus is usually based on bond lengths as it is known that in *o*-carboranes the C—C bonds are the shortest (1.61—1.62 Å), the B—B bonds are the longest (1.76—1.81 Å) and B—C bonds are 1.69—1.73 Å. In the *m*-carborane nucleus B—C bonds are also shorter than B—B bonds. In the structure of II we encountered an ambiguity: C_2 atom is reliably located as a carbon atom, whereas both C_1 and B_3 may be assigned to the second carbon atom - both have relatively short bonds with C_2 (1.62 Å) and the bond between them is also relatively short, 1.65 Å. apparently, the carbon atom (as frequently occurs in crystalline structures) is randomly distributed between the 1 and 3 positions. From the point of view of chemistry both structures are identical, i.e. the problem of the stereochemistry of the molecule is solved. Atom coordinates are given in Table 4, bond lengths in Table 5 and the stereochemistry and atom numbers in Fig. 4.

TABLE 4

4-(*para*-TOLYL)-*o*-CARBORANE. ATOMIC COORDINATES AND TEMPERATURE FACTORS [a]

Atom	*X*	*Y*	*Z*	B_j
C(1)	0.2916(9)	−0.0190(28)	0.8133(15)	4.2(3)
C(2)	0.3463(8)	0.1164(25)	0.8896(3)	4.6(3)
B(3)	0.2658(9)	0.2027(26)	0.8555(14)	4.2(3)
B(4)	0.2452(9)	0.1166(27)	0.7197(13)	4.0(3)
B(5)	0.3213(10)	−0.0261(30)	0.6735(16)	4.6(4)
B(6)	0.3885(10)	−0.0288(30)	0.7923(15)	4.5(4)
B(7)	0.3401(12)	0.3544(37)	0.8590(18)	6.7(5)
B(8)	0.2752(11)	0.3694(33)	0.7438(16)	5.3(4)
B(9)	0.3137(10)	0.2298(28)	0.6326(15)	4.5(3)
B(10)	0.4034(10)	0.1372(30)	0.6770(15)	4.6(3)
B(11)	0.4154(11)	0.2148(29)	0.8135(16)	4.8(4)
B(12)	0.3725(11)	0.3806(34)	0.7171(16)	5.6(4)
C(13)	0.1625(6)	0.0604(18)	0.6839(9)	3.4(2)
C(14)	0.1158(7)	0.1976(9)	0.6315(11)	4.1(2)
C(15)	0.0448(7)	0.1504(21)	0.5979(10)	4.2(2)
C(16)	0.0191(7)	−0.0324(19)	0.6157(11)	4.4(3)
C(17)	0.0602(7)	−0.1745(22)	0.6675(12)	5.1(3)
C(18)	0.1342(7)	−0.1156(21)	0.7013(11)	4.5(3)
C(19)	−0.0618(8)	−0.0822(24)	0.5819(13)	6.1(3)

[a] Errors of parameter determination are given parentheses.

TABLE 5

BOND LENGTHS OF 4-(*p*-TOLYL)-*o*-CARBORANE, *d* (Å) (ERRORS IN DETERMINING THE LAST DIGIT ARE GIVEN IN PARENTHESES)

Bond	*d*	Bond	*d*
C—C		B—B	
1—2	1.62(2)	3—4	1.75(2)
13—14	1.40(2)	3—7	1.69(3)
13—18	1.31(2)	3—8	1.75(3)
14—15	1.38(2)	4—5	1.77(2)
15—16	1.34(2)	4—8	1.82(3)
16—17	1.37(2)	4—9	1.78(2)
16—19	1.53(2)	5—6	1.86(3)
17—18	1.43(2)	5—9	1.80(3)
		5—10	1.86(3)
		6—10	1.79(3)
C—B		6—11	1.74(3)
1—3	1.65(2)	7—8	1.80(3)
1—4	1.67(2)	7—11	1.74(3)
1—5	1.74(3)	7—12	1.79(3)
1—6	1.77(2)	8—9	1.76(3)
2—3	1.62(2)	8—12	1.79(3)
2—6	1.70(2)	9—10	1.82(2)
2—7	1.66(3)	9—12	1.78(3)
2—11	1.68(2)	10—11	1.71(3)
13—4	1.60(2)	10—12	1.80(3)
		11—12	1.78(3)

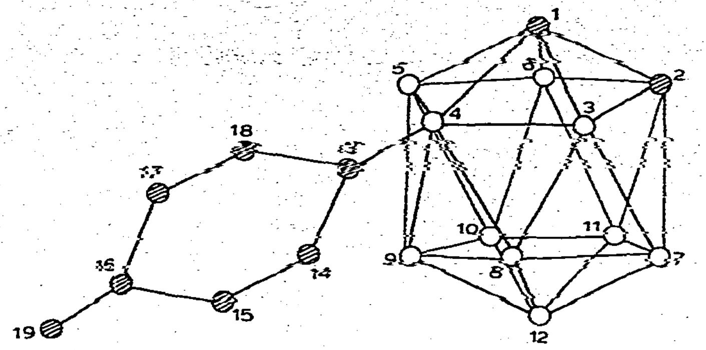


Fig. 4. Stereochemistry of 4-(p-tolyl)-o-carborane.

Structure parameters and bond lengths in the polyhedrons studied show that introduction of aryl substituents to the boron atom of the *o*-carborane nucleus practically does not change the geometry of the icosahedral backbone in relation to the unsubstituted nucleus. Terminal B—aryl bond lengths are 1.60 Å which practically coincide with B—C lengths in derivatives of three-coordinated boron [23—25].

Electronic effects of 4-o- and 9-o-carboranyl groups

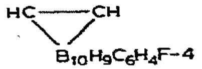
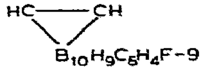
The development of methods of *B*-aryl-*o*-carborane syntheses makes it possible to study the electronic effects of 4-*o*- and 9-*o*-carboranyl groups. On account of the nonuniform distribution of electron density in the *o*-carborane nucleus, electronic effects of carboranyl groups depend on the location of the substituent in the nucleus [26,27]. A comprehensive investigation of the electronic effects of 1-*o*- and 3-*o*-carboranyl groups established that they act as electron-acceptor substituents [27—29]. A qualitative conclusion about the decrease of electronic effects of *B*-*o*-carboranyl groups in the series 3- > 4- > 8- > 9- was drawn from the values of ionization constants of *B*-hydroxy-*o*-carboranes [5].

In order to estimate quantitatively the electronic effects of 4-*o*- and 9-*o*-carboranyl groups we investigated the ^{19}F NMR spectra of 4-(*p*- and *m*-fluorophenyl)-*o*-carboranes and 9-(*p*- and *m*-fluorophenyl)-*o*-carboranes in several solvents and calculated the inductive and resonance constants of these groups (σ_I and σ_R^0) according to Taft's method [30].

The obtained data are presented in Table 6. As can be seen, 4-*o*- and 9-*o*-carboranyl groups are electron-donating substituents, the mechanism being inductive; the electron-releasing effect of the 9-*o*-carboranyl group is higher than that of the 4-*o*-carboranyl group. The strong electron-donating effect of the former confirms our previous assumption [27] made on the basis of the theoretically calculated distribution of electron density in the *o*-carborane nucleus [31]. Quantitative determination of the electronic effects of these groups also supports the series proposed [32] for the change of electronic effects of carboranyl groups: 1-*o*- ($\sigma_I = 0.38$) > 3-*o*- ($\sigma_I = 0.11$) > 4-*o*- ($\sigma_I = -0.04$) > 9-*o*- ($\sigma_I = -0.23$). The established electron-donor effects of 4-*o*- and 9*o*-carboranyl groups is the first example of the existence of such effects in electron-deficient neutral carboranes.

TABLE 6

^{19}F CHEMICAL SHIFTS IN *B*-FLUOROPHENYL-*o*-CARBORANES (ppm) IN RELATION TO FLUOROBENZENE AND CALCULATED σ CONSTANTS FOR 4-*o*- AND 9-*o*-CARBORANYL GROUPS

Solvent	 $HC\text{—}CH$, $B_{10}H_9C_6H_4F\text{-}4$				 $HC\text{—}CH$, $B_{10}H_9C_6H_4F\text{-}9$			
	δ_p^F	δ_m^F	δ_I	σ_R^0	δ_p^F	δ_m^F	σ_I	σ_R^0
CCl_4	+0.09	+0.86	−0.04	+0.02	+2.93	+2.24	−0.23	−0.02
Dioxane	+0.72	+1.02	−0.06	+0.01	+3.02	+2.22	−0.23	−0.03
THF	+0.70	+1.23	−0.09	+0.02	+3.25	+2.41	−0.26	−0.03
HMPT	+1.22	+1.38	−0.11	+0.01	+3.17	+2.21	−0.23	−0.03

As in the case of the 3-*o*-carboranyl group [28], the electron-donor effect of the 4-*o*-carboranyl group slightly increases with the proton-acceptor capacity of the solvent in the series: carbon tetrachloride < dioxane < tetrahydrofuran < HMPT.

This is connected with formation of H bonds by the acidic CH groups of the *o*-carborane nucleus. However, the range of variation ($\Delta\sigma_I$) when passing from neutral CCl_4 to the strongly aprotonic HMPT is less for 4-*o*-carboranyl groups ($\Delta\sigma_I = 0.07$) than for the 3-*o*-carboranyl group [28]. This is due to the fact that, unlike 3-substituted *o*-carboranes where the substituent is attached to the boron atom that is adjacent to both CH bonds, in 4-substituted *o*-carborane one CH bond is in *ortho* and the other in *meta* positions in relation to the substituent, and the effect of H-bond formation is less pronounced. In 9-(*p*- and *m*-fluorphenyl)-*o*-carboranes the H bond effect is practically absent, as in the case of (1-(*p*- and *m*-fluorophenyl)-*m*-carboranes [28].

To additionally confirm the value of the electronic effect of the 4-*o*-carboranyl group we synthesized *p*- and *m*-(4-*o*-carboranyl) benzoic acids, determined their ionization constants in 75% ethanol and calculated Hammet constants σ_n and σ_m for the 4-*o*-carboranyl group.

The close values of Hammet constants σ_n and σ_m for the 4-*o*-carboranyl group (Table 7) confirms the inductive mechanism of the effect of this group. Good agreement is observed between reaction constants for the 4-*o*-carboranyl group obtained by both methods (Tables 6 and 7).

TABLE 7

APPARENT IONIZATION CONSTANTS OF SUBSTITUTED RC_6H_4COOH BENZOIC ACIDS IN 75% ETHANOL AND HAMMET CONSTANTS σ_n AND σ_m OF R GROUPS.

Substituent R	pK_a	Hammet constant
p-(4-*o*-carboranyl)	6.64	−0.05
m-(4-*o*-carboranyl)	6.61	−0.03
p-(3-*o*-carboranyl) [27]	6.26	0.19
m-(3-*o*-carboranyl) [27]	6.25	0.19
H	6.58	0

TABLE 8

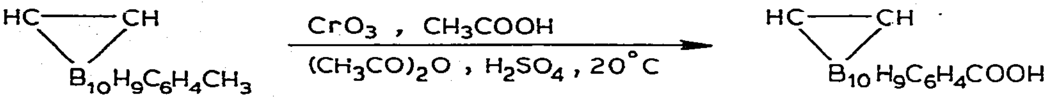
MELTING POINTS, ^{1}H NMR SPECTRA RECORDED IN CCl_4 AND ELEMENTAL ANALYSES OF THE COMPOUNDS OBTAINED

Compound	M.p. (°C)	Analysis found (calcd.) (%)					^{1}H NMR spectra[a]
			C	H	B	F	
3-Phenyl-*o*-carborane	110—111[b]						
4-Phenyl-*o*-carborane	86—87	$C_8H_{16}B_{10}$	43.53 (43.61)	7.51 (7.32)	48.87 (48.87)		3.55(CH-2); 7.35(C_6H_5-5)
3-(*p*-Tolyl)-*o*-carborane	98—99[c]						3.55(CH-2); 7.35(C_6H_4-4); 2.40(CH_3-3)
4-(*p*-Tolyl)-*o*-carborane	90—91	$C_9H_{18}B_{10}$	46.55 (46.13)	7.54 (7.74)	45.34 (46.13)		3.55(CH-2); 7.35(C_6H_4-4); 2.40(CH_3-3)
3-(*m*-Tolyl)-*o*-carborane	64—65[d]						3.60(CH-2); 7.35(C_6H_4-4); 2.40(CH_3-3)
4-(*m*-Tolyl)-*o*-carborane	90—91	$C_9H_{18}B_{10}$	46.94 (46.13)	7.67 (7.74)	45.28 (46.13)		3.55(CH-2); 7.35(C_6H_4-4); 2.35(CH_3-3)
3-(*p*-Fluorophenyl)-*o*-carborane	107—108[e]						3.85(CH-2); 7.55(C_6H_4F-4)
4-(*p*-Fluorophenyl)-*o*-carborane	101—102	$C_8H_{15}B_{10}F$	40.31 (40.4)	6.20 (6.35)	45.09 (45.4)	 (7.99)	3.85(CH-2); 7.55(C_6H_4F-4)
9-(*p*-Fluorophenyl)-*o*-carborane	69—70	$C_8H_{15}B_{10}F$	(40.4)	(6.35)	(45.4)	7.63 (7.99)	3.85(CH-2); 7.55(C_6H_4F-4)
3-(*m*-Fluorophenyl)-*o*-carborane	62—63[f]						3.85(CH-2); 7.55(C_6H_4F-4)
4-(*m*-Fluorophenyl)-*o*-carborane	47—48	$C_8H_{15}B_{10}F$	40.52 (40.4)	6.44 (6.35)	44.56 (45.4)	 (7.99)	3.65(CH-2); 7.25(C_6H_4F-4)
9-(*m*-fluorophenyl)-*o*-carborane	129—129.5		40.02	6.37	44.49		3.65(CH-2); 7.35(C_6H_4F-4)
1,2-dimethyl-3-phenyl-*o*-carborane	154—155[g]						1.85(CH_3-6); 7.35(C_6H_5-5)
1,2-Dimethyl-4-phenyl-*o*-carborane	100—101	$C_{10}H_{20}B_{10}$	48.53 (48.36)	7.98 (8.12)	43.54 (43.53)		1.90(CH_3-3); 2.20(CH_3-3); 7.55(C_6H_5-5)
1,2-Dimethyl-9-phenyl-*o*-carborane	120—121	$C_{10}H_{20}B_{10}$	48.61 (48.36)	8.20 (8.12)	43.67 (43.53)		2.03(CH_3-6); 7.35(C_6H_5-5)

[a] Chemical shifts are given in relation to TMS, used as internal reference Assignments and relative integral intensities are given in parentheses. [b] Mp. 108—109°C [7]. [c] Mp. 99—99.5°C [27]. [d] Mp. 64—65°C [27]. [e] Mp. 104.5—105°C [28]. [f] Mp. 64—64.5°C [28]. [g] Mp. 158—159°C [7].

p- and *m*-(4-*o*-Carboranyl) benzoic acids were synthesized by oxidation of 4-(*p* and *m*-tolyl)-*o*-carboranes with chromic anhydride in acetic acid [27] (Scheme 4). From comparison of inductive constants obtained in the present work for 4-*o*- and 9-*o*-carboranyl groups and published data for 1-*o*- and 3-*o*-carboranyl groups with values of effective charges on skeletal C and B atoms of the *o*-carborane nucleus [33]:

SCHEME 4



	C(1)	B(3)	B(4)	B(9)
Charge	0.22	0.07	0.02	—0.17
σ_I	0.38	0.11	—0.04	—0.23

it may be concluded that the values of electronic effects of carboranyl groups are mainly determined by the values of charges on the corresponding atoms of the polyhedron.

Experimental

The purity of the starting materials and products was determined by GLC on a "Tsvet-4" chromatograph at 230—250°C using columns (d = 4 mm, l = 2 m) packed with Celite-245 treated with 15% silicon-301. Neutral alumina, 1 100/160 -grade silica gel and plates with "Silufol" silica gel were employed for column and thin layer chromatography.

Reaction of ArMgX or ArLi with decarbadodecaborate(14) dianion (equimolar ratio of reagents)

An ether solution of ArMgX or ArLi was added to dicarbadodecaborate(14) dianion in THF. A white precipitate was formed. The reaction mixture was stirred for 1 h at 20°C, then cooled to 0° and an excess of dry $CuCl_2$ was added in small portions while stirring. After 0.5 h the solvent was evaporated in vacuo and benzene was added to the dry residue. The residue was then filtered and the filtrate was twice washed with water and dried over $CaCl_2$. After evaporating benzene the residue was passed through an alumina column using a 1 : 3 benzene/hexane mixture. Unreacted *o*-carborane and naphthalene were removed by sublimation (120°C/2 mmHg). Distillation and column chromatography on silica gel yielded B-substituted *o*-carboranes.

Melting points, ^1H NMR spectra recorded in CCl_4 and elemental analyses of the obtained compounds are given in Table 8.

Reaction of the dianion prepared from o-carborane with phenylmagnesium bromide (1 : 4 molar ratio)

The reaction was carried out as described above. Chromatography on an alumina column using a 1 : 1 mixture ethersmethanol gave a mixture of B-di, tri-, tetra- and penta-phenyl-*o*-carboranes (determined by mass spectrometry).

Reaction of the dianion prepared from m-carborane with phenylmagnesium bromide

To 50 ml of liquid NH_3 at —40°, 1.44 g (0.01 mol) of *m*-carborane in 20 ml of absolute ether followed by 0.46 g (0.02 g at.) of Na were added. The mixture was stirred for 10 min, NH_3 evaporated, and the ether removed in vacuo. 20 ml of THF followed by an ether solution of phenylmagnesium bromide (prepared from 1.7 g of C_6H_5Br and 0.3 g of Mg) were added to the dry residue. After an hour the reaction mixture was oxidized with $CuCl_2$, placed in a separating funnel, the organic layer was washed with water, dilute HCl and then dried over $CaCl_2$. After sublimation of *o*-carborane the residue was chromatographed and analyzed by GLC.

Preparation of dianion from 3-(p-tolyl)-o-carborane and its oxidation with $CuCl_2$

0.4 g (0.017 g-at.) of Na and 0.1 g of naphthalene were added, under argon, to freshly distilled THF. After appearance of a green color, 1.1 g (0.005 mol) of 3-(*p*-tolyl)-*o*-carborane was added and the solution decolorized. The reaction mixture was stirred until a green color appeared again and then for another two hours. The excess of Na was removed and 2 g of dry $CuCl_2$ was added. After stirring for 0.5 h THF was removed in vacuo, benzene was added and the residue filtered. The filtrate was washed with water and the organic phase dried over $CaCl_2$. Benzene was evaporated and naphthalene sublimated. The residue was analyzed by GLC. The mixture contained 3-(*p*-tolyl)-*o*-carborane (40%), 4-(*p*-tolyl)-*o*-carborane (48%), 8- and 9-(*p*-tolyl)-*o*-carboranes (12%). The ratio of B-substituted *o*-carboranes did not change on storing the solution of dianion for 24 h.

Oxidation of the dianion prepared from 4-(*p*-tolyl)-*o*-carborane carried out in a similar manner yielded a mixture of the same composition.

Complexation of the dianion prepared from 3-(p-tolyl)-o-carborane with Co^{3+} and subsequent oxidation

0.2 g of anhydrous $CoCl_2$ was added to the dianion prepared from 0.5 g of 3-(*p*-tolyl)-*o*-carborane in THF and the mixture was stirred for 2 h at 20°C. 0.7 g of $CuCl_2$ was then added and the reaction mixture was stirred another 2 h. GLC established 2-(*p*-tolyl)-*p*-carborane and *B*-(*p*-tolyl)-*o*- and *m*-carboranes in the obtained mixture.

p-(4-o-Carboranyl) benzoic acid

To a solution of 1 g of 4-(*p*-tolyl)-*o*-carborane in a mixture of 60 ml of CH_3COOH, 15 ml of $(CH_3CO)_2O$ and 3 ml of conc. H_2SO_4, 6 g of CrO_3 were gradually added at 20—25° whilst stirring. After 2 h the reaction mixture was poured into 0.5 litre of cold water, the acid formed was filtered, washed with water and dried over P_2O_5. Sublimation in vacuo and recrystallization from an ethanol—water mixture rendered 0.7 g (65%) of *p*-(4-*o*-carboranyl) benzoic acid, m.p. 243—243.5°C. (Found: C, 40.87; H, 5.97; B, 4069. $C_9H_{16}B_{10}O_2$ calcd.: C 4089; H 6.10; B 40.90%.) ν(CO) 1690, ν (B—H) 2580, ν(C—H) 3075 cm^{-1}.

m-(4-*o*-Carboranyl) benzoic acid was obtained similarly, m.p. 252—253°C. (Found: C, 41.14; H 5.94; B 39.81%.) ν(CO) 1680, ν(C—H) 2590, ν(B—H) 3075 cm^{-1}.

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