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Designed Synthesis of New *ortho*-Carborane Derivatives: from Mono- to Polysubstituted Frameworks

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The use of nucleophilic and electrophilic processes allow the designed synthesis of several B-iodinated derivatives of *o*-carborane. Because of the straightforward Pd-catalyzed conversion of B−I to B−C bond with Grignard reagents, such as methylMgBr and biPhenylMgBr, both, symmetrical 3,6-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ and asymmetrical 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ could be obtained. Not only conventional reactions in solution have been studied but also a highly efficient, clean and fast solvent-free procedure has provided successful results to regioselectively produce B-iodinated *o*-carborane derivatives by a careful control of the reaction conditions. The high number of nonequivalent leaving groups in boron iodinated *o*-carborane derivatives opens the possibility through B−C coupling to materials with novel possibilities and to self-assembling due to the enhanced polarizability of the C−H bond.

Introduction

Because the utility of carborane units is dependent upon their functionalization,[1] the introduction of functional groups at the boron atoms is an important target. The substitution of the carbon hydrogen in carborane clusters is easy because the C−H vertices may be deprotonated with strong bases. Conversely, the chemistry of boron-substituted carboranes is less developed than that of the carbon-substituted analogues because of the higher difficulty of introducing functional groups at the boron atoms of the carborane cage. Calculated Mulliken charges on 1,2-*closo*-$C_2B_{10}H_{12}$ by geometry optimizations at B3LYP/6−31G* level of theory[2,3] show that B(8,9,10,12) are richer in electron density than B(3,6). Figure 1 shows vertex numbering in *o*-carborane.

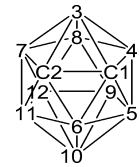

Figure 1. Vertex numbering in 1,2-*closo*-$C_2B_{10}H_{12}$, *o*-carborane.

Zakharkin et al. reported the synthesis of 3-isonitrile-1,2-*closo*-$C_2B_{10}H_{11}$, which was prepared from 3-amino-1,2-*closo*-$C_2B_{10}H_{11}$.[4] The electrophilic monoiodination at the 9 position[5,6] and diiodination at the 9 and 12 vertices[5,7] of the *o*-carborane cage is achieved by treatment with I_2 in the presence of $AlCl_3$.[7,8] A highly iodinated *o*-carborane, 4,5,7,8,9,10,11,12-I_8-1,2-*closo*-$C_2B_{10}H_4$, was later obtained by reaction with ICl

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(1) (a) Grimes, R. N. *Carboranes*, Academic Press: New York, 1970. (b) Mehta, S. C.; Lu, D. R. *Pharm. Res.* **1996**, *13*, 344. (c) Barth, R. F.; Soloway, A. H.; Brugger, R. M. *Cancer Invest.* **1996**, *14*, 534. (d) Grimes, R. N. *J. Chem. Educ.* **2004**, *81*, 658. (e) Plešek, J. *Chem. Rev.* **1992**, *92*, 269.
(2) *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
(3) Teixidor, F.; Barberà, G.; Vaca, A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *J. Am. Chem. Soc.* **2005**, *127*, 10158.
(4) (a) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V. *Synth. Inorg. Met.-Org. Chem.* **1971**, *1*, 45. (b) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V.; Dzarasova, G.S. J. *Organomet. Chem.* **1969**, *16*, 371. (c) Valliant, J. F.; Schaffer, P. *J. Inorg. Biochem.* **2001**, *85*, 43.
(5) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, *3*, 575.
(6) (a) Zakharkin, L. I.; Ol'shevskaya, V. A.; Poroshin, T. Y.; Balagurova, E. V. *Zh. Obshch. Khim.* **1987**, *57*, 2012. (b) Andrews, J. S.; Zayas, J.; Jones, M., Jr. *Inorg. Chem.* **1985**, *24*, 3715.
(7) Li, J.; Logan, C. F.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 4866.
(8) (a) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk. SSSR. Ser. Khim.* **1968**, *3*, 685. (b) Brattsev, V. A.; Stanko, V. I. *Zh. Obshch. Khim.* **1970**, *40*, 1664. (c) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk. SSSR. Ser. Khim.* **1970**, *40*, 2653. (d) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A.; Shaugumbekova, Z. S. *J. Organomet. Chem.* **1982**, *226*, 217.

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and triflic acid.[9] The recent development of a fast, solvent-free synthetic procedure has allowed the preparation of 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$ derivatives by direct reaction of *o*-carborane and iodine in sealed tubes.[10] Not only are iodinated carboranes the derivatives obtained by electrophilic substitution but also B-methylated carboranes[11,12] have also been successfully produced.

Alternatively, another way to B-functionalize the *o*-carborane, specifically at the 9 position, is by activating a B−I bond via conversion of a B-carboranyl iodide.[13]

Using the procedures named above, it is possible to derivatize all *o*-carborane cluster positions except B(3)/B(6) because these boron atoms, adjacent to both cluster carbons, are not susceptible to electrophilic substitution. Although studies of a metal-induced selective B(3)/B(6)-disubstitution of *ortho*-carborane-1,2-dithiolate have been done,[14] the disubstitution of C-unsubstituted 1,2-$C_2B_{10}H_{12}$ requires a combination of nucleophilic and boron-insertion reactions. The synthesis of 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ has been recently achieved starting from 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ by combining nucleophilic and boron-insertion processes.[15,16] Electrophilic iodination of these 3-iodo and 3,6-diiodo species led to nona- and deca-B-iodinated *o*-carboranes, respectively.[15,17]

B-iodinated *o*-carboranes have an elevated versatility to obtain B-derivatives by performing the Pd-catalyzed B−C cross-coupling reaction with Grignard reagents.[18]

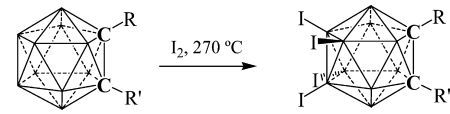
As each vertex possesses different electron density, each vertex has different reactivity. This leads to boron regioselective designed synthesis methods to selectively achieve the different B-substituted *o*-carborane derivatives in high yields.

Results and Discussion

Synthetic Studies.

a) Boron Iodinated *closo-o*-Carborane Derivatives by Electrophilic Iodination in Solvent-Free Reactions. As described in a previous communication, a solvent-free regioselective tetraiodination on *o*-carboranes is effectively achieved by reaction of 1-R-2-R′-1,2-*closo*-$C_2B_{10}H_{10}$ (R, R′ = H, Me, Ph) and elemental iodine in excess into sealed tubes (Scheme 1).[10] In this article, an extension of this fast, efficient, and solvent-free procedure is described. We have tested the reaction of *o*-carborane and iodine in sealed tubes

Scheme 1. - General Tetraiodination of 1-R-2-R′−1,2-*closo*-$C_2B_{10}H_{10}$ by Reaction with Iodine in Sealed Tubes (R, R′ = H, Me or Ph)



under varied experimental conditions (reagents ratio, temperature, and reaction time). The results given as a molar fraction (%) of the different iodinated compounds are shown in Table 1. Always, after the reaction is complete, the Pyrex tube is carefully opened and gaseous HI is removed by evaporation, leaving the crude product as a solid that is analyzed by ESI-MS and $^1H\{^{11}B\}$ NMR. The latter technique allows the determination of the molar ratio of the different iodinated compounds from the integration of the $C_{cluster}$−H peaks. Almost all of the excess iodine (95%) could be recovered from the mixture by sublimation under reduced pressure, avoiding the need for quenching with $NaHSO_3$ and allowing further re-use of reagents.

From the results in Table 1, it can be observed that this method is regioselective for the synthesis of 9-I-1,2-*closo*-$C_2B_{10}H_{11}$, 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, and 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$, depending on the experimental conditions. The best results were obtained using a 1:10 *o*-carborane/I_2 ratio. As expected, the first boron vertices to be iodinated are those furthest removed from the cluster carbon atoms. Thus, B(9) monoiodination can be achieved with high selectivity (97%) after 2.5 h at 115 ± 2 °C (entry *1*). The crude product was >97% pure in 9-I-1,2-*closo*-$C_2B_{10}H_{11}$ because the remaining starting *ortho*-carborane is removed in the iodine sublimation step. Enhanced purity can be achieved by recrystallization in hexane.

Small increments in temperature, keeping the reagents ratio constant, lead to important changes in the outcome of the reaction. Above 160 ± 2 °C, the major product is 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (entry *3*). The optimized conditions for the preparation of this compound are 170 °C and 3.5 h (entry *6*). Nevertheless, significant amounts of the isomer 8,9-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ are found in the composition of the crude product. Therefore, recrystallization in hexane/chloroform (6:1 by volume) is needed for the isolation of pure 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$.

After 3.5 h at 270 ± 2 °C (entry *11*), the crude solid contained ca. 3% of 8,9,12-I_3-1,2-*closo*-$C_2B_{10}H_9$, ca. 93% of 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$, and ca. 4% of higher iodinated *ortho*-carboranes, based on $^1H\{^{11}B\}$ NMR spectroscopy. As previously reported,[10] this is the first efficient synthetic procedure for the preparation of 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$. Longer reaction times did not substantially improve this result. Although being less regioselective (entry *10*), this species could also be produced by the reaction of 1,2-*closo*-$C_2B_{10}H_{12}$ with the stoichiometric amount of elemental iodine (4 equiv) at 270 ± 2 °C for 24 h. The crude product contained 74% of 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$. The crude solids were recrystallized from 1:1 ethanol/water to give pure 8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_8$ in a high yield.

To explore the versatility of the method, mono- and di-C-alkyl- and C-aryl-substituted *ortho*-carboranes were iodi-

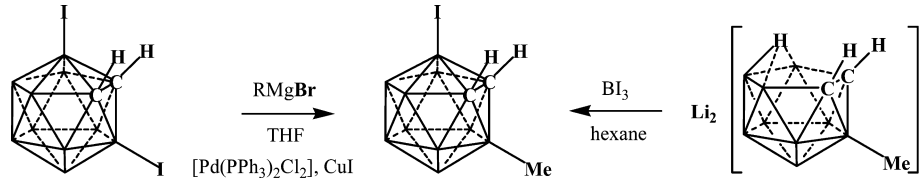
(9) Srivastava, R. R.; Hamlin, D. K.; Wilbur, D. S. J. *Org. Chem.* **1996**, *61*, 9041.
(10) Vaca, A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Viñas, C. *Dalton Trans.* **2006**, 4884.
(11) Herzog, A.; Maderna, A.; Harakas, G. N.; Knobler, C. B.; Hawthorne, M. F. *Chem.—Eur. J.* **1999**, *5*, 1212.
(12) Zheng, Z.; Knobler, C. B.; Mortimer, M. D.; Kong, G.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 1235.
(13) Grushin, V. V. *Acc. Chem. Res.* **1992**, *25*, 529.
(14) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 24.
(15) Teixidor, F.; Barberà, G.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Inorg. Chem.* **2006**, *45*, 3496.
(16) (a) Barberà, G. *Doctoral Thesis*, Universitat Autònoma de Barcelona, Bellaterra, 2002,http://www.tdcat.cesca.es/. (b) Yamazaki, H.; Ohta, K.; Endo, Y. *Tetrahedron Lett.* **2005**, *46*, 3119.
(17) Barberà, G.; Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Eur. J. Inorg. Chem.* **2003**, 1511.
(18) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095.

Table 1. Composition (%) of Iodination Crude Products of *ortho*-Carborane as a Function of I_2 Molar Ratio (1,2-*closo*-$C_2B_{10}H_{12}/I_2$), Temperature, and Reaction Time[a]

Exp.	I_2 ratio	*T* (°C)	*t* (h)	9-I-	8,9-I_2-	9,12-I_2-	8,9,12-I_3-	8,9,10,12-I_4-	I_n > $_4$-
1	**(1:10)**	**115**	**2.5**	**97**[b]					
2	(1:10)	120	2.5	95		5			
3	(1:10)	160	3.5	23	14	62	1		
4	(1:10)	170	3	4	16	77	3		
5	(1:8)	170	3.5	4	16	72	5		
6	**(1:10)**	**170**	**3.5**	1	13	**82**	4		
7	(1:10)	180	3.5		16	70	14		
8	(1:10)	195	4.5			57	43		
9	(1:2)	270	24		8	54	37	1	
10	(1:4)	270	24				18	74	8
11	**(1:10)**	**270**	**3.5**				3	**93**	4
12	(1:10)	290	2.5					83	17
13	(1:15)	300	110				2	21	77

[a] The molar ratio of the iodinated products has been calculated based on the integration of the peaks of $C_{clúster}$-H from ^{1}H NMR spectra. [b] The remaining 3% was starting material, removed by sublimation.

Scheme 2. - Syntheses of Asymmetric 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ via a Cross-Coupling Reaction and via a B−I Boron Insertion Reaction on the [3-Me-7,8-*nido*-$C_2B_9H_{10}]^{2-}$ Anion



nated under similar conditions. Slightly shorter reaction times were needed for the same degree of substitution compared to the parent *o*-carborane. Heating 1-R-1,2-*closo*-$C_2B_{10}H_{11}$ (R = Me, Ph) with I_2 at 270 ± 2 °C for 3.5 h gave the corresponding 1-R-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_7$ (R = Me, Ph) derivatives selectively in high yields (>75%). The C-disubstituted counterparts, 1,2-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ (R = Me, Ph) were iodinated in an analogous way, and the crude products obtained were analyzed by ESI-MS. 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ underwent tetraiodination selectively after 3.5 h, whereas 1,2-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$ was more susceptible to electrophilic substitution and only 2.5 h were required for completion of the reaction. This result is consistent with both theoretical[19] and experimental data[20] reported by Lipscomb and co-workers, which showed that the electron-donating effect of methyl groups bonded to the $C_{cluster}$ atoms causes a uniform increase in electron density on the B atoms while having little, or no effect on the sequence of substitution.

The synthesis of penta- and hexa-iodinated derivatives, taking 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ and 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ as starting materials, has also been achieved.

b) Boron Alkylated and Arylated *o*-Carborane Derivatives: Alkyl and Aryl-Dehalogenation Reactions at B(3) and B(6). In extending the chemistry of 3-R-6-R′-*o*-carborane derivatives, aryl and alkyl-dehalogenation reactions were performed on 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, using either an alkyl or an aryl reagent. The reaction consists of the B−C cross coupling Kumada reaction on 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ in the presence of $[PdCl_2(PPh_3)_2]$ and CuI, using the appropriate aryl or alkylmagnesium bromide reagent as a source of the organic group, in THF solution under reflux. Using 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$/Grignard reagent in a 1:10 ratio, new 3,6-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ (R = methyl, biphenyl) species were obtained in high yields (97, 96%, respectively).

Referring to asymmetric carborane derivatization, 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ could be obtained following two synthetic procedures (Scheme 2). The first one, based on the reaction of 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ with methylmagnesium bromide in a 1:5 ratio, produces the asymmetric compound in low yield (16%). The second one, that afforded a higher yield (81%), consisted of the combination of deboronation on 3-Me-1,2-*closo*-$C_2B_{10}H_{11}$, and subsequent B−I insertion through the reaction of [3-Me-7,8-*nido*-$C_2B_9H_{10}]^{2-}$ with BI_3.

Following a reported procedure on methylation reaction,[21] 3-Me-1,2-$C_2B_{10}H_{11}$ reacted with methyl iodide in the presence of aluminum trichloride under reflux for 2 days. After working up, 3,4,5,7,8,9,10,11,12-Me_9-1,2-*closo*-$C_2B_{10}H_3$ was obtained in 98% yield.[17] Treatment of 3,6-Me_2-1,2-$C_2B_{10}H_{10}$ with MeI/$AlCl_3$ at reflux for 2 days produces 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-Me_8-1,2-*closo*-$C_2B_{10}H_2$, whose ^{11}B-NMR spectrum indicates a mixture of species.[3] The ^{11}B{^{1}H}-NMR spectrum was practically identical, suggesting that all or most of the BHs had been substituted. The ^{1}H NMR spectrum confirmed this observation. The carborane C−H region between 2.6 and 4.6 ppm was very informative. Resonances due to C−H, in ppm with relative areas in parentheses, were observed at 4.47 (2.97), 3.16 (1), 2.99 (1), 3.04 (5), 2.94 (5), 2.77 (2.65), and 2.74 (2.65). This indicates that four dominant species, one of them being symmetrical,

(19) (a) Newton, M. D.; Boer, F. P.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1966**, *88*, 2353. (b) Boer, F. P.; Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1966**, *5*, 1301.

(20) Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1966**, *5*, 1483.

(21) Jiang, W.; Knobler, C. B.; Mortimer, M. D.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1332.

are formed in this reaction. The most abundant compound displays its cluster C−H's at 3.04 and 2.94 ppm, the second in importance at 2.77 and 2.74 ppm, the third at 4.47 ppm, this being most probably symmetrical, and the less abundant at 3.16 ppm and 2.99 ppm. The abundances would be approximately 49%, 26%, 15%, and 10%, respectively. Suitable colorless crystals were obtained from hexane that indicated that octaboron methyl substitution of the C_2B_{10} icosahedron at positions 3,4,5,6,7,8,10 and 11 had taken place. The remaining positions at B(9) and B(12) are partially occupied by halogen and hydrogen atoms. Similarly to 4,5,7,8,9,10,11,12-Me_8-$C_2B_{10}H_4$,[11] there are only eight Me groups on the cluster 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-Me_8-1,2-*closo*-$C_2B_{10}H_2$. It may appear that boron permethylation in 1,2-*closo*-$C_2B_{10}H_{12}$ is severely hampered due to the -I effect of Me.

The existence of three species with H in the 9,12 positions, (I,H), (H,H), and (H,Cl), whereas all other B positions are methyl substituted, could induce to reason that positions 9,12 are not the first to suffer electrophilic attack in 3,6-Me_2-1,2-$C_2B_{10}H_{10}$. To discard this possibility, a careful monitoring of the methylation reaction by ^{11}B-NMR has allowed us to find a synthetic procedure for 3,6,8,9,10,12-Me_6-1,2-$C_2B_{10}H_6$ in 68% yield. Reducing the reaction time to 4 h, 3,6,8,9,10,12-Me_6-1,2-*closo*-$C_2B_{10}H_6$ could be produced with high selectivity. This experiment proves that B(9) and B(12) are among the first four boron positions to be methylated. There is no evidence of at which stage of the methylation process the attack by other nucleophiles to the B(9)-Me and B(12)-Me groups takes place, but what seems clear is that the cluster evolves to remove the high load of positive charge (created by the Me groups bonded to the B vertexes) by incorporating groups (Cl, I, H) that either are less electron-withdrawing (H) or that by back-donation (Cl, I) can refill the cluster of electron density. Substitution of antipodal to cluster carbon B-Me group by nucleophiles had been observed in methyl derivatives of [*closo*-$CB_{11}Me_{12}$]$^-$.[22]

c) Study of the Deboronation Process of B-Methylated and B-Iodinated Derivatives. All of these boron-substituted carboranes were reacted with KOH/EtOH. Under these conditions, the low electron density at B(3) in pristine *o*-carborane facilitates its removal, whereas with 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$, the presence of methyl groups in B(3) and B(6) prevents its deboronation. The same happens for 3,6-(biPh)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$. Moreover, 3,4,5,7,8,9,10,11,12-Me_9-1,2-*closo*-$C_2B_{10}H_3$ remained also unreacted under the typical deboronation conditions, even though B(6) is still bonded to a hydrogen atom.

However, the deboronation of the 3,6-diiodinated compound with EtO^- under reflux conditions and subsequent precipitation with [$HNMe_3$]Cl led to the formation of [$HNMe_3$][3-I-7,8-*nido*-$C_2B_9H_{11}$]. In the deboronation reaction on the per-B-iodinated compound, 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$, that has both B(3) and B(6) atoms bonded to iodine, the nucleophilic attack takes place on one of these vertices, producing [1,2,3,4,5,6,9,10,11-I_9-7,8-*nido*-$C_2B_9H_2$]$^{2-}$

(22) Janousek, Z.; Lehmann, U.; Castulík, J.; Císarova, I.; Michl, J. *J. Am. Chem. Soc.* **2004**, *126*, 4060.

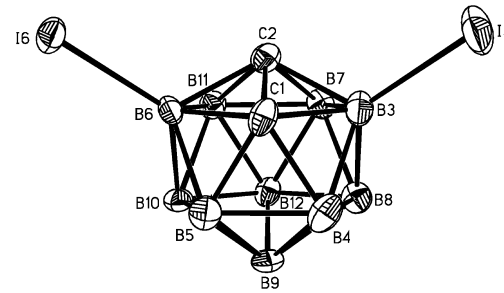


Figure 2. Molecular structure of 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$. Hydrogen atoms are omitted.

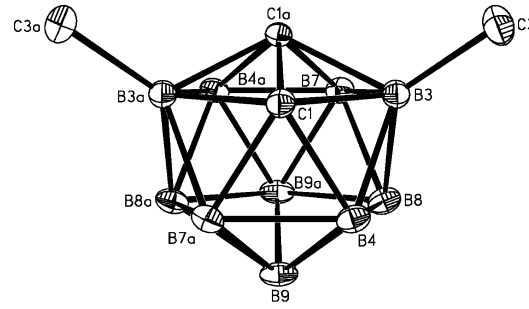


Figure 3. Molecular structure of 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$. Hydrogen atoms are omitted. Small letter "a" refers equivalent position $-x, y, -z + {}^3/_2$.

in 86% yield. In this case, the MALDI-TOF-MS spectrum shows only one envelope of peaks centered at 1266.8 *m*/*z* that corresponds to [1,2,3,4,5,6,9,10,11-I_9-7,8-*nido*-$C_2B_9H_3$]$^-$. In the same way, the deboronation reaction of 4,5,7,8,9,10,11,12-I_8-*closo*-$C_2B_{10}H_4$ produces pure [1,2,4,5,6,9,10,11-I_8-7,8-*nido*-$C_2B_9H_3$]$^{2-}$ in 86% yield. Conversely, the deboronation of 3,4,5,7,8,9,10,11,12-I_9-1,2-*closo*-$C_2B_{10}H_3$ produced a mixture of the fully B-iodinated [1,2,3,4,5,6,9,10,11-I_9-7,8-*nido*-$C_2B_9H_2$]$^{2-}$ and [1,2,4,5,6,9,10,11-I_8-*nido*-7,8-$C_2B_9H_3$]$^{2-}$ dianions in approximately a 50:50 mixture.

Then, deboronation studies confirm that either B(3)−I or B(6)−I vertices on *o*-carborane can be easily removed under nucleophilic conditions. This deboronation process is in contrast to the case of having B(3)−alkyl/B(6)−alkyl or B(3)−aryl/B(6)−aryl vertices for which no reaction has taken place, not even with a crowded species such as 3,4,5,7,8,9,10,11,12-Me_9-$C_2B_{10}H_3$.

All boron-substituted *o*-carborane derivatives were obtained in good yields and were initially characterized by microanalysis and IR spectroscopy. ^{11}B-, ^{13}C{^{1}H}-, and ^{1}H-NMR and MS for the compounds are fully consistent with the proposed formulas.

Molecular and Crystal Structures of 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$ and 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$. The species 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$, and 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ have been studied in crystalline state. Their molecular structures are presented in Figures 2, 3, and 4, respectively. Selected bond lengths and angles for the compounds are listed in Table 2, and crystallographic data are summarized in Table 3.

The structures of 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$, 3,6-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$, and 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ are formed of well-separated molecules without any strong intermolecu-

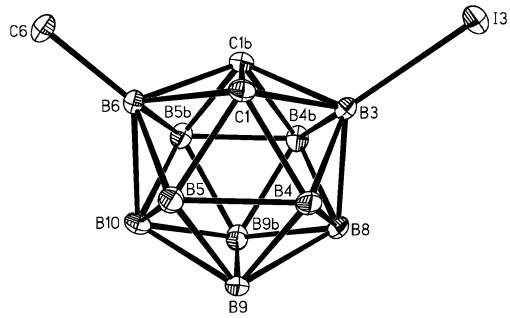


Figure 4. Molecular structure of 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$. Hydrogen atoms are omitted. Small letter "b" refers equivalent position $-x, y, z$.

lar interactions. Only some weak interactions can be found in the three compounds like the I···I contact of 3.5918(13) Å in 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$ and a BH···I contact, with the H···I and B···I distances of 3.03 and 4.150(3) Å, in 3-I-6-Me-1,2-closo-$C_2B_{10}H_{10}$.

The molecule of 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$ has approximate C_{2v} symmetry but the crystallographic symmetry of the compound is C_1. 3,6-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$ assumes crystallographic 2-fold symmetry with the axis going through the midpoints of the bonds C1−C1[a] and B9−B9[a] ([a] refers equivalent position $-x, y, -z + {}^3/_2$). However, approximate symmetry of the latter molecule is C_{2v}. 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ assumes mirror symmetry with the symmetry plane containing the atoms I3, B3, B6, C6, B8, and B10. Therefore, the symmetry element is bisecting the C1−C1[b] and B9−B9[b] bonds ([b] refers equivalent position $-x, y, z$).

In these three compounds, the $C_{cluster}-C_{cluster}$ distances vary in the range 1.613(5)−1.625(4) Å. These values agree well with the corresponding values observed for the 1,2-unsubstituted *o*-carborane derivatives.[23] $C_{cluster}-C_{cluster}$ distances can be modified by substituting the cluster carbons. Thus, the shortest distances are found for *o*-carborane derivatives carrying H atoms at both cluster carbons, like the present compounds, but much longer distances have been found for the derivatives bearing aryl groups, phosphorus, or sulfur substituents at the cluster carbons.[23a,24]

Conclusions

The combination of nucleophilic and electrophilic reactions and the choice of the proper experimental conditions allow the designed synthesis of several *o*-carborane derivatives with different patterns of substitution. Several iodinated compounds, from mono- to per-B-substituted, are now accessible on demand. The synthetic importance of B-iodo-*o*-carboranes relies on the possibility of exchanging iodine with organic moieties using the Kumada cross-coupling reaction, opening new possibilities of constructing macromolecules. The study of the boron-degradation reaction on several B-substituted *o*-carborane derivatives shows that the ease of boron vertex removal follows the order: B−H > B−I ≫ B-alkyl, B-aryl. Selective asymmetric disubstitution at the equivalent B(3) and B(6) vertexes of the *o*-carborane that opens a new route for cluster application uses has been achieved. These boron-substituted *o*-carborane derivatives can in turn serve as synthons for many others.

Experimental Section

General Procedures. Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^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 with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3 \leftarrow OEt_2$ and those for ^1H, $^1H\{^{11}B\}$, and $^{13}C\{^1H\}$ NMR spectra were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants in hertz. MS spectra for ionic species were recorded using a Bruker Biflex MALDI-TOF mass spectrometer and using a FIA-ES/MS (Shimadzu AD VP/ API 150) instrument for neutral species.

Unless otherwise noted, all manipulations were carried out under a nitrogen atmosphere using standard vacuum-line techniques. Diethyl ether and THF were distilled from sodium benzophenone prior to use. Hexane was dried over molecular sieves and deoxygenated before use. A 1.6 M solution of *n*-butyllithium in hexanes, iodine monochloride, aluminum trochloride, triflic acid, 4-biPhenylmagnesium bromide, methylmagnesium bromide, methyl iodide from Aldrich; BI_3 from Alfa and 1,2-*closo*-$C_2B_{10}H_{12}$ from Katchem Ltd. (Prague) were used as purchased. 3-I-1,2-*closo*-$C_2B_{10}H_{11}$,[7] 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$,[15] and [$HNMe_3$][3-I-7,8-*nido*-$C_2B_9H_{11}$][25] were synthesized according to the literature.

Synthesis of 1,2-I_2-1,2-*closo*-$C_2B_{10}H_{10}$. To a stirring solution of 1,2-*closo*-$C_2B_{10}H_{12}$ (98 mg, 0.68 mmol) in diethyl ether (10 mL) cooled to 0 °C in an ice−water bath was added, dropwise, a solution of butyllithium in hexane (0.89 mL, 1.6 M, 1.43 mmol) under nitrogen atmosphere. The suspension was stirred at room temperature for 0.5 h, then cooled again to 0 °C, at which point I_2 (365.8 mg, 1.44 mmol) was added in a single portion. The resulting solution was stirred at 0 °C for 30 min and at room temperature for further 30 min, then extracted with 5% aqueous $Na_2S_2O_3$ (10 mL) and washed with water (2 × 5 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated in vacuo to give a pale-yellow solid. The crude product was purified by silica gel flash chromatography at −10 °C under argon atmosphere, using diethyl ether as the eluting solvent to yield 1,2-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (188 mg, 70%). Elemental analysis of $C_2B_{10}H_{10}I_2$: Calcd C, 6.07; H, 2.55; found C, 6.29; H, 2.55. ESI-MS: 394.8 (M - H^+, 100%). FTIR (KBr), ν (cm^{-1}) = 2596 (s, B−H), 2574 (s, B−H). ^1H NMR ($CDCl_3$), δ_H = 4.6−2.2 (6 H, br m, BH). $^1H\{^{11}B\}$ NMR ($CDCl_3$), δ_H = 2.99 (6 H, br s), 2.72 (2 H, br s), 2.24 (2 H, br s). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ_C = 21.8 (s). ^{11}B NMR ($CDCl_3$), δ_C = −1.5 (2 B, d, overlapped), −3.4 (2 B, d).

Synthesis of 9-I-1,2-*closo*-$C_2B_{10}H_{11}$. A thick-walled Pyrex tube charged with 1,2-*closo*-$C_2B_{10}H_{12}$ (0.279 g, 1.93 mmol) and iodine (4.911 g, 19.3 mmol) was put under vacuum, cooled down with liquid nitrogen, and sealed. The tube was then placed in a furnace, and the temperature was gradually raised to 115 °C during 30 min,

(23) (a) Teixidor, F.; Viñas, C. In *Science of Synthesis, Ed.*; Thieme: Stuttgart, 2005, Vol. *6*, p 1235,and references therein. (b) Novák, C.; šubrtová, C.; Línek, A.; Hašek, J. *Acta Crystallogr.* **1983**, *C39*, 1393. (c) šubrtová, C.; Línek, A.; Hašek, J. *Acta Crystallogr.* **1980**, *B36*, 858.

(24) Kivekäs, R.; Flores, M. A.; Viñas, C.; Sillanpää, R. *Acta Crystallogr.* **2002**, *C58*, 570, and references cited therein.

(25) Barberà, G.; Viñas, C.; Teixidor, F.; Welch, A. J.; Rosair, G. M. *J. Organomet. Chem.* **2002**, *657*, 217.

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$, and 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$

3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$		3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$		3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$	
I3−B3	2.156(11)	C1−C1[a]	1.613(5)	I3−B3	2.132(3)
I6−B6	2.146(9)	C1−B3	1.738(4)	C1−C1[b]	1.625(4)
C1−C2	1.623(13)	C1−B3[a]	1.742(4)	C1−B3	1.718(4)
C1−B3	1.723(14)	C3−B3	1.572(4)	C1−B6	1.736(4)
C1−B6	1.711(12)			C6−B6	1.571(5)
C2−B3	1.700(14)				
C2−B6	1.727(13)				
C1−B3−I3	120.1(7)	C3−B3−C1	119.4(2)	C1−B3−I3	121.5(2)
C2−B3−I3	119.4(7)	C3−B3−C1[a]	119.8(2)	C1[b]−B3-I3	121.5(2)
I3−B3−B8	128.8(7)	C3−B3−B8	132.1(2)	I3−B3−B8	127.7(3)
C1−B6−I6	119.8(6)			C1−B6−C6	120.8(2)
C2−B6−I6	119.9(6)			C1[b]−B6-C6	120.8(2)
I6−B6−B10	129.5(6)			C6−B6−B10	130.9(3)

[a] Equivalent position $-x, y, -z + {}^3/_2$. [b] Equivalent position $-x, y, z$.

Table 3. Crystallographic Data and Structural Refinement Details for 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (**1**), 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$ (**2**), and 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ (**3**)

compound	(**1**)	(**2**)	(**3**)
empirical formula	$C_2H_{10}B_{10}I_2$	$C_2H_{16}B_{10}$	$C_3H_{13}B_{10}I$
fw	396.00	172.27	284.13
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*P*212121	*C*2/*c*	*Pmn*21
a (Å)	9.0602(4)	14.8528(7)	7.2615(2)
b (Å)	17.4247(17)	6.8281(3)	9.6534(3)
c (Å)	7.7457(16)	11.5332(6)	8.0861(2)
β (deg)	90	114.220(5)	90
V (Å^3)	1222.8(3)	1066.70(9)	566.82(3)
Z	4	4	2
T (°C)	21	−100	−100
λ (Å)	0.71069	0.71073	0.71073
ρ (g•cm^{-3})	2.151	1.073	1.665
μ (cm^{-1})	50.88	0.46	27.66
GOF	1.071	1.044	1.076
R^a [$I > 2\sigma(I)$]	0.0332	0.0965	0.0278
$R_w{}^b$ [I > 2σ(I)]	0.0847	0.2576	0.0560

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

maintained for 2.5 h, and allowed to drop slowly to room temperature. Excess of both iodine and 1,2-*closo*-$C_2B_{10}H_{12}$ were effectively separated by sublimation from the reaction mixture at 50 °C under reduced pressure, yielding practically pure (<1% of I_2-1,2-$C_2B_{10}H_{11}$ based on ^{1}H NMR) 9-I-1,2-*closo*-$C_2B_{10}H_{11}$ (0.505 g, 97%). Elemental analysis of $C_2H_{11}B_{10}I$: Calcd C, 8.89; H, 4.10; found: C, 9.06; H, 3.92. ESI-MS: *m*/*z* 268.9 (M - H$^+$, 100%). FTIR (KBr), ν (cm^{-1}) = 3047 (s, $C_{cluster}$−H), 2584 (vs, B−H). ^{1}H NMR (CD_3COCD_3), δ_H 4.96 (1 H, br s, CH), 4.75 (1 H, br s, CH) and 3.8 − 1.2 (9 H, m BH). ^{1}H{^{11}B} NMR (CD_3COCD_3), δ_H 4.96 (1 H, br s, CH), 4.75 (1 H, br s, CH), 2.82, 2.65, 2.52, 2.40, and 2.16 (9 H, br s, BH). ^{11}B NMR (CD_3COCD_3), δ_B −1.1 (1 B, d, ^1J(B,H) = 151), −7.2 (2 B, d, ^1J(B,H) = 153), −12.0, −12.7 and −13.6 (7 B, m) and −16.4 (1 B, s, B(9)I). ^{13}C{^{1}H} NMR (CD_3COCD_3), δ_C = 57.9 and 53.2 ($C_{cluster}$−H).

Synthesis of 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$. A thick-walled Pyrex tube charged with 1,2-*closo*-$C_2B_{10}H_{12}$ (0.253 g, 1.75 mmol) and iodine (4.451 g, 17.5 mmol) was put under vacuum, cooled down with liquid nitrogen, and sealed. The tube was then placed in a furnace and the temperature gradually raised to 170 °C during 30 min, maintained for 3.5 h, and allowed to drop slowly to room temperature. Excess iodine was effectively separated by sublimation from the reaction mixture at 50 °C under reduced pressure. The residual solid was composed of 9-I-1,2-*closo*-$C_2B_{10}H_{11}$ (2%), 8,9-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (13%), 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (82%), and 8,9,12-I_3-1,2- $C_2B_{10}H_9$ (3%) based on ^{1}H NMR. 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ could be obtained pure by fractional recrystallization of the crude product from hexane/$CHCl_3$ 6:1 by volume. FTIR (KBr), ν (cm^{-1}) = 3032 (s, $C_{cluster}$−H), 2615, and 2584 (s, B−H). ^{1}H NMR (CD_3COCD_3), δ_H = 5.15 (2 H, br s, CH) and 3.8−1.5 (8 H, m, BH). ^{1}H{^{11}B} NMR (CD_3COCD_3), δ_H = 5.15 (2 H, br s, CH), 2.73, 2.65, and 2.95 (8 H, br s, BH). ^{11}B NMR (CD_3COCD_3), δ_B = −5.1 (2 B, d, ^1J(B,H) = 156, B(8,10)), −11.6 (4 B, d, B(4,5,7,11)), −13.0 (2 B, d, B(3,6)) and −13.8 (2 B, s, B(9,12)). ^{13}C{^{1}H} NMR (CD_3COCD_3), δ_C = 54.5 ($C_{cluster}$−H).

Synthesis of 3,8,9,10,12-I_5-1,2-*closo*-$C_2B_{10}H_7$. A thick-walled Pyrex tube charged with 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ (0.060 g, 0.22 mmol) and iodine (0.558 g, 2.20 mmol) was put under vacuum, cooled down with liquid nitrogen, and sealed. The tube was then placed in a furnace, and the temperature was gradually raised to 270 °C during 15 min, maintained for 6 h, and allowed to drop slowly to room temperature. Excess iodine was effectively separated by sublimation from the reaction mixture at 50 °C under reduced pressure. The resulting solid was recrystallized from 1:1 ethanol/water mixture to yield 3,8,9,10,12-I_5-1,2-*closo*-$C_2B_{10}H_7$ (0.135 g, 79%). MALDI-TOF MS: *m*/*z* = 773 (M - H$^+$). FTIR (KBr), ν (cm^{-1}) = 3015 (s, $C_{cluster}$−H), 2613 and 2572 (s, B−H). ^{1}H NMR (CD_3COCD_3), δ_H = 5.98 (2 H, br s, CH). ^{1}H{^{11}B} NMR (CD_3COCD_3), δ_H = 3.13, 3.25, and 3.54 (5 H, br s, BH) and 5.98 (2 H, br s, CH). ^{11}B NMR (CD_3COCD_3), δ_B = −25.7 (1 B, s, B(3)), −15.3 (2 B, s), −8.9, (5 B, m) and −2.0 (2 B, d, ^1J(B,H) = 161).

Synthesis of 3,6,8,9,10,12-I_6-1,2-*closo*-$C_2B_{10}H_6$. A thick-walled Pyrex tube charged with 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (0.080 g, 0.20 mmol) and iodine (0.508 g, 2.00 mmol) was put under vacuum, cooled down with liquid nitrogen, and sealed. The tube was then placed in a furnace and the temperature gradually raised to 270 °C during 15 min, maintained for 6 h, and allowed to drop slowly to room temperature. Excess iodine was effectively separated by sublimation from the reaction mixture at 50 °C under reduced pressure. The resulting solid was recrystallized from a 1:1 ethanol/water mixture to yield 3,6,8,9,10,12-I_6-1,2-*closo*-$C_2B_{10}H_6$ (0.138 g, 76%). MALDI-TOF MS: *m*/*z* = 899 (M - H$^+$). FTIR (KBr), ν (cm^{-1}) = 3012 (s, $C_{cluster}$−H), 2613 (s, B−H). ^{1}H NMR (CD_3COCD_3), δ_H = 6.22 (2 H, br s, CH). ^{1}H{^{11}B} NMR (CD_3COCD_3), δ_H = 3.25 (4 H, br s, BH) and 6.22 (2 H, br s, CH). ^{11}B NMR (CD_3COCD_3), δ_B = −23.7 (2 B, s, B(3,6)), −12.0 (2 B, s), −8.7 (2 B, s), and −3.4 (4 B, d, ^1J(B, H) = 188, B(4, 5, 7,11)).

Synthesis of 3-Me-1,2-*closo*-$C_2B_{10}H_{11}$. To a stirred solution of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ (0.5 g, 1.85 mmol) in THF (20 mL) at 0 °C, was added, dropwise, a solution of methylmagnesium bromide (3.1 mL, 3 M, 9.3 mmol). After stirring at room temperature for 30 min, *cis*-[$PdCl_2(PPh_3)_2$] (52.0 mg, 4% equiv) and CuI (14.1 mg, 4% equiv) were added in a single portion; then the reaction was

heated to reflux overnight. The solvent was removed and 20 mL of diethyl ether was added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic phase was washed with water and dried over $MgSO_4$. The final compound was purified by flash silica gel chromatography using hexane as the eluting solvent to give 3-Me-1,2-*closo*-$C_2B_{10}H_{11}$. Yield: 285 mg (97%). Elemental analysis of $C_3B_{10}H_{14}$: Calcd C, 22.77; H, 8.92; found C, 22.38; H, 8.48. FTIR (KBr), ν (cm^{-1}) = 3063 ($C_{cluster}$−H), 2957, 2924, 2855 (C_{alkyl}−H), 2629, 2598, 2575 (B−H). ^{1}H NMR ($CDCl_3$), δ_H = 3.43 (2H, br s, $C_{cluster}$−H), 3.0−1.0 (8H, br m, B−H), 0.65 (3H, s, CH_3). ^{1}H{^{11}B} NMR ($CDCl_3$), δ_H = 3.43 (2H, br s, $C_{cluster}$−H), 2.26 (br s, B−H), 2.15 (br s, B−H), 0.65 (3H, s, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$), δ_C = 58.1 (s; $C_{cluster}$), −0.2 (br q, CH_3). ^{11}B NMR ($CDCl_3$), δ_B = −1.8 (d, ^1J(B,H) = 148, 2B), −4.0 (s, 1B), −7.8 (d, ^1J(B,H) = 150, 1B), −11.7 (d, ^1J(B,H) = 126, 2B), −12.9 (d, ^1J(B,H) = 150, 4B).

Synthesis of 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$.

Method *A*. In an analogous manner, 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (0.50 g, 1.26 mmol) in THF (20 mL) at 0 °C, was added, dropwise, a solution of methylmagnesium bromide (2.1 mL, 3 M, 6.3 mmol). After stirring at room temperature for 30 min, *cis*-[$PdCl_2(PPh_3)_2$] (17.7 mg, 4% equiv) and CuI (4.8 mg, 4% equiv) were added in a single portion, and then the reaction was heated at reflux for 5 h. The solvent was removed and 20 mL of diethyl ether were added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic phase was washed with water and dried over $MgSO_4$. The final compound was purified by flash silica gel chromatography using dicloromethane/hexane (3:5) as the eluting solvent to give 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$. Yield 57.3 mg (16%).

Method *B*. To the stirred solution of [$HNMe_3$][3-Me-7,8-*nido*-$C_2B_9H_{11}$] (3.5 g, 16.9 mmol) in anhydrous diethyl ether (40 mL) at 0 °C was added dropwise *n*-butyllithium (21.1 mL, 1.6 M, 33.8 mmol). Once the addition was completed, the reaction mixture was stirred at room temperature for an additional 2 h and then heated to reflux for 4 h. After evaporation of the solvent, anhydrous hexane (40 mL) was added to the remaining solid. A solution of BI_3 (9.9 g, 25.35 mmol) in 40 mL of hexane was then added dropwise with stirring at 0 °C. Stirring was continued for 5 h at room temperature once the addition was completed. The excess boron triiodide was carefully decomposed by the addition of 10 mL of water. The organic layer was separated from the mixture and the aqueous layer extracted with hexane (3 × 10 mL). The combined organic phase was dried over $MgSO_4$, and the solvent was removed at the rotary evaporator. The crude product was recrystallized from hexane to obtain 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$. Yield 3.9 g (81%). Crystals suitable for an X-ray diffraction experiment were grown by slow evaporation from a concentrated dichloromethane solution. Elemental analysis of $C_3H_{13}B_{10}I$: Calcd C, 12.68; H, 4.61; found C, 12.58; H, 4.60. FTIR (KBr), ν (cm^{-1}) = 3032 ($C_{cluster}$−H), 2964, 2930 (C_{alkyl}−H), 2594, 2586 (B−H). ^{1}H NMR ($CDCl_3$), δ_H = 3.73 (2H, s, $C_{cluster}$−H), 3.00−1.00 (8H, br m, B−H), 0.70 (s, 3H; CH_3). ^{1}H{^{11}B} NMR ($CDCl_3$), δ_H = 3.73 (2H, s, $C_{cluster}$−H), 2.70 (1H, s, B−H), 2.50 (2H, s, B−H), 2.35 (2H, s, B−H), 2.24 (2H, s, B−H), 2.12 (1H, s, B−H), 0.70 (3H, s, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$), δ_C = 62.5 (s, $C_{cluster}$). ^{11}B NMR ($CDCl_3$), δ_B = −1.7 (d, ^{1}J(B,H) = 162, 2B), −3.0 (s, 1B; B(6)), −11.4 (d,^{1}J(B,H) = 155, 6B), −28.8 (s, 1B, B(3)).

Synthesis of 3,6-(biPh)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$. To a stirring solution of 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (396 mg, 1 mmol) in THF (10 mL) at 0 °C, was added, dropwise, a solution of 4-biphenylmagnesium bromide (5 mL, 2 M, 10 mmol) in the same solvent. After stirring at room temperature for 30 min, *cis*-[$PdCl_2(PPh_3)_2$] (28 mg, 4% equiv) and CuI (7.6 mg, 4% equiv) were added in a single portion, following which the reaction was heated to reflux for 4 days. The solvent was removed, and 20 mL of diethyl ether was added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic phase was washed with water and dried over $MgSO_4$. The solvent was removed, and the residue was extracted with hexane. The final compound was purified by flash silica gel chromatography using dicloromethane/hexane (4:1) as the eluting solvent to give 3,6-(biPh)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$. Yield 0.43 g (96%). Elemental analysis of $C_{26}H_{28}B_{10}$: Calcd C, 69.60; H, 6.29; found C, 69.90; H, 6.30. FTIR (KBr), ν (cm^{-1}) = 3076, 3049, 3044 (C_{aryl}-H), ($C_{cluster}$−H), 2584, 2547 (B−H). ^{1}H NMR ($CDCl_3$), δ_H = 7.73−7.30 (m, 18H; H_{aryl}), 3.92 (br s, 2H; $C_{cluster}$−H), 3.00−1.50 (8H, br m, B−H). ^{1}H{^{11}B} NMR ($CDCl_3$), δ_H = 7.73−7.30 (18H, m, H_{aryl}), 3.92 (2H, br s, $C_{cluster}$−H), 2.62 (br s, B−H), 2.47 (br s, B−H). ^{13}C{^{1}H} NMR ($CDCl_3$), δ_C = 143.4, 142.0, 141.2, 134.3, 130.3, 129.4, 128.4, 127.8 (C_{aryl}), 59.8 (s, $C_{cluster}$). ^{11}B NMR ($CDCl_3$), δ_B = −2.0 (d, ^1J(B,H) = 150, 2B), −4.7 (s, 2B), −12.6 (d, 6B).

Synthesis of [$HNMe_3$][3-Me-7,8-*nido*-$C_2B_9H_{12}$]. To a solution of KOH (0.89 g, 15.79 mmol) in degassed EtOH (50 mL), 3-Me-1,2-*closo*-$C_2B_{10}H_{11}$ (500 mg, 3.16 mmol) was added. The solution was refluxed for 3 h. After cooling down to room temperature, the solvent was removed under reduced pressure, and the solid residue was dissolved in 20 mL of water. The solution was neutralized with HCl 1 M. Afterward, aqueous [$HNMe_3$]Cl was added dropwise to the solution to precipitate the compound. The white solid was rinsed with water and diethyl ether obtaining [$HNMe_3$][3-Me-7,8-*nido*-$C_2B_9H_{12}$]. Yield: 550 mg (84%). Elemental analysis of $C_6H_{24}B_9N$: Calcd C, 34.72; H, 11.65; N, 6.74; found C, 34.69; H, 11.56; N, 5.62. FTIR (KBr), ν (cm^{-1}) = 2908, 2856 (C_{alkyl}, H), 2513 (B−H). ^{1}H NMR (CD_3COCD_3), δ_H = 3.21 (s, 9H; [$HNMe_3$]), 2.08 (br s, 2H; $C_{cluster}$−H), 2.09 (s; 3H, CH_3), −2.71 (1H; B−H−B). ^{13}C{^{1}H} NMR (CD_3COCD_3), δ_C = 47.5 (m; $C_{cluster}$), 45.1 (s; [$HNMe_3$]), 25.24 (s; CH_3). ^{11}B NMR (CD_3COCD_3), δ_B = −10.0 (s, 1B), −10.0 (d, ^{1}J(B,H) = 138, 2B), −15.6 (d, ^{1}J(B,H) = 130, 2B), −20.3 (d, ^{1}J(B,H) = 147, 2B), −35.6 (d, ^{1}J(B,H) = 149, 2B).

X-ray Structure Determinations of 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$, 3,6-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$, and 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$. Single-crystal data collection for 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ was performed at ambient temperature on a Rigaku AFC5S diffractometer, and data collections for 3,6-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$ and 3-I-6-Me-*closo*-1,2-$C_2B_{10}H_{10}$ were performed with Enraf Nonius FR590 diffractometer at −100 °C using monochromatic Mo Kα radiation.

The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[26]

For 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ and 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$, non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as riding atoms using the *SHELX97* default parameters. 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ crystallizes in non-centrosymmetric space group and absolute configuration of the compound was determined by refinement of Flack's *x* parameter.

For 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$, non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as riding atoms using the *SHELX97* default parameters. The methyl group is disordered showing rotational disorder with each hydrogen atom occupying two positions. 3-I-

6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ crystallizes in non-centrosymmetric space group and absolute configuration of the compound was assigned by refinement of Flack's *x* parameter.

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Supporting Information Available: Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 641600−641602 for 3,6-I_2-1,2-$C_2B_{10}H_{10}$, 3,6-Me_2-1,2-$C_2B_{10}H_{10}$, and 3-I-6-Me-$C_2B_{10}H_{11}$, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or at http://pubs.acs.org/. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Sheldrick G. M. *SHELX97.* University of Göttingen: Germany, 1997.