Journal of Organometallic Chemistry, 226 (1982) 217—222
Elsevier Sequoia S A , Lausanne — Printed in the Netherlands

SYNTHESIS OF B-ORGANO-SUBSTITUTED 1,2-, 1,7-, AND 1,12-DICARBACLOSODODECABORANES(12) *

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(Received September 17th, 1981)

Summary

A convenient new method is proposed for the synthesis of 9-organo-substituted *o*- and *m*-carboranes and 2-organo-substituted *p*-carborane by the substitution of iodine in 9-iodine-*o*-, 9-iodine-*m*-, and 2-iodine-*p*-carboranes by an organic group from an organomagnesium compound in the presence of catalytic amounts of phosphine complexes of palladium. For the first time the halogen in boron halogen carboranes has been substituted by an organic group.

Introduction

Studies of functionally substituted carboranes show that their properties depend on the position of the substituent on the carborane nucleus. Until recently, C derivatives of carboranes have been examined rather widely while B derivatives have been studied to a much smaller degree. In the series of B derivatives of carboranes, B-organo-substituted carboranes with a B—C bond are of a major interest since the variety of properties of the organic substituents opens broad prospects for syntheses. However, few methods of obtaining these derivatives are available, the methods mostly being complicated and laborous The following methods of obtaining B-organo-substituted carboranes with a B—C bond are known. Alkylation of *o*- and *m*-carboranes with alkyl halides in the presence of $AlCl_3$ gives a mixture of polyalkylated carboranes [1,2]. The reaction between the mixture 1- and 2-ethyl decarboranes and acetylene furnishes 8- and 9-ethyl *o*-carboranes [3]. The reaction of 7,8- and 7,9-dicarbollide ions with alkyl (vinyl, aryl) boron dichlorides gave rise to 3- and 3,6- mono- and dialkyl (vinyl, aryl) *o*-carboranes and 2-alkyl (vinyl, aryl)

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[*] 1 2-, 1,7- and 1 12-dicarbaclosododecaboranes(12) will be referred to as *o*-, *m*-, and *p* carboranes and denoted as *o*- *m*-, and *p*-$HCB_{10}H_{10}CH$ respectively

m-carboranes, respectively [4—14] Alkylation of *o*-, *m*-, and *p*-carboranes with vinyltrichlorosilane in the presence of $AlCl_3$ produced B-(trimethylsilyl)-ethyl derivatives of 9-*o*-, 9-*m*-, and 2-*p*-carboranes, respectively [15,16]. The interaction between dicarbadodecaborate(14) dianions and organo-Li and -Mg compounds followed by oxidation with $CuCl_2$ leads to the formation of a mixture of 3-, 4-, 8-, and 9-alkyl (alkenyl, aryl) *o*-carboranes and a mixture of B-aryl *m*-carboranes [17—21].

After the synthesis of B-halogen carboranes [22], it was of interest to synthesise B-substituted carboranes by the substitution of the halogen by a nucleophilic group. However, previous studies have shown that the halogen in B-halogen carboranes is extremely inert towards substitution [23]; until now, attempts to substitute the halogen atom by an organic group have been unsuccessful

Results and discussion

We found * that the iodine atom in B-iodine carboranes can be readily substituted by an organic group by treatment with organomagnesium compounds in the presence of triphenylphosphine complexes of zerovalent palladium in catalytic amounts. In the present study we used there readily available 9-iodine-*o*- and -*m*-carboranes and 2-iodine-*p*-carborane as starting compounds. We noticed that only B-iodine carboranes enter the reaction Palladium compounds, such as tetrakis(triphenylphosphine)palladium and bis(triphenylphosphine)-palladium dichloride, are efficient catalysts. Preference was given to the latter complex since it is stable in air The amount of the catalyst used was 1—2 per cent of the starting iodine carborane. Similar nickel complexes are far less efficient The reaction mixtures were boiled in ether; for 9-iodine-*o*- and 9-iodine-*m*-carboranes the reaction was run for 30—40 h and is depicted as follows

$$\text{9-I-}o\text{- or 9-I-}m\text{-}HCB_{10}H_9CH + RMgX \xrightarrow[\text{ether}]{L_n \text{ or } L_2MCl_2} \text{9-R-}o\text{- or 9-R-}m\text{-}HCB_{10}H_9CH$$

2-Iodine-*p*-carborane reacts in a similar way but much slower: heating for 60 h was required

$$\text{2-I-}p\text{-}HCB_{10}H_9CH + RMgX \xrightarrow{L_nM \text{ or } L_2MCl_2} \text{2-R-}p\text{-}HCB_{10}H_9CH$$

In these equations $n = 3, 4$; $L = (C_6H_5)_3P$, M = Pd, Ni, R = alkyl, alkenyl, benzyl, aryl.

Data for the B-substituted *o*-, *m*-, and *p*-carboranes obtained are given in Table 1. Alkyl- and aryl-magnesium bromides, and allyl- and benzyl-magnesium chlorides were used in the reaction.

The interaction between 9-iodine-*o*- or 9-iodine-*m*-carborane and aryl- or benzyl-magnesium bromide is accompanied by a side reaction giving a product from reaction of two organomagnesium radicals, i e. a corresponding biaryl or dibenzyl, in 10—15 per cent yields. The reduction product, *o*- or *m*-carborane, is formed in trace amounts (less than 1 per cent). However, the reactions do not reduce the yield of the corresponding B-aryl or B-benzyl carborane to a notice-

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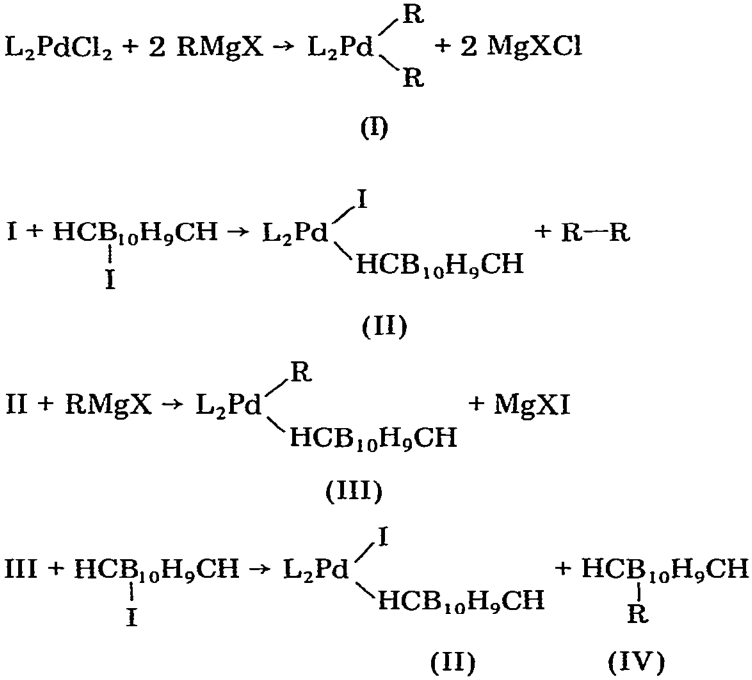
* Preliminary communication [24].

able degree; the yield is almost quantitative. On the other hand, the reaction between 9-I-*o*- and 9-I-*m*-carboranes and alkylmagnesium halides results in the formation of a reduction product, *o*- or *m*-carborane, in 5—20 per cent yields, this results in a lower yield of a corresponding B-alkyl carborane.

Apparently, the reaction follows a mechanism similar to that of the reaction between aryl halides and organomagnesium compounds in the presence of palladium and nickel complexes [25]



$$L_2PdCl_2 + 2\,RMgX \rightarrow L_2Pd\begin{array}{l}\diagup R\\ \diagdown R\end{array} + 2\,MgXCl$$

(I)

$$I + \underset{\displaystyle I}{\underset{|}{HCB_{10}H_9CH}} \rightarrow L_2Pd\begin{array}{l}\diagup I\\ \diagdown HCB_{10}H_9CH\end{array} + R{-}R$$

(II)

$$II + RMgX \rightarrow L_2Pd\begin{array}{l}\diagup R\\ \diagdown HCB_{10}H_9CH\end{array} + MgXI$$

(III)

$$III + \underset{\displaystyle I}{\underset{|}{HCB_{10}H_9CH}} \rightarrow L_2Pd\begin{array}{l}\diagup I\\ \diagdown HCB_{10}H_9CH\end{array} + \underset{\displaystyle R}{\underset{|}{HCB_{10}H_9CH}}$$

(II) (IV)

$L = (C_6H_5)_3P$

RMgX interacts with L_2PdCl_2 with the formation of compound I which undergoes successive elimination and oxidative addition reactions giving rise to R– R and compound II. Next, compound II interacts with RMgX with the formation of compound III, which under the effect of B-iodine carborane undergoes reductive elimination and oxidative addition to give B-organo-substituted carborane (IV) and compound II which returns into the cycle of reactions Similar processes apparently take place when L_4Pd is used as a catalyst

Experimental

9-I-*o*-Carborane [26], 9-I-*m*-carborane [26], 2-I-*p*-carborane [27], $[(C_6H_5)_3P]_4$-Pd [28], $[(C_6H_5)_3P]_2PdCl_2$ [29], and organomagnesium compounds were obtained according to the known procedures Organomagnesium compounds were synthesized in ether with magnesium in excess and then magnesium was removed by filtration. The yields of B-organo-substituted carboranes and the identity of compounds were determined with the help of GLC on a LKhM-8MD chromatograph. A catharometer was used as a detector, the length of the column

TABLE 1

YIELDS AND ANALYTICAL DATA FOR B ORGANO SUBSTITUTED CARBORANES $R—C_2B_{10}H_{11}$

Compound	R	B pt (°C) (mmHg) [M pt (°C)]	Yield (%) [a]		Found (%)			Formula	Calculated (%)		
			A	B	C	H	B		C	H	B
9 R-1,2-$C_2B_{10}H_{11}$	C_2H_5	74—75 (1)	98	77	28 14	9 75	62 57	$C_4H_{16}B_{10}$	27 88	9 36	62 75
	iso C_3H_7	97—98 (1)	99	80	32 43	9 83	57 68	$C_5H_{18}B_{10}$	32 23	9 74	58 03
	n C_4H_9	110—111 (1)	99	75	36 17	10 14	53 64	$C_6H_{20}B_{10}$	35 97	10 06	53 96
	iso C_4H_9	108—109 (1)	98	76	36 28	9 94	54 24	$C_6H_{20}B_{10}$	35 97	10 06	53 96
	$H_2C{=}CHCH_2$	85—86 (1)	99	81	32 52	8 70	58 37	$C_5H_{16}B_{10}$	32 59	8 75	58 66
	C_6H_5	[143—143,5]	98	90	43,52	7 50	48 88	$C_8H_{16}B_{10}$	43 61	7,32	49 06
	$C_6H_5CH_2$	[102—103]	99	91	46 20	7 82	46 22	$C_9H_{18}B_{10}$	46 13	7 74	46,13
	m $CH_3C_6H_4$	[140—141]	100	85	46 12	7 96	46 00	$C_9H_{18}B_{10}$	46 13	7 74	46 13
	p $CH_3C_6H_4$	[129—129 5]	100	87	46 01	7 82	45 91	$C_9H_{18}B_{10}$	46 13	7 74	46 13
9 R 1,7 $C_2B_{10}H_{11}$	C_2H_5	70—71 (1)	75	60	27 94	9 58	62 81	$C_4H_{16}B_{10}$	27 89	9 36	62 75
	iso C_3H_7	71—72 (1)	85	69	32 26	9 92	58 04	$C_5H_{18}B_{10}$	32 23	9 74	58 03
	n C_4H_9	82—83 (1)	97	71	36 28	10 09	53 77	$C_6H_{20}B_{10}$	35 97	10 06	53 96
	iso C_4H_9	80—81 (1)	77	62	36 15	9 99	54 11	$C_6H_{20}B_{10}$	35 97	10 06	53 96
	$H_2C{=}CHCH_2$	78—79 (1)	97	78	32 40	8 85	58 51	$C_5H_{16}B_{10}$	32 59	8 75	58 56
	C_6H_5	[69—70]	98	91	43 59	7 17	49 09	$C_8H_{16}B_{10}$	43 61	7 32	49 06
	$C_6H_5CH_2$	[102—103]	100	76	46 25	7 66	45 99	$C_9H_{18}B_{10}$	46 13	7 74	46 13
	m $CH_3C_6H_4$	[78—79]	100	74	46 11	7 59	46 07	$C_9H_{18}B_{10}$	46 13	7 74	46 13
	p $CH_3C_6H_4$	[73—74]	100	73	46 12	7 92	45 98	$C_9H_{18}B_{10}$	46 13	7 74	46 13
2 R 1,12 $C_2B_{10}H_{11}$	m FC_6H_4	120 (1)	100	68	40 41	6 31	44 84	$C_8H_{15}B_{10}F$	40 32	6 34	45 30
	p FC_6H_4	[50—51]	100	79	40 33	6 37	44 83	$C_8H_{15}B_{10}F$	40 32	6 34	45 30

[a] A, product yield determined by GLC, B, isolated in pure form

was 2 m, diameter 0.3 mm, the carrier was chromaton-N-AW-HMDS, the stationary phase was SKTFT-50Kh (10 per cent), the column temperature was 190—250°C and, the flow rate of carrier gas (helium) was 100 ml/min PMR spectra of 9-allyl-*o*- and *m*-carboranes were measured on a RYa 2309 spectrometer with a 90 MHz working frequency.

9-Organo-substituted o- and m-carboranes General procedure

A mixture of 10 mmol of 9-I-*o*- or 9-I-*m*-carborane, 20—40 mmol of alkyl-(allyl-, benzyl-, aryl-)magnesium halide, and 0 2 mmol of $[(C_6H_5)_3P]_2PdCl_2$ or $[(C_6H_5)_3P]_4Pd$ in 30 ml of absolute ether was refluxed for 25—30 h in a N_2 atmosphere until complete disappearance of 9-iodine carborane (GLC check). The mixture was decomposed with water, washed with diluted HCl, water, and dried with $CaCl_2$. The B-organo-substituted carboranes obtained were purified with the help of column adsorption chromatography on silica gel *L* 40—100 mm; the eluent was a mixture of benzene and petroleum ether with b p 40—70°C (15 . 85) Subsequently solid compounds were sublimed in a 1 mmHg vacuum at 100—120°C and recrystallised from hexane; liquids were distilled in vacuum. Yields, elemental analyses and other data of the B-organo-substituted carboranes are given in Table 1, The PMR spectrum of 9-allyl-*o*-carborane (δ, ppm with respect to TMS, in CCl_4). 1.52 (CH_2), 3 23 (CH of carborane nucleus), 4.46 (*cis* H of $=CH_2$), 4 48 (*trans* H of $=CH_2$), 5 37 ($=CH$), *J* (Hz): 10 (*cis* HC=CH), 15 (*trans* HC=CH), 8 (C=CH—CH—B).

2-(m- and p-Fluorophenyl)-p-carboranes

A mixture of 3.7 mmol of 2-iodine-*p*-carborane, 14 8 mmol of *p*- or *m*-fluorophenylmagnesium bromide, and 0 14 mmol of $[(C_6H_5)_3P]_2PdCl_2$ or $[(C_6H_5)_3P]_4$-Pd in 30 ml of absolute ether was refluxed under a N_2 atmosphere for 60 h until complete disappearance of 2-iodone-*p*-carborane (GLC check) Reaction products were isolated as before Experimental data of the compounds are given in Table 1.

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