Journal of Organometallic Chemistry 798 (2015) 171–181

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Poly-iodinated *closo* 1,2-C_2B_{10} and *nido* $[7,8\text{-}C_2B_9]^-$ carborane frameworks: Synthesis and consequences

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ARTICLE INFO

Article history:
Received 10 April 2015
Received in revised form
26 May 2015
Accepted 27 May 2015
Available online 20 June 2015

Dedicated to Prof. Russell N. Grimes, a true pioneer in the field of Boron chemistry that contributed substantially to the understanding and evolution of Boron clusters, on the occasion of his 80th birthday.

Keywords:
Carboranes
Iodination
Acidity
Solvent free

ABSTRACT

The preparation of C_c-monosubstituted *closo* and *nido* carborane derivatives, mono-, di and tetraiodinated is reported. Some of these mono-to poly-iodinated *nido* carboranes are studied in terms of the acidity of the open face bridging proton, their chemical shift position in the ^{1}H NMR, and the lesser tendency to η^5-coordination in parallel to a larger number of iodo groups.

1. Introduction

Highly iodinated molecules have been of interest in materials science and medical applications [1] including the potential use of iodinated *ortho*-carboranes as next-generation radiopaque contrast agents for X-ray diagnostic imaging [2]. These compounds have a much larger ratio of iodine in their structures than the iodinated organic compounds currently used in X-ray contrast agents. Clean and effective syntheses are still the critical issue for the consideration of highly iodinated *o*-carboranes as realistic candidates for X-ray contrast agents [3]. However, the recent development of a fast, solvent free synthetic procedure has allowed the preparation of 1-R-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_7$ and 1,2-R_2-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_6$ (R = H, Me, Ph) derivatives by direct reaction of *o*-carboranes (1,2-*closo*-$C_2B_{10}H_{12}$, 1-R-1,2-*closo*-$C_2B_{10}H_{11}$ and 1,2-R_2-1,2-*closo*-$C_2B_{10}H_{10}$) and iodine in sealed tubes [4,5]. Appealingly, the procedure does not require any solvent-based workup and the iodine excess is recovered and re-utilized. The C-substituted counterparts require slightly shorter reaction times, for the same degree of iodination, than the parent *o*-carborane. This result is consistent with both theoretical [6] and experimental data [7] reported by Lipscomb and co-workers, which showed that the electron-donating effect of methyl groups bonded to the C_{cluster} atoms (C_c) causes a uniform increase in electron density on the B atoms, while having little or no effect on the sequence of substitution.

Although halogenated *nido* carboranes have potential relevance to important topics such as radioiodine carrier [8] and as boron neutron capture therapy (BNCT) reagents [9], relatively few B-iodinated $[7,8\text{-}nido\text{-}C_2B_9]^-$ derivatives are known. Two ways have been reported for the synthesis of *nido* B-iodine *o*-carborane derivatives: i) by electrophilic iodination of the boron vertexes of the anionic $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$ cluster, leading to *nido* carboranes substituted at the 9 and 11 positions, that are the sites of highest electron density as a result of their position in the open pentagonal face of the *nido* cluster [10] and, ii) by partial deboronation of related B–I *closo* clusters. The reported B–I *nido* carboranes are: the monoiodinated $[5\text{-I-}nido\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]^-$ [11–13] and $[9\text{-I-}nido\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]^-$ [11,14], the diiodinated $[7,8\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ [11], $[9,11\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ [11,14,15] and [5,6-I_2-

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http://dx.doi.org/10.1016/j.jorganchem.2015.05.053

7,8-*nido*-$C_2B_9H_{10}]^-$ [13], triiodinated [5,6,9-I_3-7,8-*nido*-$C_2B_9H_9]^-$ [13], and tetraiodinated [1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_8]^-$ [16]. The vertexes numbering of neutral 1,2-*closo*-$C_2B_{10}H_{12}$ and anionic [7,8-*nido*-$C_2B_9H_{12}]^-$/[7,8-*nido*-$C_2B_9H_{11}]^{2-}$ platforms are indicated in Chart 1.

In this paper, we describe the syntheses of a set of *closo* B-iodinated derivatives of monosubstituted 1-R-*closo*-$C_2B_{10}H_{11}$ clusters and the consequences of their deboronation that lead to highly regioselective B-iodinated *nido* counterparts, and to study the influence of the iodo groups in their acidity particularly on the open face bridging hydrogen.

2. Materials and methods

All manipulations were carried out under inert atmosphere. 1,2-dimethoxyethane (DME) and THF were distilled from sodium benzophenone prior to use. Reagents were obtained commercially and used as purchased. 1,2-*closo*-$C_2B_{10}H_{12}$, 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$, 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ were obtained from Katchem. IR spectra (ν, cm^{-1}; ATR or KBr pellets) were obtained on a Shimadzu FTIR-8300 spectrophotometer. The ^1H- and $^1H\{^{11}B\}$-NMR (300.13 MHz), $^{13}C\{^1H\}$-NMR (75.47 MHz) and ^{11}B- and $^{11}B\{^1H\}$-NMR (96.29 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in acetone-d_6 at 22 °C. The ^{11}B- and $^{11}B\{^1H\}$-NMR shifts were referenced to external $BF_3 \cdot OEt_2$, while the ^1H, $^1H\{^{11}B\}$ and $^{13}C\{^1H\}$-NMR shifts were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. The mass spectra were recorded in the negative ion mode using a BrukerBiflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)].

2.1. *Synthesis of the mixture 1-Me-9-I-1,2-closo-$C_2B_{10}H_{10}$ and 1-Me-12-I-1,2-closo-$C_2B_{10}H_{10}$*

A 25 mL round-bottomed flask was charged with 1-Me-1,2-*closo*-$C_2B_{10}H_{10}$ (250 mg, 1.57 mmol) and iodine (4.00 g, 15.97 mmol), closed and sealed to air with Teflon. The flask was then introduced in an oil bath at a temperature of 120 °C, maintained for 45 min and then allowed to cool slowly to room temperature. Excess iodine was effectively separated by sublimation from the reaction mixture at 50 °C under reduced pressure to give 1-Me-9-I-1,2-*closo*-$C_2B_{10}H_{10}$/1-Me-12-I-1,2-*closo*-$C_2B_{10}H_{10}$ as a yellowish solid. (330 mg, 74%). IR (KBr): $\nu = 3040$ (C_c-H), 2932, 2868 (C_{alkyl}-H), 2579 (B—H). ^1H NMR ($CDCl_3$): $\delta = 3.91$ (s, 1H, C_c-H), 3.72 (s, 1H, C_c-H), 2.66–2.27 (B—*H*), 2.08 (s, 3H, CH_3), 1.94 (s, 3H, CH_3). $^1H\{^{11}B\}$ (CD_3COCD_3): $\delta = 3.88$ (s, 1H, C_c-H), 3.69 (s, 1H, C_c-H), 2.66 (s, B—*H*), 2.60 (s, B—*H*), 2.42 (s, B—*H*), 2.30 (s, B—*H*), 2.27 (s, B—*H*), 2.08 (s, 3H, CH_3), 1.94 (s, 3H, CH_3). ^{11}B NMR ($CDCl_3$): $\delta = -0.4$ (d, ^1J(B,H) = 152), −5.6 (d, ^1J(B,H) = 201), −7.7 (d, ^1J(B,H) = 165), −10.4 (d, ^1J(B,H) = 88), −11.7 (d, ^1J(B,H) = 130), −12.9 (d, ^1J(B,H) = 118), −16.3 (br s, 1B, B—I), −19.4 (br s, 1B, B—I).

2.2. *Synthesis of the mixture 1-Ph-9-I-1,2-closo-$C_2B_{10}H_{10}$ and 1-Ph-12-I-1,2-closo-$C_2B_{10}H_{10}$*

The initial procedure was as before, in a 25 mL flask, 1-Ph-1,2-*closo*-$C_2B_{10}H_{10}$ (50 mg, 0.22 mmol) and iodine (574 mg, 2.25 mmol). The flask was then introduced in an oil bath at a temperature of 120 °C, maintained for 75 min at this temperature, and then allowed to cool slowly to room temperature. Then, diethyl ether enough to dissolve the product and a 10% aqueous solution of sodium metabisulphite were added to the residue. The mixture was vigorously shaken and the two layers were separated. The organic layer was washed in this way several times, until the complete quenching of the excess iodine. The organic phase was then dried over $MgSO_4$, filtered and the solvent removed under reduced pressure, to give 1-Ph-9-I-1,2-*closo*-$C_2B_{10}H_{10}$/1-Ph-12-I-1,2-*closo*-$C_2B_{10}H_{10}$ as a yellowish oil (59 mg, 75%). IR (KBr): $\nu = 3040$ (aromatic CH), 2932 (C_c-H), 2601 (B—H). ^1H NMR ($CDCl_3$): $\delta = 7.52$–7.39 (m, 5H, C_6H_5), 4.29 (s, 1H, C_c-H), 4.09 (s, 1H, C_c-H), 2.99–2.38 (B—*H*). $^1H\{^{11}B\}$ (CD_3COCD_3): $\delta = 7.52$–7.39 (m, 5H, C_6H_5), 4.29 (s, 1H, C_c-H), 4.09 (s, 1H, C_c-H), 2.99 (s, B—H), 2.80 (s, B—H), 2.70 (s, B—H), 2.61(s, B—H), 2.38 (s, B—*H*). ^{11}B NMR ($CDCl_3$): $\delta = -0.7$ (d, ^1J(B,H) = 159), −3.3 (d, ^1J(B,H) = 151), −7.5 (d, ^1J(B,H) = 158), −10.7 (d, ^1J(B,H) = 130), −11.4 (d, B—H), −12.7 (d, B—H), −16.4 (br s, 1B, B—I), −17.1 (br s, 1B, B—I).

2.3. *Synthesis of 1-Me-9,12-I_2-1,2-$C_2B_{10}H_9$*

A thick-walled Pyrex tube charged with 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ (250 mg, 1.57 mmol) and iodine (4.00 g, 15.79 mmol) was put under vacuum, cooled down with liquid nitrogen and sealed. The tube was then placed in a furnace and the temperature was raised to 170 °C during 30 min, maintained at this temperature for 3.5 h and then allowed to cool slowly to room temperature. Excess of iodine was effectively separated by sublimation from the reaction mixture at 50 °C under reduced pressure to give 1-Me-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$ as a yellowish solid. (485 mg, 75%). IR (KBr): $\nu = 3041$ (C_c-H), 2936, 2863 (C_{alkyl}-H), 2621, 2575 (B—H).^1H NMR ($CDCl_3$): $\delta = 4.01$ (br s, 1H, C_c-H), 3.75–1.75 (B—*H*), 1.98 (s, 3H, CH_3). $^1H\{^{11}B\}$ (CD_3COCD_3): $\delta = 4.01$ (br s, 1H, C_c-H), 2.85 (br s, 2H, B—*H*), 2.78 (br s, 4H, B—*H*), 2.49 (br s, 2H, B—*H*), 1.98 (s, 3H, CH_3). $^{13}C\{^1H\}$ ($CDCl_3$): $\delta = 68.11$ (s, C_c-CH_3), 59.17 (s, C_c-H), 25.49 (s, CH_3). ^{11}B NMR ($CDCl_3$): $\delta = -10.5$ (d, ^1J(B,H) = 156, 2B), −14.8 (d, ^1J(B,H) = 177, 2B), −15.9 (d, ^1J(B,H) = 173, 2B), −16.7 (d, ^1J(B,H) = 184, 2B), −18.4 (br s, 1B), −21.7 (br s, 1B). MALDI-TOFMS: *m*/*z* = 408.69 (23%) [M], 525.09 [M + I -B] (100%), 536.25 [M + I] (75%). Crystals suitable for X ray diffraction study were grown from mixture hexane/ethyl acetate (1/1).

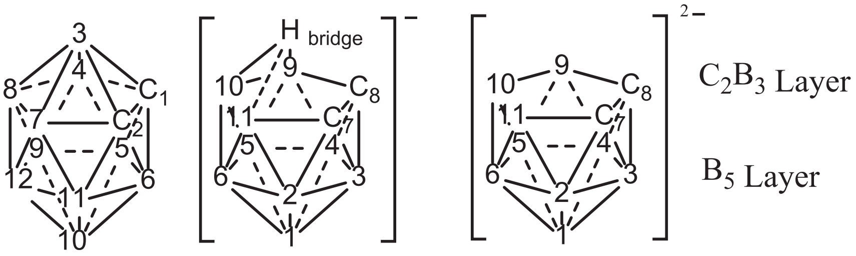


Chart 1. Icosahedral neutral 1,2-*closo*-$C_2B_{10}H_{12}$, monoanionic [7,8-*nido*-$C_2B_9H_{12}]^-$ and dianionic [7,8-*nido*-$C_2B_9H_{11}]^{2-}$ platforms with their numbering. Vertexes with numbers correspond to B. All vertexes, also including C, have external H or substituent.

2.4. Synthesis of 1-Ph-9,12-I_2-1,2-closo-$C_2B_{10}H_9$

A thick-walled Pyrex tube charged with 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ (250 mg, 1.12 mmol) and iodine (4.00 g, 11.29 mmol) was put under vacuum, cooled down with liquid nitrogen and sealed. The tube was then placed in a furnace and the temperature was raised to 170 °C during 30 min, maintained for 3.5 h at this temperature, and then allowed to cool slowly to room temperature. Then, diethyl ether enough to dissolve the product and a 10% aqueous solution of sodium metabisulphite were added to the residue. The mixture was vigorously shaken and the two layers were separated. The organic layer was washed in this way several times, until the complete quenching of the excess iodine. The organic phase was then dried over $MgSO_4$, filtered and the solvent removed under reduced pressure, to give 1-Ph-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$ as a brownish oil. (470 mg, 79%). IR (KBr): ν = 3042 (aromatic CH), 2923 (C_c-H), 2610 (B–H).^{1}H ($CDCl_3$): δ = 7.47 (d, 3H, ^3J(H,H) = 6, C_{aryl}-H), 7.39 (dd, 2H, ^3J(H,H) = 6, C_{aryl}-H), 4.38 (br s, 1H, C_c-H), 3.75–1.75 (B–*H*). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ = 7.47 (d, 3H, ^3J(H,H) = 6, C_{aryl}-H), 7.39 (dd, 2H, ^3J(H,H) = 6, C_{aryl}-H), 4.38 (br s, 1H, C_c-H), 4.38 (br s, 1H, C_c-H), 3.09 (br s, 2H, B–*H*), 3.00 (br s, 2H, B–*H*), 2.86 (br s, 2H, B–*H*), 2.76 (br s, 2H, B–*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 131.81, 131.00, 130.79, 130.05, 129.30, 127.52 (C_6H_5), 57.91 (C_c-H). ^{11}B NMR ($CDCl_3$): δ = −5.8 (d, ^1J(B,H) = 160, 2B), −10.4, −11.4, −12.1 (6B), −14.0 (br s, 1B), −15.1 (br s, 1B).

2.5. Synthesis of 1-Bz-2-Me-8,9,10,12-I_4-1,2-closo-$C_2B_{10}H_6$

The procedure was as for *1-Ph-9,12-I_2-1,2-closo-$C_2B_{10}H_9$* (R = Me, Ph) with1-Bz-2-Me-$C_2B_{10}H_{10}$ (0.2 g, 0.805 mmol) and iodine (2.043 g, 8.052 mmol). The tube was then placed in a furnace and the temperature gradually raised to 270 °C during 20 min, maintained for 3 h and allowed to drop slowly to room temperature. The mixture was then dissolved in diethyl ether (4 mL), and the excess of iodine quenched by addition of 5% aqueous solution $Na_2S_2O_5$ (4 mL). The mixture was thoroughly shaken and the two layers separated. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic phase was dried over $NaSO_4$, filtered and evaporated in vacuum. The resulting solid, 1-Bz-2-Me-8,9,10,12-I_4-1,2-$C_2B_{10}H_6$, was obtained in 77% yield (470 mg). Good crystals for X ray diffraction were grown from the mixture hexane/ethyl acetate (1/1). FTIR (KBr), ν (cm^{-1}): 2625, 2607 (s, B–H). ^{1}H NMR (CD_3COCD_3): δ 7.44 (5H, C_{aryl}-H), 3.80 (2H, s, CH_2), 2.43 (3H, s, C_c-CH_3). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ 7.44 (5H, C_{aryl}-H), 3.80 (2H, s, CH_2), 3.35, 3.20, 2.93 (s, B–H), 2.43 (3H, s, C_c-CH_3). ^{11}B NMR (CD_3COCD_3): δ −8.1, −9.5 (br s, 8B), −17.8 (br s, 2B–I). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.39, 130.52, 128.92, 128.55 (s, C_{aryl}), 79.37 (s, C_c), 76.77 (s, C_c), 39.74 (s, CH_2), 22.18 (s, CH_3).

2.6. Deboronation of the C_c-monosubstituted mono or polyiodinated closo o-carboranes

The carboranes described in the preceding sections have been deboranated as described in Refs. [13] and [16]. The crystal structures of [$HNMe_3$][5-I-7,8-*nido*-$C_2B_9H_{11}$] and [$HNMe_3$][7-Ph-1,8,9,12-I_4-7,8-*nido*-$C_2B_9H_7$] are reported in this paper.

2.6.1. Characterization of [NMe_4][9-I-7,8-nido-$C_2B_9H_{11}$]

The [NMe_4][9-I-7,8-*nido*-$C_2B_9H_{11}$] was prepared according to the general procedure described in the literature [14]. IR (KBr): ν (cm^{-1}) 3181, 3168 (C_c-H), 3097, 3037, 2958 (C_{alkyl}-H), 2574, 2518, 2430 (BH), 1474, 1467, 1446. ^{11}B NMR ($CDCl_3$): δ = +18.3 (s, B(9)), −5.2 (d, ^1J(B,H) = 138, 1B), −16.0 (d, ^1J(B,H) = 136, 1B), −17.8 (d, ^1J(B,H) = 148, 2B), −21.6 (d, ^1J(B,H) = 152, 1B), −24.9 (d, ^1J(B,H) = 138, 1B), −29.5 (d, ^1J(B,H) = 131, 1B), −37.4 (d, ^1J(B,H) = 140, 1B).

2.6.2. Characterization of [$HNMe_3$][9,11-I_2-7,8-nido-$C_2B_9H_{10}$]

The [$HNMe_3$][9,11-I_2-7,8-*nido*-$C_2B_9H_{10}$] was prepared according to the general procedure described in the literature [14]. IR (KBr): ν (cm^{-1}) 3140 (C_c-H), 3032, 2960 (C_{alkyl}-H), 2766 (Me_3N–H), 2584, 2561, 2539, 2521 (BH), 1474, 1449 (δ Me_3N–H). ^{11}B NMR ($CDCl_3$): δ = −12.8 (d, ^1J(B,H) = 143, 2B: B5+B6), −15.5 (d, ^1J(B,H) = 166, 1B: B3), −18.5 (d, ^1J(B,H) = 154, 2B: B4+B7), −19.9 (s, 2B: B9+B11), −28.1 (br d, ^1J(B,H) = 133, 1B: B10), −35.2 (d, ^1J(B,H) = 144, 1B: B1). ^{1}H NMR (CD_3COCD_3): δ 3.23 (s, NMe_3, 9H), 2.33 (s, C_c-H, 1H), 1.78 (s, C_c-H, 1H). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ 3.23 (s, NMe_3, 9H), 2.33 (s, C_c-H, 1H), 1.78 (s, C_c-H, 1H), 2.25, 1.98, 1.76, 1.43, 0.86, 0.65 (br s, B–H), −2.98 (t, ^1J(H,H) = 6, B–H–B).

2.7. X-ray structure analysis

X-ray crystal structure analyses for 1-Me-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$ and [$NHMe_3$][7-Ph-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$] were done with an EnrafNonius CCD area detector diffractometer with MoK_α radiation (λ = 0.71073 Å) at 123 K. The data sets were corrected for absorption using SADABS program [17]. X-ray crystal structure analysis for [$NHMe_3$][5,6,11-I_3-7,8-*nido*-$C_2B_9H_8$] was done with an Agilent Supernova diffractometer equipped with Atlas CCD area-detector using MoK_α radiation (λ = 0.71073 Å) at 123 K. The data set was corrected for absorption using a multifaceted crystal model as implemented in CrysAlisPro program package [18]. The structures were solved with the program SIR97 [19]; full-least-squares refinements on F^2 were performed with SHELXL97 [20] using anisotropic displacement parameters for most of the non-H atoms: The hydrogen atoms were treated as riding atoms using the SHELX97 default parameters or their positional parameters were refined isotropically according to the riding model. All calculations and graphics were done at WinGX platform [21]. Crystallographic data and structure refinement details are shown in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1058310–1058314. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html.

3. Results and discussion

3.1. B-iodinated closo 1-R-o-carborane (R = Me, Ph) derivatives: mono, di and tetraiodinated

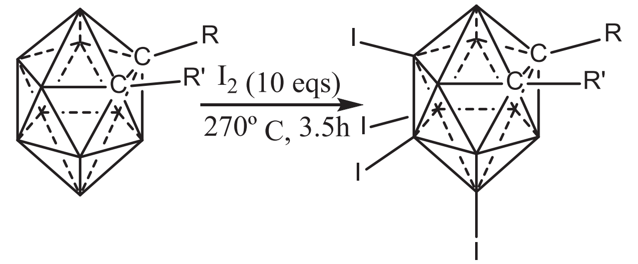
As described in a previous communication, a solvent-free regioselective tetraiodination on *o*-carboranes is effectively achieved by reaction of 1,2-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ (R = H, Me, Ph) and 1-R-1,2-*closo*-$C_2B_{10}H_{11}$ (R = Me, Ph) with excess iodine in sealed tubes (Scheme 1) [4].

In this paper, an extension of this fast, efficient and solvent free procedure was used to explore the versatility of the method in the iodination reaction to synthesize the *closo* monoiodinated compounds 1-R-9-I-1,2-*closo*-$C_2B_{10}H_{10}$/1-R-12-I-1,2-*closo*-$C_2B_{10}H_{10}$ and diiodinated 1-R-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$ as well as the C_c heterodisubstituted 1-Me-2-Bz-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_6$. We have tested the reaction of 1-R-1,2-*closo*-$C_2B_{10}H_{11}$ (R = Me, Ph) and iodine in a ratio 1:10 in sealed tubes under various experimental conditions (temperature and reaction time). The best results are shown in Table 2. Always, after the reaction is completed, volatiles, including HI, are carefully removed first by natural diffusion after mindful opening of the reaction flask glass tube, then by evaporation leaving the crude product as a solid that is analysed by $^1H\{^{11}B\}$ NMR spectra. Almost all of the iodine in excess (95%) could be

Table 1
Crystallographic data and structure refinement details for neutral *closo* carborane derivatives 1-Me-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$, **1**; 1-Me-2-Bz-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_6$, **2** compounds and the anionic *nido* derivatives [NMe_4][5-I-7,8-*nido*-$C_2B_9H_{11}$], **3**; [$HNMe_3$][5,6,11-I_3-7,8-*nido*-$C_2B_9H_9$], **4** and [$HNMe_3$][7-Ph-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$], **5**.

Compound	1	2	3	4	5
Formula	$C_3H_{12}B_{10}I_2$	$C_{10}H_{16}B_{10}I_4$	$C_6H_{22}B_9IN$	$C_5H_{19}B_9I_3N$	$C_{11}H_{22}B_9I_4N$
M_r	410.05	751.93	332.44	571.2	749.19
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group (no.)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)
a (Å)	8.9345(3)	9.421(13)	15.29(2)	6.9919(2)	13.5502(2)
b (Å)	12.7332(3)	16.59(2)	13.259(18)	17.5061(5)	12.3860(2)
c (Å)	11.4559(3)	15.685(17)	15.56(2)	14.3988(3)	14.9886(2)
α (°)	90	90	90	90	90
β (°)	97.6710(10)	113.05(6)	93.48(2)	92.382(10)	113.7250(10)
γ (°)	90	90	90	90	90
V (Å)	1291.61(6)	2256(5)	3149(7)	1760.90(8)	2302.98(6)
Z	4	4	8	4	4
D_c (g cm^{-1})	2.109	2.214	1.394	2.155	2.23
μ(MoK$_\alpha$) (mm^{-1})	4.821	5.517	2.005	5.301	5.409
T/K	123(2)	300(2)	173.5(2)	123(2)	123(2)
Observed reflections	2514	5249	5329	3026	4500
R_{int}	0.03	0.0417	0.0648	0.0264	0.0333
Parameters	137	218	310	184	235
$R[F^2 > 2\sigma(F^2)]$	0.0222	0.0605	0.1060	0.0282	0.0267
wR(F^2)[a]	0.0487	0.1646	0.3011	0.0592	0.0518
Largest peak, hole (e Å^{-3})	0.877, −0.567	1.611, −1.286	7.235, −3.241	1.962, −0.743	1.385, −0.818

[a] $w = 1/[s^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$



Scheme 1. General tetraiodination of 1-R-1,2-*closo*-$C_2B_{10}H_{11}$ (R = Me, Ph) by reaction with iodine in sealed tubes (R, R' = H, Me or Ph).

recovered from the mixture by sublimation under reduced pressure allowing further reuse of reagents.

As a representative example of these compounds, the ^{1}H NMR spectrum of the mixture of 1-Me-9-I-1,2-*closo*-$C_2B_{10}H_{10}$ and 1-Me-12-I-1,2-*closo*-$C_2B_{10}H_{10}$ display two broad singlets of the same intensity at 3.91 and 3.72 ppm and two singlets at 2.08 and 1.94 ppm corresponding to the C_c-H and the methyl groups (C_c-Me) of the two geometrical isomers. The $^{11}B\{^1H\}$ NMR spectra of these compounds also display two different resonances at high field that do not split when running ^{11}B NMR spectra in agreement with the presence of the two geometrical isomers with a B–I vertex. Fig. 1 shows the geometry of the two isomers while Fig. 2 displays the ^{1}H and ^{11}B NMR spectra of the isomers mixture.

Table 2
Mono, di and tetra iodination reaction of 1-R-1,2-*closo*-$C_2B_{10}H_{11}$ using iodine in a 1/10 M ratio.

R	T (°C)	t (h)	9-I-	9,12-I_2-	8,9,10,12-I_4-
H [5]	115	2.5	97%		
Me	120	0.75	74%		
Ph	120	1.25	75%		
H [5]	170	3.5		82%	
Me [4]	170	3.5		75%	
Ph [4]	170	3.5		79%	
H [4]	265	3.5			75%
Me [4]	265	3.5			>75%
Ph [4]	265	3.5			<75%

No attempt to separation regioisomers, 1-Me-9-I-1,2-*closo*-$C_2B_{10}H_{10}$ and 1-Me-12-I-1,2-*closo*-$C_2B_{10}H_{10}$, was made because our goal was to discern if the Me substituent bonded at one of the C_c would produce a major regioselective isomer. ^{1}H and ^{11}B NMR spectra of the mixture confirm same amount of each regioisomer and no antipodal influence of the C_c-Me on the electrophilic boron vertex substitution. The 1-R-9-I-1,2-*closo*-$C_2B_{10}H_{10}$ and 1-R-12-I-1,2-*closo*-$C_2B_{10}H_{10}$ (R = Ph, vinyl) regioisomers separation was recently reported for the investigation of polar liquid crystals [22].

In this paper, we report the single-crystal X-ray structure determination of 1-Me-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$ and 1-Me-2-Bz-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_6$.

3.2. Deboronation process of mono, di and tetraiodinated derivatives of closo 1-R-o-carborane (R = Me, Ph)

We have reported recently the partial deboronation reaction of *closo* 1-R-9-I-1,2-$C_2B_{10}H_{10}$, 1-R-12-I-1,2-$C_2B_{10}H_{10}$, 1-R-9,12-I_2-1,2-$C_2B_{10}H_9$ and 1-R-8,9,10,12-I_4-1,2-$C_2B_{10}H_7$ (R = Me, Ph) derivatives with KOH/EtOH under reflux conditions for 5 h that following precipitation with [$HNMe_3$]Cl leads to the formation of [$HNMe_3$][7-R-5-I-7,8-*nido*-$C_2B_9H_{10}$], [$HNMe_3$][7-R-6-I-7,8-*nido*-$C_2B_9H_{10}$], [$HNMe_3$][7-R-5,6-I_2-7,8-*nido*-$C_2B_9H_9$] and [$HNMe_3$][7-R-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$] in good to high yield [13]. The nucleophilic attack is produced selectively over one of the boron atoms that are directly bonded to the cluster carbons, because these boron

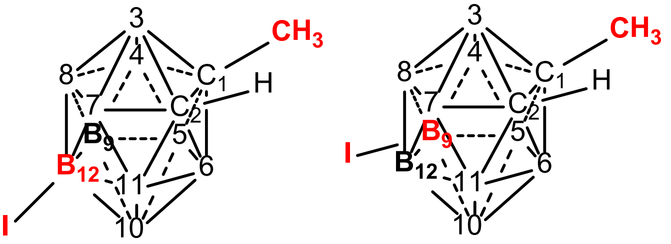


Fig. 1. The two mono B-iodinated isomers: 1-Me-12-I-*closo*-1,2-$C_2B_{10}H_{10}$ and 1-Me-9-I-*closo*-1,2-$C_2B_{10}H_{10}$.

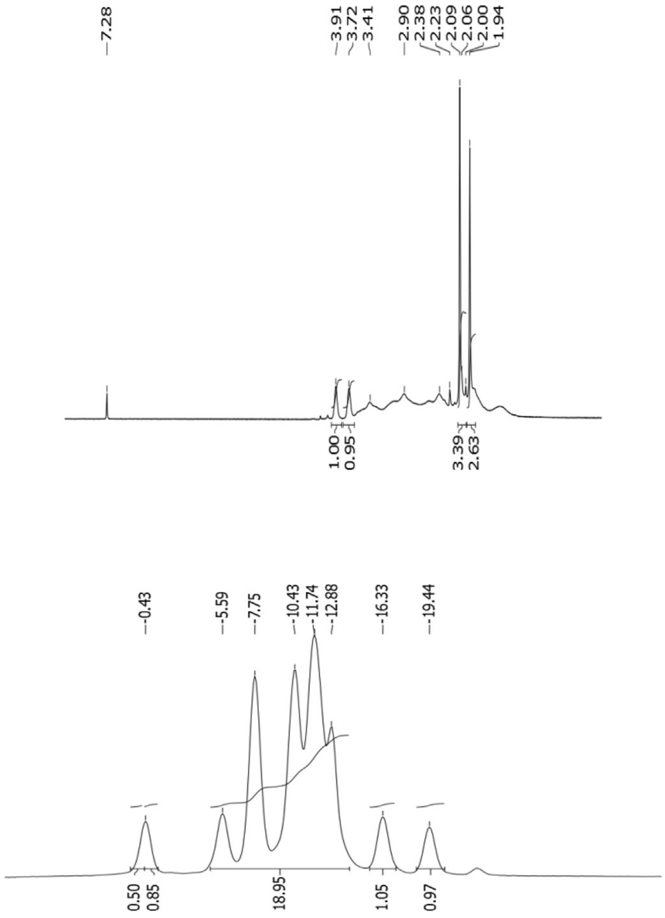


Fig. 2. ^{1}H and ^{11}B{^{1}H} NMR spectra of the mixture of isomers 1-Me-12-I-*closo*-1,2-$C_2B_{10}H_{10}$ and 1-Me-9-I-*closo*-1,2-$C_2B_{10}H_{10}$.

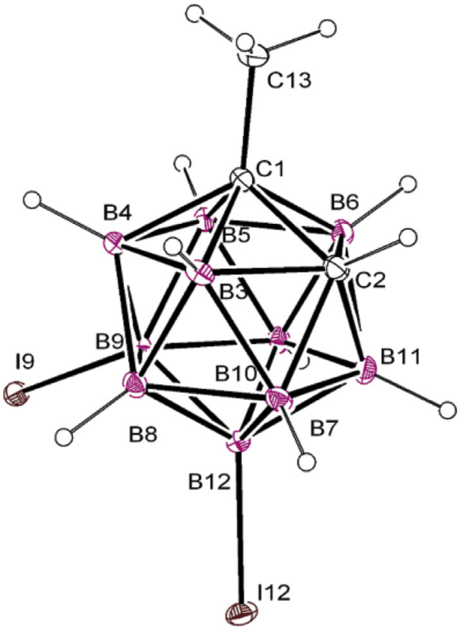
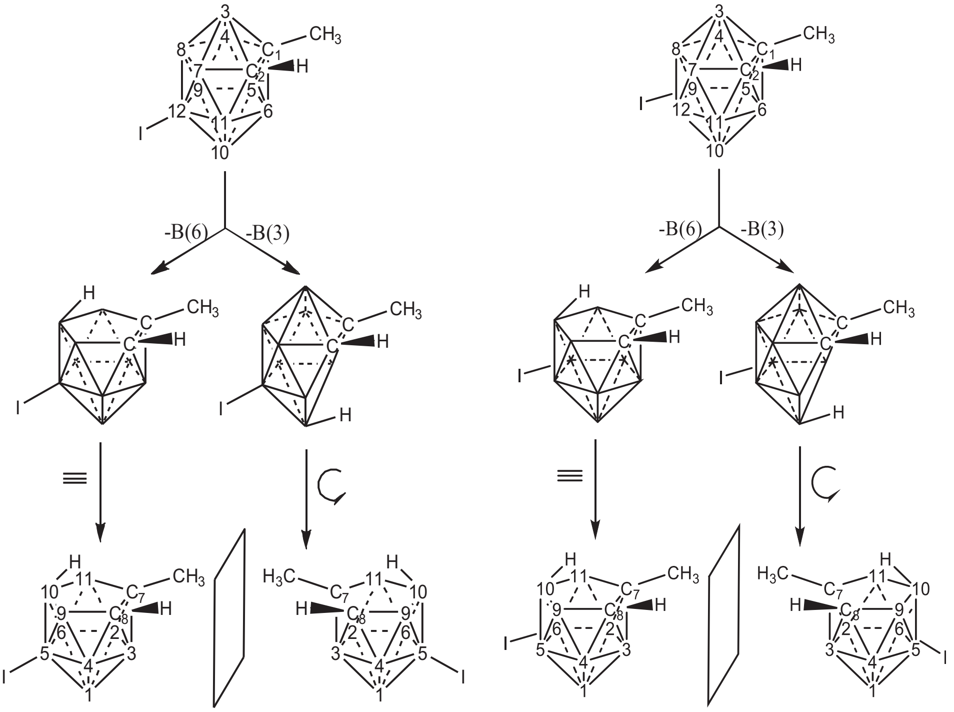


Fig. 3. ORTEP drawing of 1-Me-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$. Thermal displacement ellipsoids are drawn at 20% probability level. Selected bond lengths (Å): I9 − B9 = 2.174(4), I12 − B12 = 2.179(5), C1−C2 = 1.643(4). C1−C13 = 1.517(5).

atoms, either B(3) or B(6), are the ones most electronically impoverished (Scheme 2). The non-equivalence of the initial C_c substituents of the $[7,8\text{-}nido\text{-}C_2B_9]^-$ cluster resulted in the preparation of four isomers. No attempt to resolve the *nido*-carborane ligands into their enantiomers was made and the ligand racemic mixture was isolated.

All synthesized compounds, *closo* and *nido*, were characterized by ^{1}H-, ^{11}B, ^{13}C NMR and MALDI-TOF-MS spectroscopy [13]. The



Scheme 2. Anionic iodinated chiral ligands, $[7\text{-R-5-I-7,8-}nido\text{-}C_2B_9H_{10}]^-$ and $[7\text{-R-6-I-7,8-}nido\text{-}C_2B_9H_{10}]^-$.

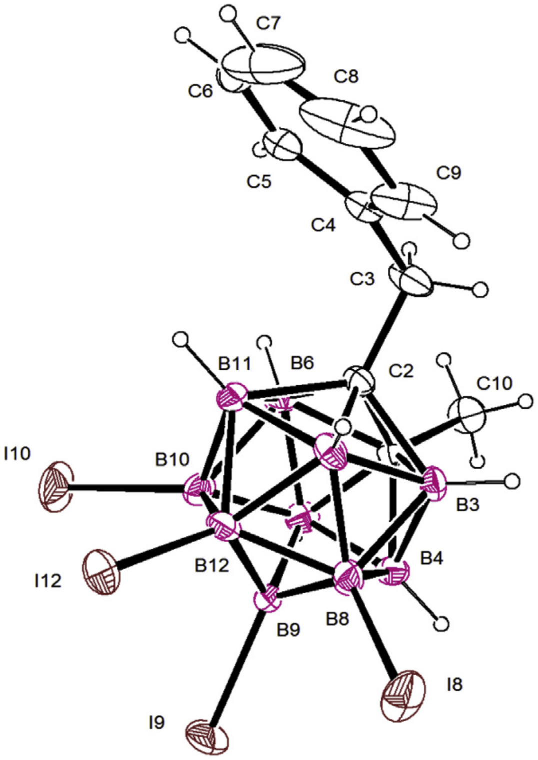


Fig. 4. ORTEP drawing of 1-Me-2-Bz-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_6$. Thermal displacement ellipsoids are drawn at 20% probability level.

single-crystal X-ray structure determination for $[NMe_4][5\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]$, $[HNMe_3][5,6,11\text{-}I_3\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]$ and $[HNMe_3][7\text{-}Ph\text{-}1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]$ are reported.

3.3. X-ray structure determination

Closo B-iodinated derivatives: Crystals suitable for X-ray diffraction of 1-Me-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$ (Fig. 3), and 1-Me-2-Bz-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_6$ (Fig. 4) were grown from a solution of hexane:ethyl acetate (1:1). *Nido* B-iodinated derivatives: Crystals suitable for X-ray diffraction of $[NMe_4][5\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]$ (Fig. 5), $[HNMe_3][5,6,11\text{-}I_3\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]$ (Fig. 6) and $[NHMe_3][7\text{-}Ph\text{-}1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]$ (Fig. 7) were grown from ethanol, water and chloroform solutions, respectively. The structural parameters in the compounds are normal. However, bond distances B11—C7 and B11—B10 are longer in tetra B-iodine compound than in tri B-iodine one (see the captions in Figs. 6 and 7).

Figs. 8 and 9 display the crystal packing showing the periodical weak C_c-H···I—B and C_c-H···H—B interactions of 1-Me-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$ and $[7\text{-}Ph\text{-}1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]^-$, respectively.

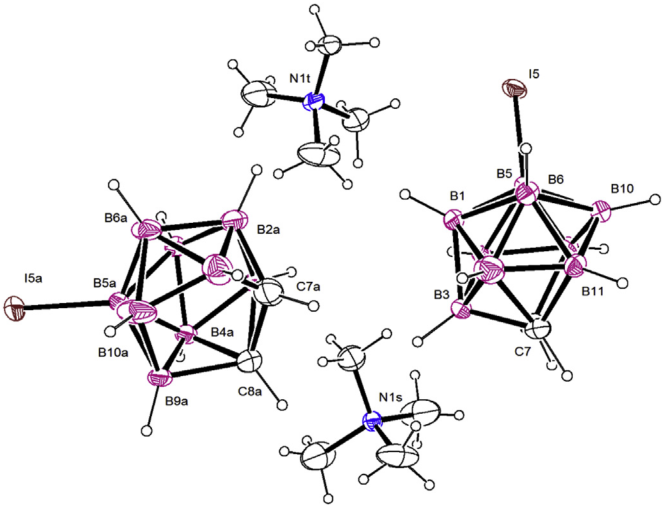


Fig. 5. ORTEP drawing of $[NMe_4][5\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]$. Thermal displacement ellipsoids are drawn at 20% probability level.

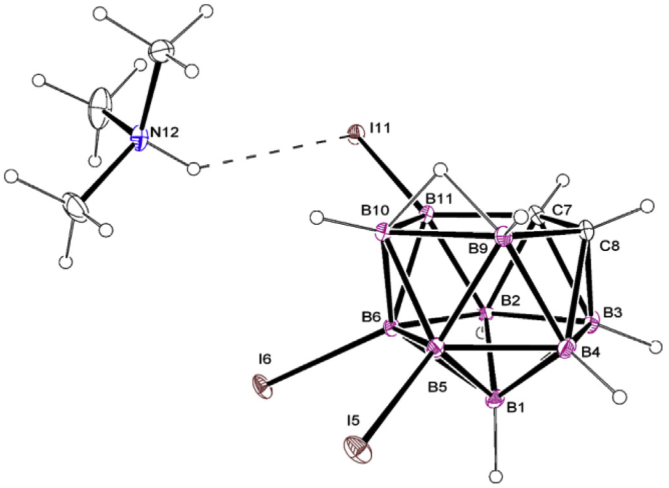


Fig. 6. ORTEP drawing of $[HNMe_3][5,6,11\text{-}I_3\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]$. Thermal displacement ellipsoids are drawn at 20% probability level. Selected bond lengths (Å): I5 — B5 = 2.183(5), I6 — B6 = 2.185(5), C7—C8 = 1.555(7), C8—B9 = 1.624(7), B9—B10 = 1.854(8), B10—B11 = 1.797(7), B11—C7 = 1.597(7).

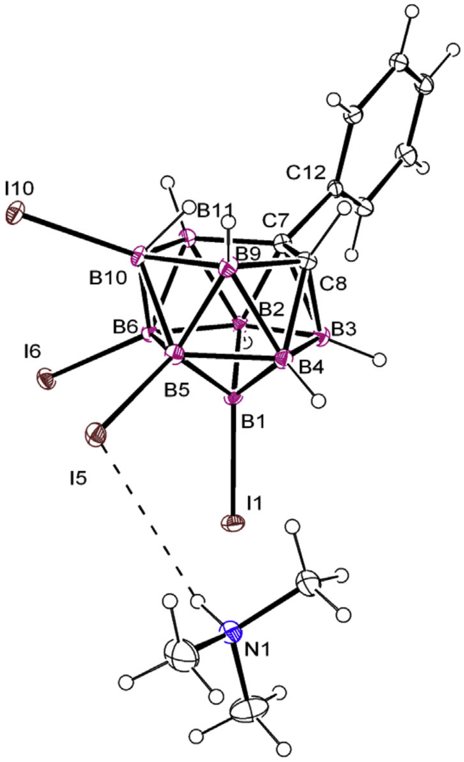


Fig. 7. ORTEP drawing of $[HNMe_3][7\text{-}Ph\text{-}1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]$. Thermal displacement ellipsoids are drawn at 20% probability level. Selected bond lengths (Å): I1 — B1 = 2.178(4), I5 —B5 = 2.190(4), I6 — B6 = 2.173(5), C7—C8 = 1.566(6), C8—B9 = 1.611(6), B9—B10 = 1.838(6), B10—B11 = 1.824(6), B11—C7 = 1.625(6).

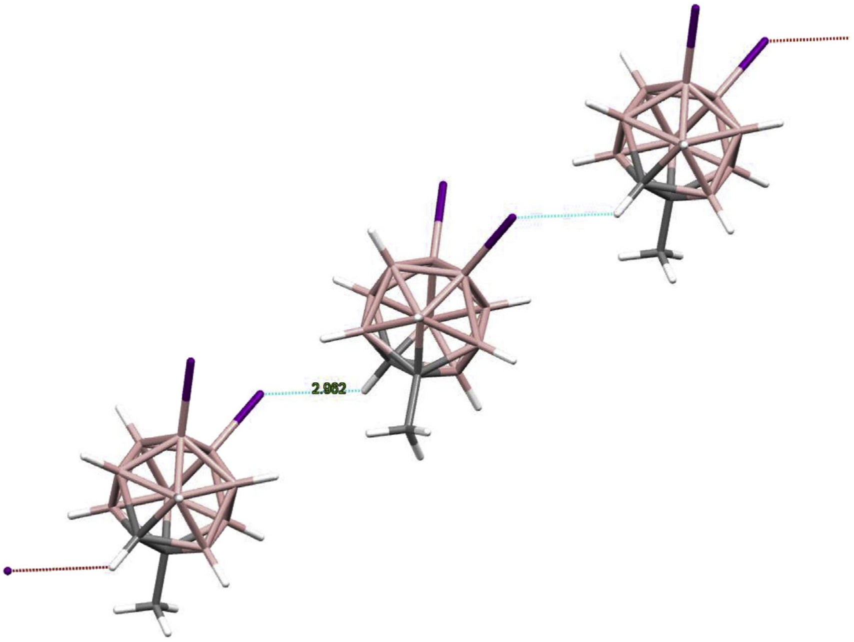


Fig. 8. Crystal structure of 1-Me-9,12-I_2-1,2-$C_2B_{10}H_9$ showing the C_c—H···I hydrogen bonding (I···H is 2.962 Å) of molecules forming an infinite zig-zag chains running parallel to the *b* crystallographic axis.

An examination of Cambridge Structural Database [23] shows just 28 X-ray structures of iodinated *closo* 1,2-C_2B_{10} carborane framework and 8 X-ray structures of iodinated *nido* [7,8-C_2B_9]$^-$ carborane framework that have been summarized in Table 3.

4. NMR spectral considerations on B-iodinated [7,8-*nido*-$C_2B_9H_{12}$]$^-$ derivatives

The sensitivity of the electron distribution in carboranes to the presence of substituents has long been apparent [24]. For icosahedral carborane derivatives of 1-R-1,2-*closo*-$C_2B_{10}H_{11}$, ^{11}B NMR studies have shown that the chemical shifts of the cage boron atoms vary with the substituent R [25], particularly on the boron atom opposite to the point of attachment of the substituent, the "antipodal atom" [26]. The ^{11}B NMR spectrum of *o*-carborane was rationalised in 1986 following a set of empirical rules incorporating antipodal, rhomboidal, butterfly and neighbour effects [27]. It was also reported that the presence of iodine atoms bonded to Boron vertexes in *closo o*-carborane modifies all the resonances of the ^{11}B NMR spectrum but the largest upfield shift is always due to the B—I [5,28]. In this paper the influence of B—I in the ^{11}B{^{1}H}-NMR as well as in the acidity of the hydrogen bridge has been studied.

4.1. Influence of the number of B—I vertexes of nido species on the ^{11}B{^{1}H}-NMR spectrum

The ^{11}B{^{1}H}-NMR spectra of [$HNMe)_3$][7,8-*nido*-$C_2B_9H_{12}$], [$HNMe_3$][5,6-I_2-7,8-*nido*-$C_2B_9H_{10}$], and [$HNMe_3$][1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_8$], are in the range −7 to −38 ppm, characteristic to *o*-carborane derived *nido* species [29]. Fig. 10 shows the influence of the successive B-iodinations on the chemical shifts of ^{11}B{^{1}H} NMR spectra of the *nido o*-carborane derivatives. The [$HNMe_3$][5,6-I_2-7,8-*nido*-$C_2B_9H_{10}$] spectrum displays the same number of resonances (2:1:2:2:1:1) of the non-iodinated [$HNMe_3$][7,8-*nido*-$C_2B_9H_{12}$] cluster parent (2:2:1:2:1:1) from low to high field but different pattern. Conversely, for the case of [$HNMe_3$][1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_8$], the pattern is 2:1:4:2 (low to high field). Neither the resonance at $\delta = -24.0$ ppm for [$HNMe_3$][5,6-I_2-7,8-*nido*-

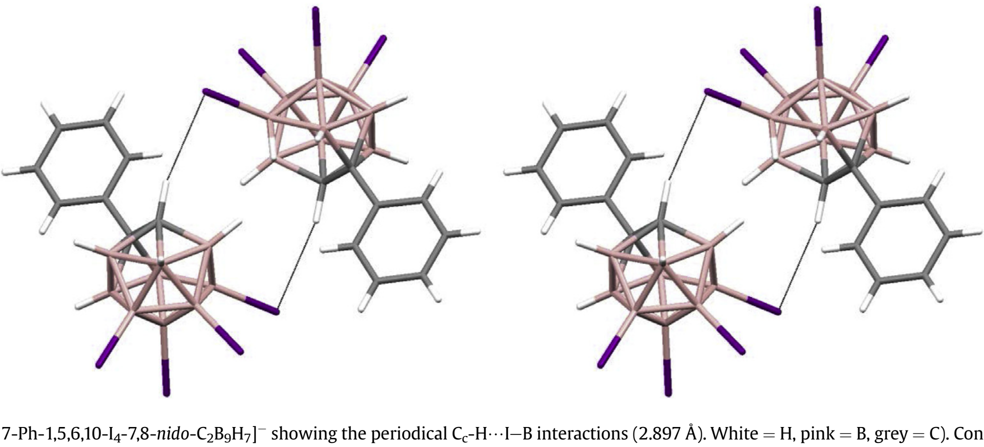


Fig. 9. Crystal packing of [7-Ph-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$]$^-$ showing the periodical C_c-H···I—B interactions (2.897 Å). White = H, pink = B, grey = C). Contacts shorter than the sum of Van der Waals radii (−0.2 Å) are plotted as dashed dark lines.

Table 3
Crystal structures reported on iodinated neutral *closo* 1,2-C_2B_{10} and monoanionic *nido* $[7,8\text{-}C_2B_9]^-$ carborane frameworks.

		Compound	CCDC code	Reference
1,2-*closo*-C_2B_{10} framework	Mono-iodinated	$[12\text{-IPh-1,2-}closo\text{-}C_2B_{10}H_{11}]I$	CARLAI	[34]
		9-I-1-SiMe$_2$*t*Bu-1,2-*closo*-$C_2B_{10}H_{10}$	HAWPAY	[35]
		12-I-1-SiMe$_2$*t*Bu-1,2-*closo*-$C_2B_{10}H_{10}$	HAWPEC	[35]
		9-I-1-CHMeOEt-1,2-*closo*-$C_2B_{10}H_{10}$	IZEYAO	[36]
		9-I-1,2-Ph$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	KIYCUQ	[37]
		9-Et-12-I-1,2-*closo*-$C_2B_{10}H_{10}$	LICJOW	[38]
		12-I-1,2-*closo*-$C_2B_{10}H_{11}$	WUNDEP	[39]
		12-I-1,2-*closo*-$C_2B_{10}H_{11}$	WUNDEP01	[40]
		9-X-12-Y-3,4,5,6,7,8,10,11-Me$_8$-1,2-*closo*-$C_2B_{10}H_2$ (X,Y = I,Cl)	XARHUU	[41]
		8-I-1,2-*closo*-$C_2B_{10}H_{11}$		[42]
		8-I-1-COOEt-1,2-*closo*-$C_2B_{10}H_{10}$		[42]
	Di-iodinated	9,12-I$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	LICJUC	[38]
		9,12-I$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	WURVOU	[43]
		3,10-I$_2$-1,2-*closo*-$C_2B_{10}H_{10}$		[42]
		9,12-I$_2$-1,2-Ph$_2$-1,2-*closo*-$C_2B_{10}H_8$	BAQZUP	[44]
		9,12-I$_2$-8,10-Ph$_2$-1,2-*closo*-$C_2B_{10}H_8$	ULOYAW	[45]
		9,12-I$_2$-1,2-Ni(PPh$_3$)$_2$—1,2-*closo*-$C_2B_{10}H_8$	OLIQEC	[46]
		9,12-I$_2$-1,2-(HgR)$_2$—1,2-*closo*-$C_2B_{10}H_8$	YAWKIQ	[47]
	Tetra-iodinated	8,9,10,12-I$_4$-1,2-*closo*-$C_2B_{10}H_8$	GERGAM	[4]
		8,9,10,12-I$_4$-1-Me-1,2-*closo*-$C_2B_{10}H_7$	WUNDUF	[39]
		8,9,10,12-I$_4$-1-Ph-1,2-*closo*-$C_2B_{10}H_7$	GERGEQ	[4]
		8,9,10,12-I$_4$-1,2-Me$_2$-1,2-*closo*-$C_2B_{10}H_6$	WUNFAN	[39]
		8,9,10,12-I$_4$-1,2-Ph$_2$-1,2-*closo*-$C_2B_{10}H_6$	WUNFER	[39]
	Octa-iodinated	4,5,7,8,9,10,11,12-I$_8$-1,2-*closo*-$C_2B_{10}H_4$	WUNDIT	[39]
	Nona-iodinated	3,4,5,7,8,9,10,11,12-I$_9$-1,2-*closo*-$C_2B_{10}H_3$	HAFZOE	[48]
	Deca-iodinated	3,4,5,6,7,8,9,10,11,12-I$_{10}$-1,2-*closo*-$C_2B_{10}H_2$	CEHWOC	[49]
		3,4,5,6,7,8,9,10,11,12-I$_{10}$-1,2-*closo*-$C_2B_{10}H_2$	WUNDAL	[28]
		3,4,5,6,7,8,9,10,11,12-I$_{10}$-1,2-*closo*-$C_2B_{10}H_2$	WUNDOZ	[39]
$[7,8\text{-}nido\text{-}C_2B_9]^-$ framework	Mono-iodinated	$[1\text{-I-7,8-}nido\text{-}C_2B_9H_{11}]^-$		[42]
		$[6\text{-I-7,8-Ph}_2\text{-7,8-}nido\text{-}C_2B_9H_9]^-$	BARBEC	[44]
		$[9\text{-I-11-PPh}_3\text{-7,8-}nido\text{-}C_2B_9H_{10}]^-$		[50]
		$[6\text{-I-9-PPh}_3\text{-7,8-}nido\text{-}C_2B_9H_{10}]^-$		[50]
		$[5\text{-I-6,9-(PPh}_3)_2\text{-7,8-}nido\text{-}C_2B_9H_9]^-$		[50]
	Tetra-iodinated	$[1,5,6,10\text{-I}_4\text{-7,8-}nido\text{-}C_2B_9H_8]^-$	FAKGAB	[16]
	Octa-iodinated	$[1,2,4,5,6,9,10,11\text{-I}_8\text{-7,8-}nido\text{-}C_2B_9H_4]^-$	RICLUL	[33]

$C_2B_9H_{10}]$ nor these at $\delta = -16.4$ and -33.9 ppm for $[HNMe_3][1,5,6,10\text{-I}_4\text{-7,8-}nido\text{-}C_2B_9H_8]$ split into doublets in the ^{11}B NMR spectra, thus indicating that they correspond to B—I vertexes, respectively. The iodo groups affect more importantly the ipso boron atoms. The average chemical shift value, <δ>, remains practically unaltered upon the increment of the number of B—I vertexes.

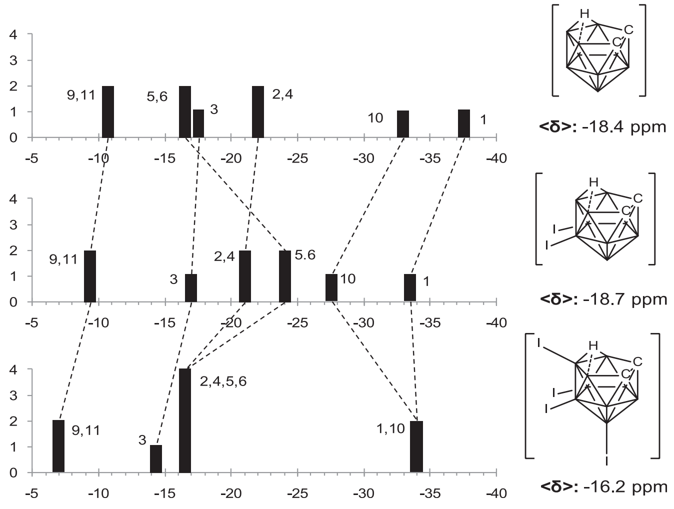


Fig. 10. Raw $^{11}B\{^1H\}$spectra with the peak assignments for unsubstituted $[HNMe_3][7,8\text{-}nido\text{-}C_2B_9H_{12}]$ and two iodinated derivatives $[HNMe_3][5,6\text{-I}_2\text{-7,8-}nido\text{-}C_2B_9H_{10}]$ and $[HNMe_3][1,5,6,10\text{-I}_4\text{-7,8-}nido\text{-}C_2B_9H_8]$ from solutions of the samples in acetone-d$_6$. Substitution of hydrogen with iodine causes significant shielding on boron atoms attached to the substituent.

4.2. Influence on the acidity of nido derivatives when increasing the number of B—I vertexes

Treatment of 1,5,6,10-I$_4$-1,2-*closo*-$C_2B_{10}H_8$ with potassium hydroxide in ethanol yielded the corresponding tetraiodo *nido* cluster

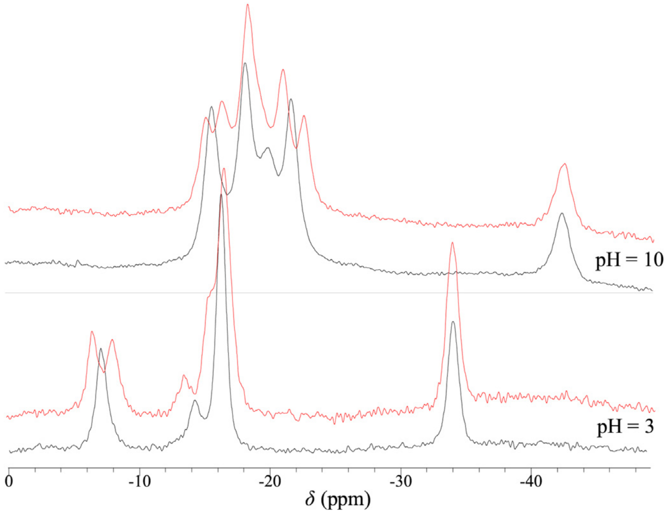


Fig. 11. $^{11}B\{^1H\}$ (black lines) and ^{11}B (red lines) NMR spectra of the acid/base pair $[1,5,6,10\text{-I}_4\text{-7,8-}nido\text{-}C_2B_9H_8]^-/[1,5,6,10\text{-I}_4\text{-7,8-}nido\text{-}C_2B_9H_7]^{2-}$ in water. The highest field peak in the spectra at pH = 3 (-33.9 ppm) is assigned to the overlapped signals of B(1) and B(10). At pH = 10, the peak of B(1) is shifted to higher field, whereas that of B(10) is shifted to low field (*ca.* -8.0 and $+12.0$ ppm, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

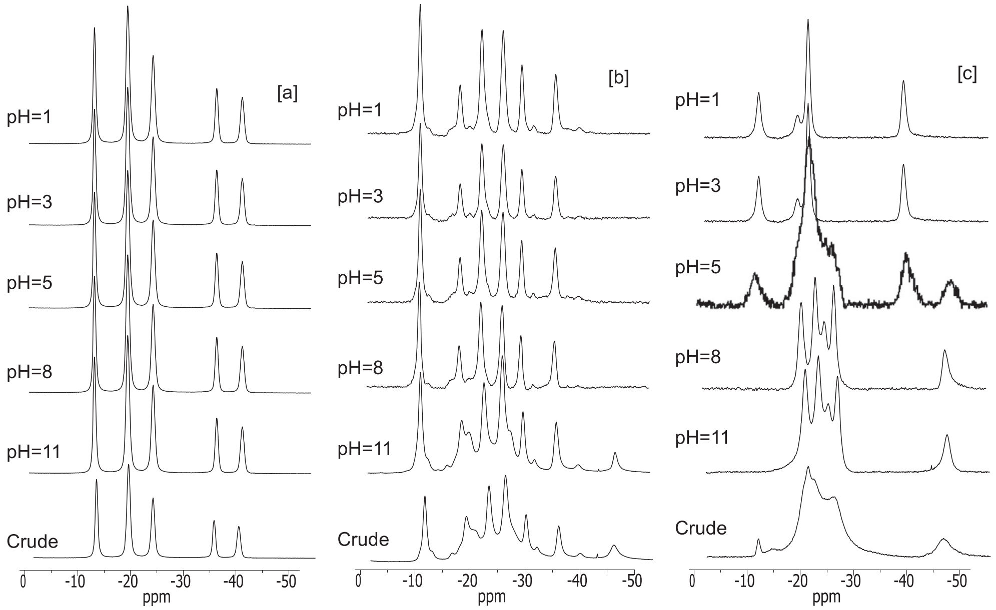


Fig. 12. $^{11}B\{^1H\}$ NMR spectra of the acid/base pairs: a) $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-/[7,8\text{-}nido\text{-}C_2B_9H_{11}]^{2-}$; b) $[5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-/[5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^{2-}$; c) $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-/[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]^{2-}$ in EtOH: H_2O at the pH range 11–1.

Table 4
^1H NMR chemical shift of bridge BHB protons in iodinated *nido*-carboranes derivatives related to the parent *nido*-*o*-carborane. Spectra were run in acetone-d_6.

Entry	Compounds	δ ^1H NMR of bridge BHB protons (ppm)	$\Delta\delta$ relative to *o*-carborane
1	$[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$	−2.90	–
2	$[9\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$	−2.98	−0.08
3	$[3\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]^-$	−2.67 [16]	+0.23
4	$[5\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]^-$	−2.41 [11]	+0.49
5	$[9,11\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$	−1.62	+1.28
6	$[5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$	−2.15 [16]	+0.75
7	$[5,6,9\text{-}I_3\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$	−2.25 [11]	+0.65
8	$[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$	−0.09 [16]	+2.81
9	$[7\text{-}Me\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]^-$	−2.68	+0.22
10	$[7\text{-}Me\text{-}5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$	−1.89 [11]	+1.01
11	$[7\text{-}Me\text{-}1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]^-$	+0.19 [11]	+3.09
12	$[7\text{-}Ph\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]^-$	−2.40	+0.50
13	$[7\text{-}Ph\text{-}5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$	−1.58 [11]	+1.32
14	$[7\text{-}Ph\text{-}1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]^-$	+0.40 [11]	+3.30

$[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$, able to generate η^5-ligands for sandwich type compounds. It was isolated for characterization as the trimethylammonium salt of the protonated monoanion, $[NHMe_3][1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]$. The bridging proton in pristine $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$ anion is relatively acidic and can be removed by the addition of strong base.

Although it is possible to approximately calculate *nido*-carborane pK_a values from DFT methods [30], there exists few experimental data in the literature [31]. We undertook a study in order to determine the acidity of the anion $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$. We wanted to avoid a typical titration to be able to observe structural changes upon the pH modification. The ^{11}B NMR spectra of its potassium salt in aqueous solution could be very informative as a function of *p*H. Significant shifts were observed from acidic to basic solutions. Fig. 11 shows a comparison of two spectra of $K[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]$ recorded at *p*H 3 and 10. The former is identical to that of $[NHMe_3][1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]$ in acetone, indicating that the monoanion is present. The one at pH 10 shows a quite different pattern; but importantly, however, is that both the monoanion $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$ and the dianion $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]^{2-}$ are stable in aqueous media. Upon deprotonation, the B(10) resonance is shifted to low field, whereas that of B(1) is shifted upfield, as occurs for $[7,8\text{-}nido\text{-}C_2B_9H_{11}]^{2-}$ [32], $[7,8\text{-}\mu\text{-}SCH_2CH_2S\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^{2-}$ [32] and $[1,2,3,4,5,6,9,10,11\text{-}I_9\text{-}7,8\text{-}nido\text{-}C_2B_9H_2]^{2-}$ [33].

For a matter of comparison $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$, $[5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ and $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$ have been studied by $^{11}B\{^1H\}$-NMR in a mixture of EtOH: H_2O in a range of pH between 11 and 1 (Fig. 12). At the lowest pH (higher concentration of acid), it was assumed that all three anions had the bridging proton on the open face, thus they were monoanions. In Fig. 12a, dedicated to $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$, it is definitely observed that the $^{11}B\{^1H\}$-NMR is invariant through all pH values. When the number of B-iodinated vertexes increases, case of $[5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$, the situation is different. As can be seen in Fig. 12b, the $^{11}B\{^1H\}$-NMR spectrum is identical from pH = 1 to pH = 8 indicating that within this pH interval the bridging proton is on the open face, but the spectrum shows signs of alteration at pH = 11 suggesting that two species, most probably $[5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ and $[5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^{2-}$ coexist at pH = 11. Finally, the same studies were performed in a higher iodo containing anion, $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$, see Fig. 12c. In this case, the $^{11}B\{^1H\}$-

NMR at a very low pH (between 1 and 3) show identical spectra, but this dramatically changes at pH = 5 at which pH the two species, monoanionic $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$ and dianion $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_7]^{2-}$, coexist. At pH 8, only the dianionic species is present. The new and very distinct resonance near −43 ppm appears at the same chemical shift as the new resonance found in $[5,6\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^{2-}$.

Expectedly, a higher number of B—I groups on the $[7,8\text{-}nido\text{-}C_2B_9]^-$ framework would lower the pH at which the dianionic species is more stable, or alternatively indicating that a higher number of B—I units produce a lower pK_a species, and also a less η^5 coordinating open face. These experiments are in agreement with the experimental pK_a of $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$ that is at 14.25 in water [31].

4.3. Influence on the chemical shift of the bridging hydrogen in the ^{1}H NMR spectrum of nido derivatives when increasing the number of B—I vertexes

We previously reported that a continuous C_c-H downfield chemical shift in the ^{1}H NMR, in acetone-d_6, was observed parallel to an increasing number of iodine atoms in the *closo* cluster [28]. This data indicates that the acidic character of the C_c-H hydrogen atom linearly increases with the number of B-bonded iodine atoms and that the effect is additive [28].

In this paper we report on a continuous H_{bridge} downfield chemical shift in the ^{1}H NMR, in acetone-d_6 (Table 4) that is parallel to an increasing number of iodine atoms in the cluster: $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$ (−2.90 ppm), $[5\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]^-$ (−2.41 ppm), $[9,11\text{-}I_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ (−1.62 ppm), $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$ (−0.09 ppm) indicating an increase of its acidic character. To notice is that the presence of iodine substituents on boron vertexes at the C_2B_3 open face produces larger deshielding effect than at the second layer B_5 (entries 5 and 6). In addition, the presence of a methyl or phenyl group bonded to the C_c in *B*-iodinated *nido* carboranes increase the deshielding effect on the H_{bridge} (entries 1 and 9; entries 1 and 12; entries 6 and 10; entries 6 and 13; entries 8 and 11; entries 8 and 14).

5. Conclusions

In this work the preparation of C_c-monosubstituted *closo* carborane derivatives, mono-, di-, tri- and tetraiodinated is reported by using green solvent-free methods that allow for the recovery of the unused I_2 reagent. Spectroscopy and some crystal structures endorse the procedure. Deboronation of these *closo* species with the conventional KOH/EtOH method leads to the corresponding iodinated *nido* anions, in which the two carbon atoms remain adjacent, and the number of iodo groups in the starting *closo* compound remains invariant in the *nido* derivative. Again spectroscopy and some crystal structures ratify the value of the deboronation process. Some of these mono-to poly-iodinated *nido* carboranes are studied in terms of the acidity of the open face bridging proton, their chemical shift position in the ^{1}H NMR, and the lesser tendency to η^5-coordination in parallel to a larger number of iodo groups. Comparison with non-iodo containing similar *nido* compounds has been paramount to interpret the consequences of increasing B—I moieties in the molecules.

Acknowledgement

This research has been financed by MEC (CTQ2013-44670-R) and Generalitat de Catalunya (2014/SGR/149). M. Lupu and A. Zaulet are enrolled in the PhD program of the UAB. M.L. thanks MICINN for FPU predoctoral grant.

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