ELSEVIER

Journal of Organometallic Chemistry 642 (2002) 16–19

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

# The B–I activation in *o*-carborane clusters: their fate towards B–H. Easy synthesis of $[7,10\text{-}C_2B_{10}H_{13}]^-$

Clara Viñas, Gemma Barberà, Francesc Teixidor *

*Institut de Ciència de Materials de Barcelona, C.S.I.C., Campus U.A.B., 08193 Bellaterra, Spain*

Received 2 April 2001; accepted 26 June 2001

## Abstract

The reaction of 3-I-*o*-carborane with Cu, Cu/PPh$_3$, [Ni(PPh$_3$)$_3$], or [Pd(PPh$_3$)$_4$] has been studied to find the suitability of B–iodine substituted carboranes as sources of new boron-derivatives. In all these reactions a hydrodehalogenation reaction to yield *o*-carborane has been produced, indicating that B–I activation takes place. It may be considered that B–I adds oxidatively to M, but alternative explanations can be given. Reaction of 3-I-*o*-carborane with Na/naphthalene also produced *o*-carborane showing that albeit an oxidative addition is impossible for sodium the same hydrodehalogenation had taken place. The same result was also formed with Mg. Addition of 1,2-dibromoethane to the Mg/*o*-carborane reaction yielded $[7,10\text{-}C_2B_{10}H_{13}]^-$. Then, the sequence 3-I-*o*-carborane → *o*-carborane → $[7,10\text{-}C_2B_{10}H_{13}]^-$ can be generated with only reducing agents. The synthetic procedure for $[7,10\text{-}C_2B_{10}H_{13}]^-$ is very simple and produces a 97% yield of $[NMe_4][7,10\text{-}C_2B_{10}H_{13}]$. Basically, $1,2\text{-}C_2B_{10}H_{12}$ and Mg in excess are refluxed in THF in the presence of $I_2$ and 1,2-dibromoethane. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Carboranes; Cluster; Iodine; *Nido*; Magnesium; Oxidative addition

## 1. Introduction

It is well known that the chemistry of boron-substituted carboranes is not as developed as that of the carbon analogues due to the difficulty of introducing functional groups at the boron atom of the carborane cage. B-halogenated carboranes would be an excellent source of new B-derivatives if they were not so inert to substitution reactions [1]. Notwithstanding so, these can be adequate starting materials through reaction of a iodocarborane with organomagnesium compounds in the presence of Ni and Pd complexes [2], or if the B–I bond is activated to the corresponding carboranyl(phenyl)iodonium salt [3,4]. None of these methods provide, however, a nucleophilic boron atom. Considering the similarities between aryl and carboranyl fragments [5] one would expect the ready formation of B-carboranyl Grignard reagents. In this case a formally negative B-carboranyl fragment could be produced. Another way of activating the B–I bond would be via the oxidative addition to metal ions in low oxidation states, as is the case in cross-coupling reactions [6]. Neither in one case nor in the other, we were able to obtain the desired final products. The recent paper by Grushin and coworkers [4] on the activation of B–I by Pd(0) motivated us to present our results which are in agreement and complement the observations indicated there.

## 2. Results and discussion

Grushing et al. utilized 9-I-*m*-carborane while we did utilize 3-I-*o*-carborane [7]. They reasoned to use the *m*-carborane to avoid the nucleophilic induced partial degradation of the *closo*-carborane framework. They used [Pd(PPh$_3$)$_4$], and precursors of [Pd(PPh$_3$)$_n$] ($n = 1$ or 2), while we did use Cu, Cu/PPh$_3$, [Ni(PPh$_3$)$_3$], and [Pd(PPh$_3$)$_4$]. The reagents are comparable and, as expected, the conclusions were, too. Our interest in these reactions was motivated to generate 3-(3′-*o*-carboranyl)-*o*-carborane as shown in Scheme 1.

Contrary to Grushing et al., who had used the metal complexes in catalytic amounts, in our case the metal complex was used in stoichiometric amounts. The reaction of 3-I-*o*-carborane with Cu, Cu/PPh$_3$, [Ni(PPh$_3$)$_3$],

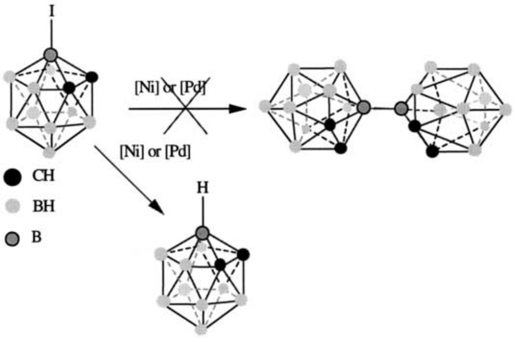
---

* Corresponding author.

PII: S0022-328X(01)01108-1

or [Pd(PPh$_3$)$_4$] has been studied. The reaction conditions are the ones used to generate coupling of organic iodides [8]. The result in all cases was a hydrodehalogenation to produce *o*-carborane. This hydrodehalogenation reaction, however, does not take place when 9-I-*m*-carborane is reacted with [Pd(PPh$_3$)$_4$] [4,9]. For this to occur, it is required to use [Pd(PPh$_3$)$_n$]($n = 1$ or 2) that provides more accessibility to the metal ion. Although this proves that some differences exist between 3-I-*o*-carborane and 9-I-*m*-carborane, which are the result of the different electronic surroundings, it seems clear that B–I activation takes place by M(0) transition metal complexes. This is, however, not synthetically satisfactory as it reverts to *o*-carborane. It may happen, as it has been indicated, that B–I adds oxidatively to M. In fact there is data that seems to support it [4], although from our point of view the source of H is controversial. Due to the special characteristics of the cluster an interaction such as the one shown in Fig. 1 could not be excluded.

To discern on the fate of the Pd complex, the reaction between 3-I-*o*-carborane and Pd[(PPh$_3$)$_4$] in DMF at reflux for 24 h, was carried out. The reaction was monitored by boron and phosphorous NMR spectra. The $^{11}$B{$^1$H}-NMR spectrum of the initial reaction mixture displayed a spectrum with pattern 2:1:3:3:1 in the range −1.0 to −29.0 ppm characteristic of 3-I-*o*-carborane while both the $^{31}$P{$^1$H} and $^{31}$P spectra showed a singlet at 15.66 ppm characteristic of [Pd(PPh$_3$)$_4$] complex [10]. After completion of the reaction, the $^{11}$B{$^1$H}-NMR spectrum of the reaction crude showed an independent broad resonance at −5 ppm corresponding to the removed boron vertex and a pattern spectrum 2:2:1:2:1:1 in the range −10.6 to −37.6 ppm characteristic of *nido*-[7,8-C$_2$B$_9$H$_{12}$]$^-$ species and the $^{31}$P{$^1$H} and $^{31}$P spectra showed two singlets at −5.35 and 25.9 ppm in a ratio 1:1. The resonance at −5.35 ppm could be attributed to triphenylphosphine [11] and the second one most probably to *cis*-[PdI$_2$(PPh$_3$)$_2$] [12].



Scheme 1. Hydrodehalogenation of 3-I-*o*-carborane to produce *o*-carborane. On top, the sought 3-(3′-*o*-carboranyl)-*o*-carborane dicluster.

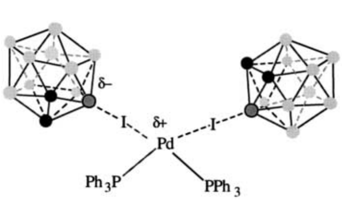
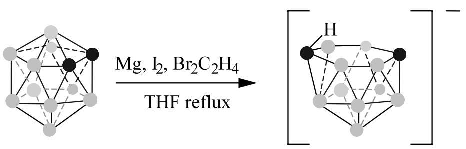


Fig. 1. Possible explanation for B–I activation and formation of [PdI$_2$(PPh$_3$)$_2$].

Electron density from the electron-rich metal would be transferred to the easily polarizable iodine, ultimately forming an electron-rich boron, which could be subjected to an electrophilic attack by a proton. An alternative pathway would be a homolytic cleavage of the B–I bond, but there seems to be evidence that it does not take place with [Pd(PPh$_3$)$_4$] [4]. To see if an electron transfer, basically a reduction, could also explain the formation of the *o*-carborane, a reducing agent that cannot undergo additive oxidation was chosen. Although the coupling of two aryl halides with sodium is impractical [13], the fate of 3-I-*o*-carborane with this metal was tested. Reaction of 3-I-*o*-carborane with Na/naphthalene produced after working up the *o*-carborane. Thus, the hydrodehalogenation has again taken place, albeit an oxidative addition is impossible in this case. We pursued this issue further by performing the reaction with Mg. It is well known that aryl iodides react directly with magnesium to give Grignard reagents, and the similarity of 3-I-*o*-carborane with iodophenyl should have produced, a priori, the Grignard derivatives of 3-*o*-carborane. Furthermore it is generally accepted that the mechanism of this reaction involves free radicals [13]. The reaction was done in THF, adding a few crystals of I$_2$ as a catalyst. Under these conditions the reaction proceeded very slowly. After 10 days at reflux, and following the sequential addition of minor amounts of I$_2$, the reaction was considered terminated. The $^{11}$B-NMR of the mother liquor, done in a concentric tube, proved that *o*-carborane had been produced. The reaction was considerably accelerated when 1,2-dibromoethane, that produces ethene, was added as a catalyst. Within 12 h at room temperature, the total conversion of 3-I-*o*-carborane to *o*-carborane had taken place. Another observation was that upon reaction of 3-I-*o*-carborane with Mg for 12 h, in THF, at reflux and with 1,2-dibromoethane, an anionic species was generated. This could be isolated as the [NMe$_4$]$^+$ salt. The $^{11}$B-NMR displayed a 2:1:1:2:2:2 pattern, with resonances at 16.4, 12.1, +0.8, −7.9, −15.8, −22.2 ppm that could be assigned to [7,10-C$_2$B$_{10}$H$_{13}$]$^-$ according to published data [14]. To ascertain if 3-I-*o*-carborane was necessary to produce this reaction, *o*-carborane was treated under the same conditions, to say in THF, at reflux, with Mg and 1,2-dibromoethane, for 9 h. The result was identical. This



Scheme 2. Synthesis of $[7,10\text{-}C_2B_{10}H_{13}]^-$.

indicates that the sequence 3-I-*o*-carborane → *o*-carborane → $[7,10\text{-}C_2B_{10}H_{13}]^-$ is the one that takes place.

It has been well documented that alkali metals can reduce the neutral carborane $C_2B_{10}H_{10}R_2$ to the carborane dianion $[nido\text{-}C_2B_{10}H_{10}R_2]^{2-}$, which is able to form the 13-vertex *closo*-metallacarboranes with the metal ions in a $\eta^6$ fashion [15]. The $[C_2B_{10}H_{12}]^{2-}$ anions have recently experienced a renewed interest [16], mainly in its capacity to produce U, Dy, Y, Er and Sm complexes. The monoanion $[7,10\text{-}C_2B_{10}H_{13}]^-$ can be produced by reduction of any of the $C_2B_{10}H_{12}$ isomers [17] although the more convenient is $1,2\text{-}C_2B_{10}H_{12}$. Upon its reduction with sodium metal, in THF at room temperature for 15 h, the dianion $[C_2B_{10}H_{12}]^{2-}$ is obtained. Treatment of the $Na_2C_2B_{10}H_{12}$ solution in THF with aqueous 0.1 N NaOH yielded after considerable working up $[NMe_4][7,10\text{-}C_2B_{10}H_{13}]$, in overall 20% yield. The procedure reported here is considerably more simple and produces a 97% yield of $[NMe_4][7,10\text{-}C_2B_{10}H_{13}]$. It uses Mg instead of Na, which already represents an advantage for the easiness of use, and requires an easy working up. Basically, $1,2\text{-}C_2B_{10}H_{12}$ and Mg in excess are refluxed in THF for 9 h in the presence of $I_2$ and 1,2-dibromoethane. After working up and treatment of the water solution with $[NMe_4]Cl$ the species $[NMe_4][7,10\text{-}C_2B_{10}H_{13}]$ is obtained.

In conclusion, in this report we have intended to produce new information concerning the reactivity of B–I in *o*-carborane. Our results are in agreement with those reported by Grushing et al., however, it is not so clear whether the mechanism goes through an oxidative addition. While the end product is the same, the *o*-carborane, we have shown that Na, which cannot undergo oxidative addition leads to the same product. Also, the statement that the reaction does not take place via a radical mechanism is not supported by the fact that the *o*-carborane is also produced by a Grignard reaction which is accepted to take place via this mechanism. Most possibly, different mechanisms take place. What seems to be clear is that the *o*-carborane formation is a favored process, probably due to kinetic considerations, which compete favorably with other desired products. More efforts are needed to activate the B–I bond, avoiding the competition of hydrogen, either radical or a proton that prevents their use as a convenient starting material.

Finally we have proven that $[7,10\text{-}C_2B_{10}H_{13}]^-$ an anion that surprisingly has not received much attention, can be synthesized in high yield by reduction with Mg with the concourse of 1,2-dibromoethane (Scheme 2).

## 3. Experimental

### 3.1. General

$^1$H-NMR (300.13 MHz), $^{11}$B-NMR, $^{11}B\{^1H\}$-NMR (96.29 MHz) and $^{31}$P-, $^{31}P\{^1H\}$-NMR (121.5 MHz) spectra were recorded in a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Most of the NMR spectra were recorded from acetone-$d^6$ concentric tubes at 25 °C. The acetone-$d^6$ was in the inner tube. The outer tube contained the sample in a non-deuterated dry solvent. Chemical shift values for $^{11}$B-NMR spectra were referenced to external $BF_3{\cdot}OEt_2$ and those for $^1$H-, $^1H\{^{11}B\}$-NMR spectra were referenced to $Me_4Si$. $^{31}$P- and $^{31}P\{^1H\}$-NMR spectra were referenced to an external 85% $H_3PO_4$. Chemical shifts are reported in units of parts per million downfield from $Me_4Si$, and all coupling constants are reported in Hz.

Unless otherwise noted, all manipulations were carried out under $N_2$ atmosphere using standard vacuum line techniques. Toluene and THF were distilled from sodium benzophenone prior to use. DMF was distilled from CaO and Py from CaH. $[Ni(PPh_3)_3]$ [18] and $[Pd(PPh_3)_4]$ [19] were synthesized by published methods.

### 3.2. Reaction of 3-I-*o*-carborane with Cu

#### 3.2.1. In the presence of $PPh_3$

3-I-*o*-Carborane (100 mg, 0.37 mmol), triphenylphosphine (97 mg, 0.37 mmol) and activated Cu metal (235 mg, 3.7 mmol) were placed in a capillary. After sealing, it was heated in the oven at 300 °C for 24 h. After it was cooled down, the residue was extracted with acetone and evaporated to dryness to get *o*-carborane (53 mg) in 100% yield.

#### 3.2.2. In the absence of $PPh_3$

As above with 3-I-*o*-carborane (100 mg, 0.37 mmol) and activated Cu metal (235 mg, 3.7 mmol) to get 25 mg of *o*-carborane in 48% yield.

### 3.3. Reaction of 3-I-*o*-carborane with $[Ni(PPh_3)_3]$

#### 3.3.1. In toluene, THF or pyridine

To a 25 ml Schlenk flask were added $[NiCl_2(PPh_3)_2]$ (653 mg, 1 mmol), $PPh_3$ (524 mg, 2 mmol), Zn (66 mg, 1 mmol) and 5 ml of the dry solvent. The mixture was heated at 50 °C in an oil bath for 1 h. A solution of 3-I-*o*-carborane (270 mg, 1 mmol) in dry solvent was added to the mixture. Stirring was continued under $N_2$

at 50 °C for 24 h. The solution contained only *o*-carborane.

### 3.3.2. In DMF

The same as above was done but in DMF, obtaining a mixture of *o*-carborane (95%) and *nido*-*o*-carborane (5%).

### 3.4. Reaction of 3-I-*o*-carborane with $[Pd(PPh_3)_4]$

To a 25 ml Schlenk flask were added $[Pd(PPh_3)_4]$ (577 mg, 0.5 mmol), $K_2CO_3$ (691 mg, 5 mmol) and 5 ml of dry DMF. The mixture was heated at 50 °C in an oil bath for 1 h. A solution of 3-I-*o*-carborane (135 mg, 0.5 mmol) in dry DMF was added to the mixture and was continued stirring under $N_2$ at 50 °C during 24 h. The solution contained *nido*-*o*-carborane in 100% yield as the only final product.

### 3.5. Synthesis of $[N(CH_3)_4][7,10\text{-}C_2B_{10}H_{13}]$

To a 100 ml Schlenk flask were added Mg metal (1.0 g, 41 mmol), 2 ml of THF and a crystal of $I_2$. Then, dibromoethane (0.5 ml, 6.0 mmol) and a solution of *o*-carborane (1.0 g, 7.0 mmol) in THF (40 ml) were added dropwise, at the same time, to the Mg suspension at 0 °C. Once the addition was completed the reaction mixture was left at room temperature for 30 min. After 9 h at reflux the mixture was evaporated to dryness in vacuo and water (60 ml) was added to the residue, filtered and the anion was precipitated from the aqueous solution with an excess of $[NMe_4]Cl$. The white solid was washed with water and $Et_2O$. The compound $[NMe_4][7,10\text{-}C_2B_{10}H_{13}]$ was obtained in 97% yield (1.5 g, 6.8 mmol). $^1$H-NMR ($CD_3COCD_3$, 25 °C): $\delta$ 3.40 (s, $N(CH_3)_4$, 12H), 3.21 (d, C–H, 1H, $J$(H,H) = 7.4 Hz), 2.81 (d, C–H, 1H, $J$(H,H) = 7.4 Hz), 2.54 (s, C–H, 1H). $^{11}$B-NMR ($CD_3COCD_3$, 25 °C): $\delta$ +16.4 (d, 2B, $J$(B–H) = 151 Hz), +12.1 (d, 1B, $J$(B–H) = 135 Hz), +0.8 (d, 1B, $J$(B–H) = 135 Hz), −7.9 (d, 2B, $J$(B–H) = 148 Hz), −15.8 (d, 2B, $J$(B–H) = 135 Hz), −22.2 (d, 2B, $J$(B–H) = 139 Hz).

## Acknowledgements

G.B. thanks CSIC and Carburos Metálicos for a grant. This work was supported by project MAT98-0921.

## References

[1] V.I. Bregadze, Chem. Rev. 92 (1992) 209.

[2] (a) L.I. Zakharkin, A.I. Kovredov, V.A. Ol'shevskaya, Zh.S. Shaugumbekova, Izv. Akad. Nauk. SSSR Ser. Khim. (1980) 1691;
(b) A.I. Kovredov, Zh.S. Shaugumbekova, P.V. Petrovskii, L.I. Zakharkin, Zh. Obshch. Khim. 59 (1989) 607;
(c) L.I. Zakharkin, A.I. Kovredov, V.A. Ol'shevskaya, Zh.S. Shaugumbekova, J. Organomet. Chem. 226 (1982) 217;
(d) Z. Zheng, W. Jiang, A.A. Zinn, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 34 (1995) 2095;
(e) W. Jiang, C.B. Knobler, C.E. Curtis, M.D. Mortimer, M.F. Hawthorne, Inorg. Chem. 34 (1995) 3491;
(f) T. Peyman, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 37 (1998) 1544;
(g) B. Grüner, Z. Janousek, B.T. King, J.N. Woodford, C.H. Wang, V. Vsetecka, J. Michl, J. Am. Chem. Soc. 121 (1999) 3122;
(h) J. Li, C.F. Logan, M. Jones Jr., Inorg. Chem. 30 (1991) 4866;
(i) C. Viñas, G. Barberà, J.M. Oliva, F. Teixidor, A.J. Welch, G.M. Rosair, Inorg. Chem. in press.

[3] (a) V.V. Grushin, Acc. Chem. Res. 25 (1992) 529;
(b) V.V. Grushin, I.I. Demkina, T.P.J. Tolstaya, J. Chem. Soc. Perkin Trans. 2 (1992) 505.

[4] W.J. Marshall, R.J. Young Jr., V.V. Grushin, Organometallics 20 (2001) 523 (and references therein).

[5] (a) G.A. Olah, G.K.S. Prasash, R.E. Williams, L.E. Fidd, K. Wade, Hypercarbon Chemistry, Wiley, New York, 1987;
(b) B.J. Gimarc, M. Zhao, Inorg. Chem. 35 (1996) 825;
(c) R. Núñez, C. Viñas, F. Teixidor, R. Sillanpää, R. Kivekäs, J. Organomet. Chem. 22 (1999) 592.

[6] (a) C. Amatore, A. Jutand, Acc. Chem. Res. 33 (2000) 314;
(b) B. Chauder, L. Green, V. Snieckus, Pure Appl. Chem. 71 (1999) 1521;
(c) D.J. Cardenas, Angew. Chem. Int. Ed. Engl. 38 (1999) 3018.

[7] J. Li, C.F. Logan, M. Jones Jr., Inorg. Chem. 30 (1991) 4866.

[8] (a) R. Boese, J.R. Green, J. Mittendorf, D.L. Mohler, P.C. Volhardt, Angew. Chem. Int. Ed. Engl. 31 (1992) 1643;
(b) R. Stümer, Angew. Chem. Int. Ed. Engl. 38 (1999) 3307;
(c) M.F. Semmelhack, P.M. Helquist, L.D. Jones, J. Am. Chem. Soc. 93 (1971) 5909.

[9] In fact trace amounts of *m*-carborane and $[PdI_2(PPh_3)_2]$ have been observed.

[10] B.E. Mann, A.J. Mesco, J. Chem. Soc. Dalton Trans. (1975) 1673.

[11] V. Mark, C.H. Dungan, M.M. Crutchfield, J.R. Van Wazer, Compilation of $^{31}$P NMR Data, Montsanto Company, St. Louis, MO, 1967 (chap. 4).

[12] Although we do not have conclusive evidence on the formation of the *cis*-$[PdI_2(PPh_3)_2]$ simply because there are no literature data neither on its synthesis nor, obviously, on their NMR, a comparison between available *cis*- and *trans*-$[PdX_2(PR_3)_2]$ complexes supports that the resonance at 25.9 ppm could be assigned to *cis*-$[PdI_2(PPh_3)_2]$.

[13] J. March, Advanced Organic Chemistry, Wiley, New York, 1992, pp. 449 and 624.

[14] D.F. Dustin, G.B. Dunks, M.F. Hawthorne, J. Am. Chem. Soc. 95 (1973) 1109.

[15] (a) A.K. Saxena, N.S. Hosmane, Chem. Rev. 93 (1993) 1081;
(b) R.N. Grimes, in: E.W. Abel, F.A.G. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 1, Pergamon, New York, 1995, p. 373;
(c) A.K. Saxena, J.A. Maguire, N.S. Hosmane, Chem. Rev. 97 (1997) 2421;
(d) G.B. Dunks, M.M. McKown, M.F. Hawthorne, J. Am. Chem. Soc. 93 (1971) 2541.

[16] (a) K. Chui, Q. Yang, T.C.W. Mak, Z. Xie, Organometallics 19 (2000) 1391;
(b) K. Chui, Q. Yang, T.C.W. Mak, W.H. Lam, Z. Lin, Z. Xie, J. Am. Chem. Soc. 122 (2000) 5758;
(c) Z. Xie, C. Yan, Q. Yang, T.C.W. Mak, Angew. Chem. Int. Ed. Engl. 38 (1999) 1761.

[17] G.B. Dunks, R.J. Wiersema, M.F. Hawthorne, J. Am. Chem. Soc. 95 (1993) 3174.

[18] A.S. Kende, L.S. Liebeskind, D.M. Braitsch, Tetrahedron Lett. 39 (1975) 3375.

[19] D.R. Coulson, Inorg. Syn. 13 (1972) 121.