Palladium-Catalyzed Amination of 2-Iodo-*para*-carborane

Irina P. Beletskaya,*,† Vladimir I. Bregadze,*,‡ Kuanysh Z. Kabytaev,† Galina G. Zhigareva,‡ Pavel V. Petrovskii,‡ Ivan V. Glukhov,‡ and Zoya A. Starikova‡

Chemistry Department, M. V. Lomonosov Moscow State University, Leninskye Gory, 119992, Moscow, Russian Federation, and A. N. Nesmeyanov Institute of Organoelement Compounds, 28 Vavilov Street, 119991 Moscow, Russian Federation

Received December 25, 2006

The palladium-catalyzed Buchwald−Hartwig amination of B-iodocarborane by various azoles and amines is described for the first time. The reactions of 2-iodo-*p*-carborane with indole, imidazole, benzimidazole, or carbazole in the system $Pd(dba)_2$−BINAP−Bu^{t}ONa in dioxane at 100 °C gave 2-*p*-carboranyl derivatives of these azoles in high yields together with 2-hydroxy-*p*-carborane as a side product. The reactions of 2-iodo-*p*-carborane with aromatic amines in the same system gave the amination products in 60−70% yields and also were accompanied by the formation of hydroxy derivatives (up to 30% yields). In a special investigation it was shown that the base Bu^{t}ONa was responsible for its formation. The principle possibility of the amination of 2-iodo-*p*-carborane by morpholine (with 30% yield) as an example of aliphatic amination was shown. The structures of *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)carbazole (**1**), *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)benzimidazole (**2**), *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)indole (**4**), and 2-hydroxy-1,12-dicarba-*closo*-dodecaborane (**5**) have been established by X-ray diffraction studies.

Introduction

There is a growing interest in the synthesis of compounds that combine carborane clusters and organic units, due to their potential applicability for nanoarchitectural and supramolecular constructions,[1−4] nonlinear optical materials,[2,5,6] or medicinal chemistry.[7] The nature of the carborane cage opens two different routes for attaching the carborane cluster to the organic moiety, using either the carbon atom or the boron atom of the carborane cage.

The substitution at the carbon atom in carborane derivatives is widely described,[8] while the preparation of boron derivatives is more challenging. New possibilities for the carborane cage functionalization at the boron atom are opened by the palladium-catalyzed cross-coupling reactions of B-halogen carboranes, in spite of the fact that there is a great difference in behavior between the C_{sp2}−Hal bond and the carborane B−Hal bond in oxidative addition. Until now all attempts to detect the formation of a Pd-intermediate with a B−Pd−I bond have failed;[9] however a few Pd-catalyzed cross-coupling reactions at the B−I bond have been carried out.[10,11]

The carborane derivatives with a boron−carbon bond can be prepared by cross-coupling reactions of B-iodocarboranes with active organometallic compounds,[3,10−12] terminal alkynes,[3,12] and

* To whom correspondence should be addressed. E-mail: (I.B.) beletska@org.chem.msu.ru; (V.B.) bre@ineos.ac.ru.

† Chemistry Department, M. V. Lomonosov Moscow State University.

‡ A. N. Nesmeyanov Institute of Organoelement Compounds.

(1) (a) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719. (b) Mueller, J.; Base, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721. (c) Schöberl, U.; Magnera, T. E.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907. (d) Schwab, P.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863.

(2) (a) Murphy, D. M.; Mingos, D. M. P.; Forward, J. M. *J. Mater. Chem.* **1993**, *3*, 67. (b) Murphy, D. M.; Mingos, D. M. P.; Haggitt, J. L.; Powell, H. R.; Westcott, S. A.; Marder, T. B.; Taylor, N. J.; Kanis, D. R. *J. Mater. Chem.* **1993**, *3*, 139.

(3) (a) Jiang, W.; Knobler, C. B.; Curtis, C. E.; Mortimer, M. D.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 3491. (b) Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 3056. (c) Jiang, W.; Harwell, D. E.; Mortimer, M. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 4355. (d) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267. (e) Bayer, M. J.; Herzog, A.; Diaz, M.; Harakas, G. A.; Lee, H.; Knobler, C. B.; Hawthorne, M. F. *Chem.−Eur. J.* **2003**, *9*, 2732.

(4) (a) Colquhoun, H. M.; Herbertson, P. L.; Wade, K.; Baxter, I.; Williams, D. J. *Macromolecules* **1998**, *31*, 1694. (b) Alekseyeva, E. S.; Fox, M. A.; Howard, J. A. K.; Macbride, J. A. H.; Wade, K. *Appl. Organomet. Chem.* **2003**, *17*, 499.

(5) (a) Lamrani, M.; Hamasaki, R.; Mitsuishi, M.; Miyashita, T.; Yamamoto, Y. *Chem. Commun.* **2000**, 1595. (b) Tsuboya, N.; Lamrani, M.; Hamasaki, R.; Ito, M.; Mitsuishi, M.; Miyashita, T.; Yamamoto, Y. *J. Mater. Chem.* **2002**, *12*, 2701.

(6) (a) Kaszynski, P.; Douglas, A. G. *J. Organomet. Chem.* **1999**, *581*, 28. (b) Piecek, W.; Kaufman, J. M.; Kaszynski, P. A. *Liq. Cryst.* **2003**, *30*, 39. (c) Pahomov, S.; Young, V. G.; Kaszynski, P. *Inorg. Chem.* **2000**, *39*, 2243. (d) Kaszynski, P.; Pahomov, S.; Young, V. G. *Collect. Czech. Chem. Commun.* **2002**, *67*, 1061.

(7) (a) Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F.-G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 1515. (b) Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **1999**, *99*, 3421. (c) Valliant, J. F.; Guenther, K. J.; King A. S. *Coord. Chem. Rev.* **2002**, *232*, 173. (d) Endo, Y.; Iijima, T.; Yamakoshi, Y.; Fukasawa, H.; Miyaura, C.; Inada, M.; Kubo, A.; Itai, A. *Chem. Biol.* **2001**, *8*, 341. (e) Bregadze, V. I.; Sivaev, I. B.; Glazun, S. A. *Anti-Cancer Agents Med. Chem.* **2006**, *6*, 75.

(8) (a) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970. (b) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209.

(9) Marshall, W. J.; Young, R. J., Jr.; Grushin, V. V. *Organometallics* **2001**, *20*, 523.

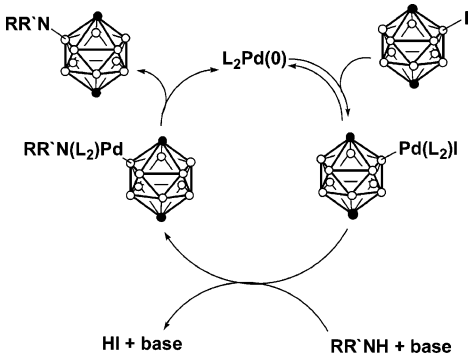
(10) (a) Zakharkin, L. I.; Kovredov, V. A.; Ol'shevskaya, V. A. *Bull. Akad. Sci. USSR Div. Chem. Sci.* **1981**, 1775. (b) Zakharkin, L. I.; Kovredov, V. A.; Ol'shevskaya, V. A.; Shaugumbekova, Z. S. *J. Organomet. Chem.* **1982**, *226*, 217. (c) Zakharkin, L. I.; Ol'shevskaya, V. A. *Russ. J. Gen. Chem.* **1987**, *57*, 317. (d) Kovredov, V. A.; Shaugumbekova, Z. S.; Petrovskii, P. V.; Zakharkin L. I. *Russ. J. Gen. Chem.* **1989**, *59*, 537.

(11) (a) Li, J.; Logan, C. F.; Jones, M. *Inorg. Chem.* **1991**, *30*, 4866. (b) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095. (c) Vinas, C.; Barbera, G.; Oliva, J. M.; Teixidor, F.; Welch, A. J.; Rosair, G. M. *Inorg. Chem.* **2001**, *40*, 6555.

(12) (a) Zakharkin, L. I.; Ol'shevskaya, V. A. *Synth. React. Inorg. Met.-Org. Chem.* **1991**, *21*, 1041. (b) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 888.

10.1021/om0611756 CCC: $37.00
Publication on Web 03/27/2007

Scheme 1



arylboronic acids,[13] as well as by the carboranylation of styrenes (i.e., the boron analogue of the Heck reaction).[14] Recently we have demonstrated that boron-substituted pyridyl- and quinolylethynyl derivatives of *m*- and *p*-carboranes can be prepared by the palladium-catalyzed cross-coupling of 9-iodo-*m*- and 2-iodo-*p*-carborane and the corresponding acetylenes or their magnesium derivatives.[15]

These results allowed us to anticipate a possible extension of Pd-catalyzed reactions to boron−heteroatom bond forming processes and especially to the amination of carboranes at the boron atom using the Buchwald−Hartwig procedure.[16] Herein we report that this type of reaction has been accomplished for the first time for 2-iodo-1,12-dicarba-*closo*-dodecaborane (2-iodo-*p*-carborane) under the action of azoles or aromatic and aliphatic amines. The catalytic cycle of this reaction is presented in Scheme 1.

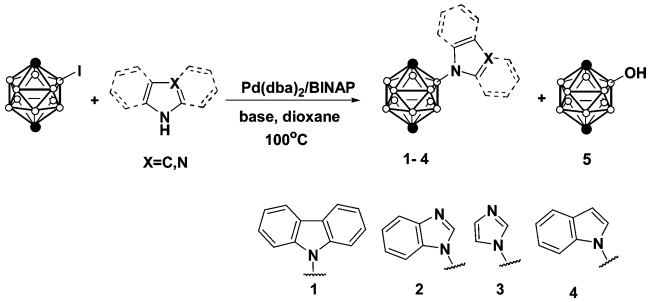
It is known that the amino group can be introduced at the boron atom of *o*-carborane by the reaction of ammonia with *o*-carborane dianion in liquid ammonia solution.[17] In the same way the *N*-piperidyl derivative of *o*-carborane was obtained.[17b] Although the mechanism of this reaction is unknown, it was suggested that two additional electrons in the *o*-carborane dianion increase the hydride lability of hydrogen at the boron atom, and the reaction of this dianion with ammonia leads to the evolution of H_2 and the formation of the B−N bond.[17b,c] The mechanism of this reaction was also considered as the bimolecular nucleophilic substitution of the hydride anion with an amide anion.[17c] Only the amino derivatives of *o*-carborane can be obtained by this method because *m*- and *p*-carborane dianions undergo isomerization into *o*-carborane under these conditions.[17b] Amino derivatives of *m*-carborane with the B−N bond could be prepared by indirect ways: either by insertion of diphenylaminodichloroborane into *nido*-carborane $[m\text{-}C_2B_9H_{12}]^-$ [18] or by the reaction of 1,7-$C_2H_2B_{10}H_9$(2-COOH) with HN_3.[19a,b] The only known B-substituted amino derivative of *p*-carborane, 2-amino-*p*-carborane, was obtained by the latter method.[19c]

Table 1. Reaction of 2-Iodo-*p*-carborane with Carbazole[a]

entry	$Pd(dba)_2$/ligand, %	base	time, h	yield[b] B−N (**1**), %	yield[b] B−OH (**5**), %
1	5/5 BINAP	Bu^{t}ONa	48	69 (57)	29
2	5/7.5 BINAP	Bu^{t}ONa	48	67	28
3	5/7.5 Tol-BINAP	Bu^{t}ONa	48	58	31
4	5/5 BINAP	NaH	48	90[c] (78)	3
5	5/5 BINAP	Cs2CO3	48	7	0

[a] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane, 0.1 mmol of carbazole, 1.2 mmol of base, catalyst, 1 mL of dioxane, 100 °C. [b]Yield determined by ^{11}B NMR; the yield of isolated product is shown in parentheses. [c]Carbazole pretreated with NaH was added to the reaction mixture.

Scheme 2



Results and Discussion

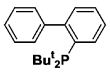
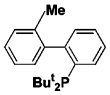
Amination of 2-Iodo-*p*-carborane by Azoles. It is known that almost each Pd-catalyzed amination requires its "own" ligand depending on the nature of haloarenes and amine. The yields of such reactions usually depend on the L/Pd ratio and the nature of the base. Therefore we have carried out a wide optimization of the reaction conditions, mainly using carbazole as an example. It was shown that the Buchwald−Hartwig reaction can be applied to the amination of 2-iodo-*p*-carborane by azoles (Scheme 2).

However there is a peculiarity in the reaction with carbazole. Under classical conditions—$Pd(dba)_2$−BINAP−Bu^{t}ONa in dioxane at 100 °C—a comparable amount of the hydroxy derivative of carborane (B−OH) (**5**) (∼30%) was formed along with the amination product (∼70%) (Table 1, entries 1−3). The formation of phenols has been never described during the amination of haloarenes. The application of Cs_2CO_3, commonly used in the arylation of azoles, turned out to be inefficient (Table 1, entry 5). The problem was solved by the use of NaH as a base, resulting in a high yield of the product (∼90%) (Table 1, entry 4). The isolated yields are generally much lower than the yields estimated by ^{11}B NMR due to losses during the chromatography.

Unlike carbazole, all other azoles with different values of pK_a (benzimidazole 12.8, imidazole 14.5, indole 17) in the presence of Bu^{t}ONa gave good results and formation of B−OH (**5**) was negligible. In some cases less expensive MeONa can also be used successfully (Table 2, entry 4; Table 3, entry 4). The best results have been obtained for 5 mol % [Pd] (Pd:BINAP = 1:1). The decrease of catalyst concentration leads to a reduction of product yields (Table 2, entries 2 and 5; Table

(13) Eriksson, L.; Beletskaya, I. P.; Bregadze, V. I.; Sivaev, I. B.; Sjöberg, S. *J. Organomet. Chem.* **2002**, *657*, 267.
(14) Eriksson, L.; Winberg, K.-J.; Claro, R. T.; Sjöberg, S. *J. Org. Chem.* **2003**, *68*, 3569.
(15) (a) Beletskaya, I. P.; Bregadze, V. I.; Ivushkin, V. A.; Petrovskii, P. V.; Sivaev, I. B.; Sjöberg, S.; Zhigareva, G. G. *J. Organomet. Chem.* **2004**, *689*, 2920. (b) Beletskaya, I. P.; Bregadze, V. I.; Ivushkin, V. A.; Zhigareva, G. G.; Petrovskii, P. V.; Sivaev, I. B. *Russ. J. Org. Chem.* **2005**, *41*, 1359.
(16) (a) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (b) Wolfe, J. P.; Wagaw, S.; Marcous, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805.
(17) (a) Zakharkin L. I.; Kalinin V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2585. (b) Zakharkin L. I.; Kalinin V. N.; Gedymin V. V. *J. Organomet. Chem.* **1969**, *16*, 371. (c) Brattsev, V. A.; Stanko, V. I. *Russ. J. Gen. Chem.* **1969**, *39*, 2144.
(18) Roscoe J. S.; Kongpricha S.; Papetti S. *Inorg. Chem.* **1970**, *9*, 1561.
(19) (a) Zakharkin L. I.; Kalinin, V. N.; Gedymin, V. V. *Synth. React. Inorg. Met. Org. Chem.* **1973**, *3*, 93. (b) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V. *Russ. J. Gen. Chem.* **1973**, *43*, 1974. (c) Zakharkin, L. I.; Kalinin, V. N.; Kobelkova, N. I. *Russ. J. Gen. Chem.* **1980**, *50*, 919.

Table 2. Reaction of 2-Iodo-*p*-carborane with Benzimidazole[a]

entry	Pd(dba)$_2$ / ligand, %	base	time, h	yield[b] B-N (**2**), %	yield[b] B-OH (**5**), %
1	5 / 5 BINAP	Bu^{t}ONa	24	95 (71)	5
2	2 / 2 BINAP	Bu^{t}ONa	24	43	0
3	5 / 5 BINAP	MeONa	24	77	0
4	5 / 5 BINAP	MeONa	72	80	1
5	2 / 2 BINAP	MeONa	72	25	0
6	5 / 5 dppf	MeONa	24	34	0
7	5 / 10 P(o-tolyl)$_3$	MeONa	96	20	0
8	5 / 10 PBu$^t_3$·HBF$_4$	MeONa	72	11	0
9	5 / 7.5 	MeONa	48	3	0
10	5 / 7.5 	MeONa	48	4	0

[a] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane, 0.1 mmol of benzimidazole, 1.2 mmol of base, catalyst, 1 mL of dioxane, 100 °C. [b]Yield determined by ^{11}B NMR; the yield of isolated product is shown in parentheses.

Table 3. Reaction of 2-Iodo-*p*-carborane with Indole[a]

entry	Pd(dba)$_2$/ ligand, %	base	time, h	yield[b] B−N (**4**), %	yield[b] B−OH (**5**), %
1	5/5 BINAP	Bu^{t}ONa	48	89 (63)	10
2	2/2 BINAP	Bu^{t}ONa	48	13	0
3	5/5 BINAP	MeONa	24	59	0
4	5/5 BINAP	MeONa	72	64	0
5	2/2 BINAP	MeONa	72	8	0
6	5/5 dppf	MeONa	24	27	0

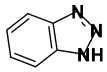
[a] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane, 0.1 mmol of indole, 1.2 mmol of base, catalyst, 1 mL of dioxane, 100 °C. [b]Yield determined by ^{11}B NMR; the yield of isolated product is shown in parentheses.

3, entries 2 and 5). An attempt to change BINAP to other mono- or bidentate ligands including Buchwald's ligands (Table 2, entries 6−10) has been unsuccessful. Increasing the amount of ligand or the use of Tol-BINAP in place of BINAP has led to no improvement of yields and selectivity (Table 1, entries 2 and 3).

Thus for azoles having pK_a values in the range 12.8−17 we found the conditions for N-carboranylation in high yields. It is difficult to discuss the influence of the pK_a value on the reactivity of azoles because the high acidity produces the N-anion more easily but decreases at the same time the nucleophilicity of this anion.

Very acidic azoles, triazole and benzotriazole (pK_a 10.3 and 8.2, correspondingly), gave poor yields due to their low nucleophilicity (Table 4, entries 2 and 3). A small amount of **5** is formed in these reactions due to consumption of Bu^{t}ONa by

Table 4. Reaction of 2-Iodo-*p*-carborane with Imidazole and Triazoles[a]

entry	azole, pK_a	yield[b] B-N, %	yield[b] B-OH (**5**), %
1	 14.5	**comp. 3** 83 (68)	0
2	 10.3	5	7
3	 8.2	5	10

[a] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane, 0.1 mmol of azole, 1.2 mmol of Bu^{t}ONa, catalyst 5% Pd(dba)$_2$/5% BINAP, 1 mL of dioxane, 100 °C, 48 h. [b]Yield determined by ^{11}B NMR; the yield of isolated product is shown in parentheses.

Table 5. Amination of 2-Iodo-*p*-carborane by Aromatic Amines[a]

entry	amine	base (equiv)	product	yield[b] B−N,%	yield[b] **5**, %
1	$C_6H_5NH_2$	Bu^{t}ONa (1.2)	**6**	68 (59)	32
2	*p*-$ClC_6H_4NH_2$	Bu^{t}ONa (1.2)	**7**	68[c]	32
3	*p*-$MeOC_6H_4NH_2$	Bu^{t}ONa (1.2)	**8**	66 (47)	34
4	*p*-$MeOC_6H_4NH_2$	MeONa (1.2)	**8**	11	7
5	*p*-$MeOC_6H_4NH_2$	Cs_2CO_3 (1.2)	**8**	25	0
6	*p*-$MeOC_6H_4NH_2$	NaOH (1.6)	**8**	34	5
7	*p*-$MeOC_6H_4NH_2$	K_2CO_3 (1.4) + 18-crown-6 (1.4)	**8**	56	0

[a] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane, 0.1 mmol of amine, base, Pd(dba)$_2$ 5 mol %, BINAP 5 mol %, 1 mL of dioxane, 100 °C. [b]Yield determined by ^{11}B NMR; isolated yield is shown in parentheses. [c]Cannot be separated from **5**.

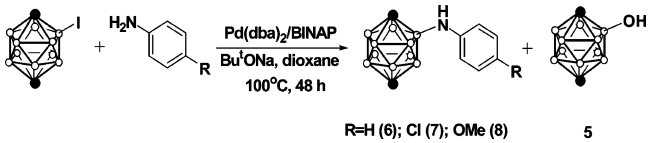
azole under formation of an anion. The use of CuI as a well-known cocatalyst in the arylation of azoles[16] was not successful in this case.

Amination of 2-Iodo-*p*-carborane by Aromatic Amines. The reaction of 2-iodo-*p*-carborane with aromatic amines *p*-$XC_6H_4NH_2$ (X = H, Cl, OMe) in the system 5% Pd(dba)$_2$−5% BINAP−Bu^{t}ONa in dioxane (100 °C) gave the products in good yields but was also accompanied by the formation of **5** in 30% yield (Scheme 3).

The yield of amination product is practically the same for amines with both electron-withdrawing and electron-donating substituents (Table 5).

The attempt to replace Bu^{t}ONa by other bases and avoid the formation of B−OH product was not successful. In all cases

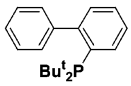
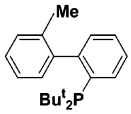
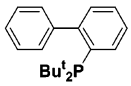
Scheme 3



(Table 5, entries 4−7) a decrease in the yields was observed. The only exception is the system K_2CO_3−18-crown-6 ether, which allowed an increase in yield of up to 56% (Table 5, entry 7).

Amination of 2-Iodo-*p*-carborane by Aliphatic Amines. The amination of 2-iodo-*p*-carborane by morpholine (Scheme

Table 6. Reaction of 2-Iodo-*p*-carborane with Morpholine[a]

entry	[ligand],%	yield **9**, %	yield **5**, %	*p*-carborane, %
1	BINAP 5	30	20	19
2	 10	39	3	9
3	$PBu^t_3 \cdot HBF_4$ 10	43	7	14
4	P(o-tolyl)$_3$ 10	31	14	16
5	PCy_3 10	34	15	15
6	IMes·HCl 10	12	16	21
7[b]	$PBu^t_3 \cdot HBF_4$ 10	15	5	15
8	 8	20	5	16
9	Cy_2Xantphos 7	11	17	17
10[c]	 10	8	0	19

[a] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane, 0.12 mmol of morpholine, 0.1 mmol of Bu^tONa, 1 mL of dioxane, 100 °C, 48 h, 5 mol % $Pd(dba)_2$, yield based on ^{11}B NMR. [b]Solvent: toluene. [c]5 mol % $Pd(OAc)_2$, solvent toluene.

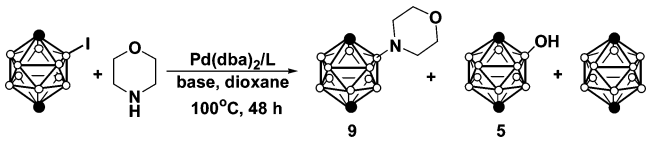
Table 7. Preparation of 2-Hydroxy-*p*-carborane (5)[a]

entry	base (equiv)	time, h	**5**, %
1	Bu^tONa (1)	20	16
2	Bu^tONa (3)	20	90
3	K_3PO_4[b] (2)	65	0
4	NaOH (2)	40	0

[a] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane, 5% $Pd(dba)_2$, 5% BINAP, 1 mL of dioxane, 100 °C, yield based on ^{11}B NMR. [b]In the presence of 0.2 mmol of water.

4) as an example of the reaction with aliphatic amines under the same conditions gave poor results. The system $Pd(dba)_2$−BINAP−Bu^tONa has been found to be unselective, giving along with the B−N compound significant amounts of **5** and the product of reduction (*p*-carborane) (Table 6, entry 1). After 48 h we have found 30% **9**, 20% **5**, and 19% *p*-carborane.

Scheme 4



The use of other ligands such as P(*o*-tolyl)$_3$, PCy_3, and IMes·HCl, as well as the bidentate ligand Cy_2Xantphos was also ineffective (Table 6, entries 4−6, 9). Only in the presence of di(*tert*-butyl)biphenylphosphine or $(t\text{-Bu})_3P \cdot HBF_4$ did the desired product yield increase to 39% and 43%, respectively (Table 6, entries 2, 3). The use of toluene as solvent and $Pd(OAc)_2$ as catalyst precursor gave worse results (Table 6, entry 10). It is known that the amination of haloarenes by aliphatic amines containing β-hydrogen atoms is often accompanied by the reduction of the halogen−carbon bond.[16] This process was found to compete (together with formation of **5**) with the amination of 2-iodo-*p*-carborane by morpholine. Neither BINAP nor other ligands carried out this reaction selectively (Table 6).

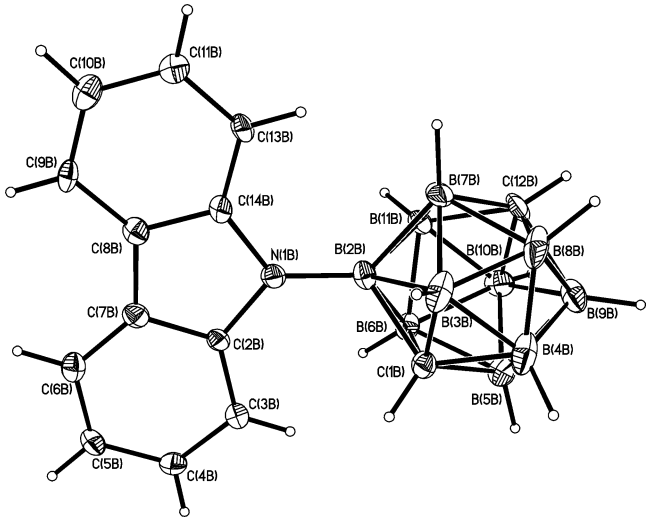


Figure 1. Molecular structure of one of the independent molecules (B) of *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)carbazole (**1**) (50% probability thermal ellipsoids). Selected bond distances (Å) for A[B] molecules: N(1)−B(2) 1.481(5) [1.472(5)], C(1)−B(2) 1.743(6) [1.725(6)], C(1)−B(3) 1.745(5) [1.655(6)], C(1)−B(4) 1.747(6) [1.677(6)], C(1)−B(5) 1.673(8) [1.691(6)], C(1)−B(6) 1.660(8) [1.719(6)], C(12)−B(7) 1.687(6) [1.651(7)], C(12)−B(8) 1.704(6) [1.718(9)], C(12)−B(9) 1.704(6) [1.705(7)], C(12)−B(10) 1.659-(7) [1.659(6)], C(12)−B(11) 1.713(6) [1.648(7)]. Bond angle C(2)−N(1)−C(14): 105.0(5)° [107.5(5)°].

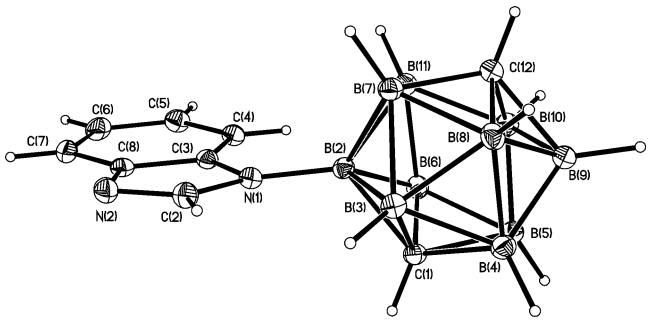


Figure 2. Structure of *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)-benzimidazole (**2**) (50% probability thermal ellipsoids). Selected bond distances (Å): N(1)−B(2) 1.481(2), C(1)−B(3) 1.713(3), C(1)−B(4) 1.700(3), C(1)−B(5)1.707(3), C(1)−B(6) 1.6933, C(12)−B(7) 1.700(3), C(12)−B(8) 1,702(3), C(12)−B(9) 1.707(3), C(12)−B(10) 1.714(3), C(12)−B(11) 1.705(3). Selected bond angles (deg): C(2)−N(1)−C(3) 104.4(2), C(2)−N(2)−C(8) 106.5(2).

Reaction of 2-Iodo-*p*-carborane with Different Bases. A special investigation has been carried out in order to elucidate the source of the hydroxy group in 2-hydroxy-*p*-carborane (**5**). For this purpose we have studied the reactions of 2-iodo-*p*-carborane with different bases (Table 7). The reactions of 2-iodo-*p*-carborane with NaOH (Table 7, entry 4) and with K_3PO_4 in the presence of water (Table 7, entry 3) did not lead to the formation of **5**. In the case of a 3-fold excess of Bu^tONa, **5** was formed in 90% yield (Table 7, entry 2).

The process of hydroxy derivative formation is still uncertain. It is known that this compound was formed as a side product

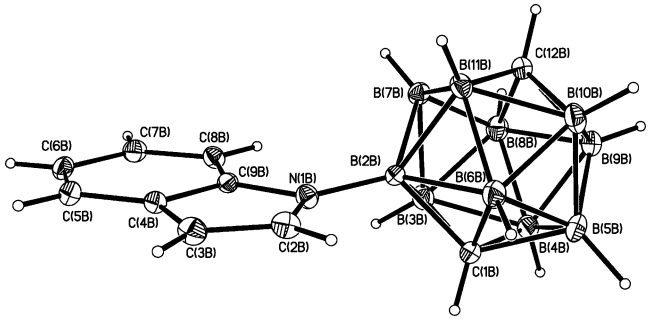


Figure 3. Structure of one of the independent molecules (B) of *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)indole (**4**) (50% probability thermal ellipsoids). Selected bond distances (Å) for A [B] molecules: N(1)−B(2) 1.468(3) [1.478(3)], C(1)−B(2) 1.737(4) [1.737(4)], C(1)−B(3) 1.717(4) [1.709(4)], C(1)−B(4) 1.701(4) [1.717(4)], C(1)−B(5) 1.702(4) [1.698(4)], C(1)−B(6) 1.695(4) [1.703(4)], C(12)−B(7) 1.707(4) [1.710(4)[. C(12)−B(8) 1.698(5) [1.718(4)], C(12)−B(9) 1.714(4) [1.702(4)], C(12)−B(10) 1.710(4) [1.697(4)], C(12)−B(11) 1.714(4) [1.705(4)]. Bond angle C(2)−N(1)−C(9): 106.8(2)° [106.5(2)°].

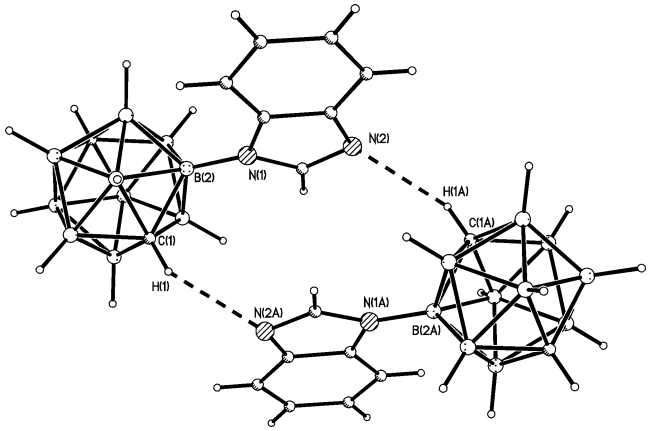


Figure 4. Centosymmetric H-bonded dimer in **2** (H-bond parameters: C(1)−H(1A) 0.95(2) Å, distances N(2)···C(1) and H(1A)···N(2) 3.239(3) and 2.46(2) Å, respectively, C(1)−H(1A)···N(2) bond angle 139°).

in the Heck reaction in the presence of water when K_3PO_4 was used as catalyst.[20] In our case the reactions of 2-iodo-*p*-carborane with NaOH and K_3PO_4 in the presence of water did not lead to the formation of hydroxy derivative **5** (Table 7, entries 3, 4). So, namely, Bu^{t}ONa is the source of the hydroxy derivative in the reaction. Indeed, we showed that the hydroxy derivative was formed in almost quantitative yield in usual reaction conditions using an excess of Bu^{t}ONa (Table 7, entry 2). We could suggest that unlike $ArPdXL_2$ the palladium intermediate *p*-$C_2H_{11}B_{10}$−PdL_2I is able to react with Bu^{t}O$^-$, giving *p*-$C_2H_{11}B_{10}$−Pd−OBu^t, which decomposes with elimination of isobutene to give *p*-$C_2H_{11}B_{10}OH$ (**5**). Compound **5** was isolated and its structure has been investigated.

The structures of the compounds obtained were confirmed by ^{1}H and ^{11}B NMR, mass spectrometry, and elemental analysis. The X-ray crystal structures of compounds **1**, **2**, **4**, and **5** were determined.

Description of the Structures. Molecular structures of *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)carbazole (**1**), *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)benzimidazole (**2**), and *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)indole (**4**) are given in Figures 1, 2, and 3.

(20) Beletskaya, I. P.; Davydov, D. V., Moreno-Manas, M. *Tetrahedron Lett.* **1998**, *39*, 5617.

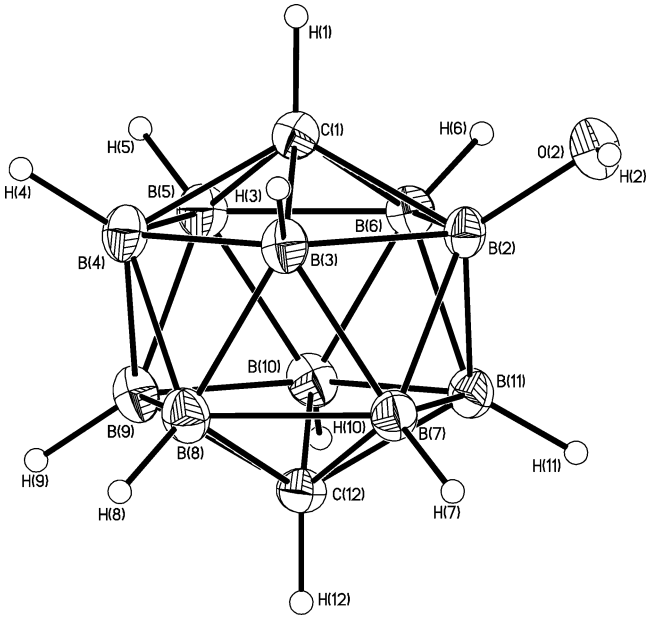


Figure 5. Molecular structure of one of the independent molecules in the crystal of 2-hydroxy-1,12-dicarba-*closo*-dodecaborane (**5**) (30% probability thermal ellipsoids). Selected average bond distances (Å, the average deviation is equal to 0.003): O(2)−B(2) 1.381, C(1)−B(2) 1.734, C(1)−B(3) 1.698, C(1)−B(4) 1.701, C(1)−B(5) 1.704, C(1)−B(6) 1.700, C(12)−B(7) 1.699, C(12)−B(8) 1.702, C(12)−B(9) 1.701, C(12)−B(10) 1.701, C(12)−B(11) 1.701.

The crystals **1** and **4** contain two crystallographically independent molecules in the unit cell (A and B), which have the same structures in **4**, but in **1** the independent molecules differ in the relative disposition of the aromatic system with respect to the carborane moiety by 30.4°; namely, they are rotamers. The dihedral angle (deg) between the plane of the B(2)−B(3)−B(4)−B(5)−B(6) atoms and the plane of the heterocyclic system is 28.2° and 58.6° (for A and B) and 24.2°, 29.0°, and 32.4° (for A and B), respectively, in the structures **1**, **2**, and **4**. Heterocyclic systems in all structures have conventional planar structures with the standard geometrical parameters.

In **1**, **2**, and **4** the B−B bonds in the *p*-carborane moiety located in the parallel five-membered rings (B(2), B(3), B(4), B(5), B(6) and B(7), B(8), B(9), B(10), B(11)) are equal (av 1.783 Å) and slightly longer than the B−B bonds between the cycles (av 1.769 Å). This means that the introduction of a substituent in position 2 of the *p*-carborane icosahedron does not change the B−B bond's nature and influences only the carbon−boron bond, increasing the bond length B(2)−C(1) (av 1.734 Å) in comparison with all other C(1)−B bonds (1.693−1.717 Å) and C(12)−C (1.697−1.718 Å) bonds. This can be explained by the π-electron back-donation from the aromatic ring to the antibonding orbital of the C−B bond, similar to the one found for C- and B-aryl derivatives of *o*- and *m*-carboranes.[21] In the unsubstituted *p*-caborane[22] the bond length distribution is the same as in **1**, **2**, and **4**: the B−B bonds in the B_5-cycles are longer (av 1.781 Å) in comparison to the bonds between the cycles (av 1.760 Å), and on average the B−C bond lengths are equal to 1.705 Å. We have not found any structure of N-substituted *o*-, *m*-, and *p*-carboranes similar to **1**, **2**, and **4** in the Cambridge Structural Database [The Cambridge Structural

(21) Glukhov, I. V.; Lyssenko, K. A.; Korlyukov, A. A.; Antipin, M. Yu. *Faraday Discuss.* **2007**, 203

(22) Davidson, M. G.; Hibbert, T. G.; Howard, J. A. K.; Mackinnon, A.; Wade, K. *Chem. Commun*. **1996**, 2285.

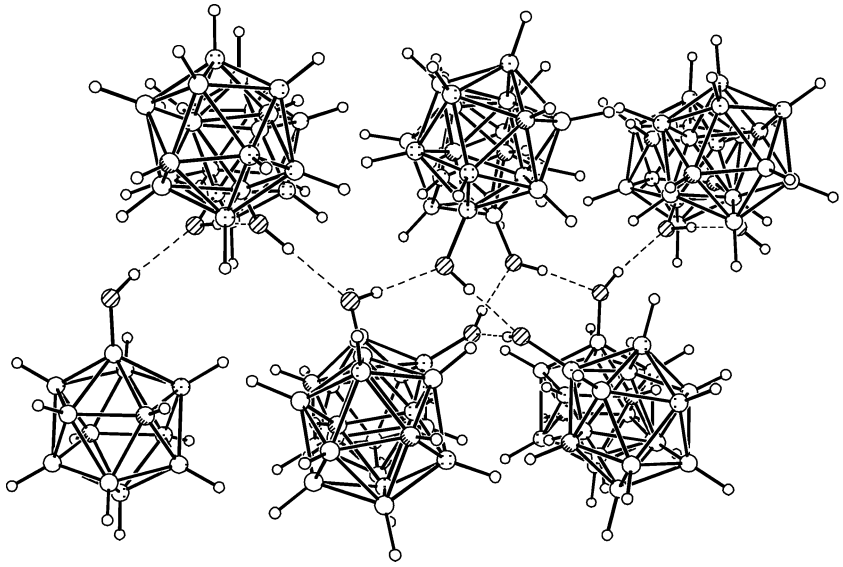


Figure 6. Double layers in the structure **5** (average H-bond parameters: O(2A)−H(2A) 0.82(2) Å, distances O(2A)···O(2B) and H(2A)···O(2B) 2.617 and 1.81 Å, respectively, O(2A)−H(2A)···O(2B) bond angle 170.2°).

Table 8. Crystal Data and Structure Refinement for 1, 2, 4, and 5

	1	**2**	**4**	**5**
formula	$C_{14}H_{19}B_{10}N$	$C_9H_{16}B_{10}N_2$	$C_{10}H_{17}B_{10}N$	$C_2H_{12}B_{10}O$
mol wt	309.40	260.34	259.35	160.22
cryst color, habit	colorless, needle	colorless, plate	colorless, needle	colorless, prism
cryst size, mm	0.25 × 0.20 × 0.15	0.4 × 0.3 × 0.2	0.6 × 0.4 × 0.2	0.21 × 0.17 × 0.13
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1$	$P\bar{1}$	$P2_1$	$C2/c$
cell constants				
a, Å	13.922(4)	7.167(1)	9.834(2)	24.445(2)
b, Å	7.835(2)	9.142(1)	13.467(2)	13.346(1)
c, Å	15.145(4)	10.977(1)	10.802(2)	23.753(2)
α, deg	90	86.316(3)	90	90
β, deg	90.420(5)	76.466(3)	90.274(3)	104.829(2)
γ, deg	90	77.876(3)	90	90
V, Å^3	1651.9(8)	683.5(2)	1430.5(4)	7491.4(11)
Z	4	2	4	32
D_{calcd}, g cm^{-3}	1.244	1.265	1.204	1.136
$2\theta_{max}$, deg	54	56	54	54
abs coeff, μ(Mo Kα), mm^{-1}	0.063	0.064	0.059	0.055
no. reflns collected	12 005	5372	8512	35 537
completeness	0.972	0.982	0.969	1.000
no. indep reflns	6343 (R_{int} = 0.0680)	3174 (R_{int} = 0.0433)	5494 (R_{int} = 0.0315)	8179
no. obsd reflns ($I > 2\sigma(I)$)	4461	1977	4780	3666
abs struct param	4(4)		0(2)	
no. of params	451	190	379	657
R_1 (on *F* for obsd reflns)	0.0780	0.0606	0.0556	0.0547
wR_2 (on F^2 for all reflns)	0.1338	0.1182	0.1230	0.1287
weighting scheme		$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, $P = 1/3(F_o^2 + 2F_c^2)$		
A	0.0016	0.0212	0.0166	0.018
B	1.1889	0.3550	1.2683	
F(000)	640	268	536	2624
GOOF	1.019	1.016	1.015	1.046
largest diff peak and hole, e Å^{-3}	0.197 and −0.241	0.271 and −0.208	0.252 and −0.218	0.263 and −0.272

Database, release 1.8 (November 2005)]. In the structures of N-substituted *o*-carboranes the B−N bond lenghts in 3-cyano- (1.463[23] and 1.467 Å[24]) and 3-aminocarbonyl-1,2-dicarba-*closo*-dodecaboranes (1.469[24] and 1.460 Å[25]) are shorter than the N(1)−B(2) bond (av 1.476 Å) in **1**, **2**, and **4**.

The packing of molecules in structures **1**, **2**, and **4** is defined by the van der Waals interactions between the atoms. Only in structure **2** are centrosymmetric dimers formed (see Figure 4) due to the presence of rather weak hydrogen bonds C(1)−H(1A)···N(2).

The structure of 2-hydroxy-*p*-carborane (**5**) is given in Figure 5. So far there have not been reported any crystal structures of monohydroxy derivatives of carboranes. The crystal **5** is monoclinic with four independent molecules in the unit cell, which have the same structure. The B−O bond lengths are within the range 1.391−1.385 Å (av 1.389 Å). The same B−O bond lengths were found for B-decahydroxy-*p*-carborane 1,12-H_2-1,12-$C_2B_{10}(OH)_{10}$ (av 1.394 Å),[26] in *closo*-2,3,4,5,6,7,8,9,-10,11-decamethoxy-1,12-bis(sulfonic acid)-1,12-dicarbadodecaborane, and for its sodium and potassium salts (av 1.390 Å).[27]

(23) Morel, P.; Schaffer, P.; Valliant, J. F. *J. Organomet. Chem.* **2003**, *668*, 25.

(24) Valliant, J. F.; Schaffer, P. *J. Inorg. Biochem.* **2001**, *85*, 43.

(25) Krasnov, V. P.; Levit, G. L.; Charushin, V. N.; Grishakov, A. N.; Kodess, M. I.; Kalinin, V. N.; Ol'shevskaya, V. A.; Chupakhin, O. N. *Tetrahedron: Asymmetry* **2002**, *13*, 1833.

All interatomic distances in **5** are typical for *p*-carboranes. The C−B bond lengths are within the range 1.691−1.711Å with the exception of the C(1)−B(2) bonds, which are longer by ca. 0.03 Å (1.731−1.737 Å) due to the electron lone pair donation from the oxygen atom of the hydroxy group to the antibonding orbital of the corresponding C−B bond. Earlier, its existence was shown by quantum-chemical calculations.[28] In the crystal **5** molecules linked by the O−H···O hydrogen bond network (see Figure 6) in the double layers are placed parallel to the *ab* plane.

Conclusion

The palladium-catalyzed cross-coupling of 2-iodo-*p*-carborane with various NH nucleophiles (azoles, anilines, and morpholine) at the boron atom is described for the first time. The best yields of aminated *p*-carboranes were reached using the system Pd(dba)$_2$−BINAP−Bu^{t}ONa in dioxane at 100 °C. A significant amount (up to 30%) of 2-hydroxy-*p*-carborane as a side product was formed in some of these reactions, most likely due to reaction of iodo-carborane with Bu^{t}ONa. The compounds with carbazole, benzimidazole, indole, and hydroxy fragments at the boron atom of *p*-carborane have been characterized by X-ray structural analysis to be the first examples of B−N derivatives of *p*-carborane with resolved structures.

Experimental Section

General Comments. All reactions were performed under argon in oven-dried glassware. Flash chromatography was carried out on Merck silica gel 60 (4360 mesh), and Merck silica 60 F254 was used for thin-layer chromatography (TLC). The TLC plates were developed with palladium chloride in acidified (hydrochloric acid) methanol solution. Dioxane was dried over sodium benzophenone ketyl and distilled under argon prior to use. The ^{1}H and ^{11}B NMR spectra were recorded on Bruker AMX-400 and Varian XL-400 spectrometers at 400 and 128.3 MHz, respectively, from solutions in $CDCl_3$. The ^{11}B chemical shifts were measured relative to $Et_2O\cdot BF_3$ as external reference. The mass spectra were obtained on a Finnigan SSQ-7000 instrument. Elemental analyses were performed in the Microanalytical Laboratory of INEOS RAS, Moscow, Russia.

General Procedure for Amination Reaction. An oven-dried 5 mL tube was charged with 2-iodo-*p*-carborane (81 mg, 0.3 mmol), amine (0.3 mmol), Bu^{t}ONa (34.6 mg, 0.36 mmol), Pd(dba)$_2$ (8.6 mg, 5%), and BINAP (9.3 mg, 5%), and 3 mL of dry dioxane was added. The tube was evacuated and back-filled with argon. Then the tube was immersed in a preheated oil bath and stirred at 100 °C for 24−48 h. The reaction was monitored by TLC using petroleum ether as eluent. The reaction was stopped *either* after precipitation of palladium black *or* when all 2-iodo-*p*-caborane was consumed. The resulting mixture was diluted with 5 mL of diethyl ether and filtered through a pad of silica gel, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography using chloroform or petroleum ether as eluent.

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)carbazole (1)** was prepared in two ways. (A) According to the general procedure a colorless crystalline solid (57%) was obtained, mp = 166−167 °C. ^{11}B NMR: −18.9 (d, 1B, J = 169 Hz), −16.4 (d, 2B, J = 131 Hz), −15.5 (d, 4B, J = 150 Hz), −14.2 (d, 2B, J = 167 Hz), −3.7 (s, 1B). ^{1}H NMR: 1.3−3.4 (m, 9 H, B−H), 2.70 (s, 1H, cage C−H), 2.99 (s, 1H, cage C−H), 7.30 (t, 2H, J = 7.7 Hz, carbazole), 7.44 (t, 2H, J = 7.7 Hz, carbazole), 8.01 (d, 2H, J = 8.1 Hz, carbazole), 8.09 (d, 2H, J = 7.7 Hz, carbazole). Anal. Calcd for $C_{14}H_{19}B_{10}N$: C, 54.34; H, 6.19; B, 34.94; N, 4.53. Found: C, 54.39; H, 6.19; B, 35.21; N, 4.06. MS: *m*/*z* 309 [M$^+$].

(B) A carbazole was added (66 mg, 0.4 mmol) to a suspension of sodium hydride (60% dispersion in mineral oil; 0.35 mmol) in dioxane (3 mL). The mixture was stirred at 100 °C for 15 min, and then 2-iodo-*p*-carborane, Pd(dba)$_2$ (8.6 mg, 5%), and BINAP (9.3 mg, 5%) were added to the mixture. The stirring was continued at 100 °C for 48 h. The resulting mixture was diluted with 5 mL of diethyl ether and filtered through a pad of silica gel, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel with an eluent of petroleum ether to afford a colorless crystalline solid (78%).

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)benzimidazole (2)** was prepared according to the general procedure to give a colorless crystalline solid (71%), mp = 196−197 °C. ^{11}B NMR: −18.6 (d, 1B, J = 164 Hz), −16 (d, 2B, J = 133 Hz), −15.1 (d, 6B, J = 139 Hz), −5.1 (s, 1B). ^{1}H NMR: 0.8−3.5 (m, 9 H, B−H), 3.01 (s, 1H, cage C−H), 3.31 (s,1H, cage C−H), 7.29 (t, 1H, J = 7.0 Hz, benzimidazole), 7.33 (t, 1H, J = 7.0 Hz, benzimidazole), 7.81 (d, 1H, J = 7.0 Hz, benzimidazole), 7.83 (d, 1H, J = 7.0 Hz, benzimidazole), 8.07 (s, 1H, benzimidazole). Anal. Calcd for $C_9H_{16}B_{10}N_2$: C, 41.52; H, 6.19; B, 41.53; N, 10.76. Found: C, 41.61; H, 6.28; B, 41.74; N, 10.48. MS: *m*/*z* 260 [M$^+$].

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)imidazole (3)** was prepared according to the general procedure to give a colorless crystalline solid (68%), mp = 115−117 °C. ^{11}B NMR: −19.1 (d, 1B, J = 178 Hz), −16.2 (d, 2B, J = 159 Hz), −15.1 (d, 4B, J = 149 Hz), −14.7 (s, 2B J = 93 Hz), −4.8 (s, 1B). ^{1}H NMR: 1.5−3.3 (m, 9H, B−H), 3.02 (s, 1H, cage C−H), 3.23 (s, 1H, cage C−H), 7.09 (s, 1H, imidazole), 7.12 (s, 1H, imidazole), 7.71 (s, 1H, imidazole). Anal. Calcd for $C_5H_{14}B_{10}N_2$: C, 28.56; H, 6.71; N, 13.32. Found: C, 29.02; H, 7.01; N, 12.94. MS: *m*/*z* 210 [M$^+$].

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)indole (4)** was prepared according to the general procedure to give a colorless crystalline solid (63%), mp = 151−153 °C. ^{11}B NMR: −19.6 (d, 1B, J = 164 Hz), −16.6 (d, 2B, J = 155 Hz), −15.5 (d, 4B, J = 147 Hz), −14.7 (d, 2B, J = 111 Hz), −3.8 (s, 1B). ^{1}H NMR: 1.5−3.4 (m, 9H, B−H), 2.98 (s, 1H, cage C−H), 3.32 (s, 1H, cage C−H), 6.63 (d, 1H, J = 3.3 Hz, indole), 7.19 (t, 1H, J = 7.6 Hz, indole), 7.29 (t, 1H, J = 7.6 Hz, indole), 7.36 (d, 1H, J = 3.3 Hz, indole), 7.65 (d, 1H, J = 7.6 Hz, indole), 7.93 (d, 1H, J = 7.6 Hz, indole). Anal. Calcd for $C_{10}H_{17}B_{10}N$: C, 46.31; H, 6.61; N, 5.40. Found: C, 46.26; H, 6.53; N, 5.01. MS: *m*/*z* 259 [M$^+$].

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)benzenamine (6)** was prepared according to the general procedure to give a colorless crystalline solid (59%), mp = 93−94 °C. ^{11}B NMR: −21.6 (d, 1B, J = 167 Hz), −17.2 (d, 2B, J = 170 Hz), −15.8 (d, 4B, J = 155 Hz), −14.9 (d, 2B, J = 135 Hz), −3.1 (s, 1B). ^{1}H NMR: 1.5−3.2 (m, 9H, B−H), 2.82 (s, 1H, cage C−H), 3.08 (s, 1H, cage C−H), 3.90 (s, 1H, NH), 6.77 (t, 1H, J = 7.3 Hz, Ph), 6.96 (d, 2H, J = 7.7 Hz, Ph), 7.18 (m, 2H, J = 7.3 Hz, J = 7.7 Hz, Ph). Anal. Calcd for $C_8H_{17}B_{10}N$: C, 40.83; H, 7.28; B, 45.94; N, 5.95. Found: C, 41.10; H, 7.32; B, 46.05; N, 5.62. MS: *m*/*z* 235 [M$^+$].

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)-4-methoxybenzenamine (8)** was prepared according to the general procedure to give a colorless crystalline solid (47%), mp = 100−102 °C. ^{11}B NMR: −21.6 (s, 1B), −17.4 (d, 2B, J = 178 Hz), −15.9 (d, 4B, J = 157 Hz), −14.9 (d, 2B, J = 137 Hz), −2.7 (s, 1B). ^{1}H NMR: 1.3−3.5 (m, 9H, B−H), 2.85 (s, 1H, cage C−H), 3.10 (s, 1H, cage C−H), 3.71 (s, 1H, NH), 3.78 (s, 3H, OMe), 6.80 (d, 2H, J = 8.4 Hz, C_6H_4), 6.92 (d, 2H, J = 8.4 Hz, C_6H_4). Anal. Calcd for $C_9H_{19}B_{10}NO$: C, 40.74; H, 7.22; B, 40.74; N, 5.28. Found: C, 41.07; H, 7.44; B, 40.40; N, 4.93. MS: *m*/*z* 256 [M$^+$].

(26) Peymann, T.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1062.

(27) Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **2001**, *123*, 12791.

(28) Oliva, J. M.; Allan, N. L.; Schleyer, P. v. R.; Viñas, C.; Teixidor, F. *J. Am. Chem. Soc.* **2005**, *127*, 13538.

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)morpholine (9)** was prepared according to the general procedure, but 10% of $(t\text{-}Bu)_3P\cdot HBF_4$ was used instead of BINAP. Yield: 33%, a colorless crystalline solid, mp =74−76 °C. ^{11}B NMR: −22.5 (d, 1B, J = 177 Hz), −17.9 (d, 2B, J = 173 Hz), −16.2 (d, 6B, J = 211 Hz), 1.1 (s, 1B). ^{1}H NMR: 1.3−3.1 (m, 9H, B−H), 2.76 (s, 1H, cage C−H), 2.95 (s, 1H, cage C−H), 2.95 (t, 4H, J = 4.2 Hz, morpholine), 3.64 (t, 4H, J = 4.2 Hz, morpholine). Anal. Calcd for $C_6H_{19}B_{10}NO$: C, 31.42; H, 8.35; N, 6.11. Found: C, 31.80; H, 8.34; N, 5.82. MS: m/z 229 [M^+].

2-Hydroxy-1,12-dicarba-*closo*-dodecaborane (5). To an oven-dried 5 mL tube charged with 2-iodo-*p*-carborane (81 mg, 0.3 mmol), Bu^{t}ONa (87 mg, 0.9 mmol), $Pd(dba)_2$ (8.6 mg, 5%), and BINAP (9.3 mg, 5%) was added 3 mL of dry dioxane. The tube was evacuated, back-filled with argon, and stirred at 100 °C for 20 h. The reaction mixture was diluted with 3 mL of diethyl ether, filtered through a pad of silica gel, and concentrated to leave a crude oil. The resulting oil was purified by flash chromatography on silica gel with chloroform as eluent to afford a colorless crystalline solid (78%), mp = 162−163 °C. ^{11}B NMR: −24.7 (d, 1B, J = 167 Hz), −18.1 (d, 2B, J = 194 Hz), −16.4 (d, 4B, J = 187 Hz), −14.5 (d, 2B, J = 163 Hz), 2.3 (s, 1B). ^{1}H NMR: 1.3−3.5 (m, 9H, B−H); 2.50 (s, 1H, cage C−H), 2.72 (s, 1H, cage C−H), 3.14 (s, 1H, O−H). MS: m/z 160 [M^+].

X-ray Crystal Structure Determination of Compounds 1, 2, 4, and 5. Crystals of **1**, **2**, **4**, and **5** suitable for X-ray crystal structure determination were grown by slow crystallization from the chloroform solution at room temperature. Single-crystal X-ray diffraction experiments for **1**, **2**, **4**, and **5** were carried out with a Bruker SMART 1000 CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure) at 120 K. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated using SAINT software[29,30] and the semiempirical method of SADABS.[31]

The structures were solved by the direct method and refined by full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms of the carborane moiety and OH groups were located from the difference Fourier syntheses, and the H(C) atoms were placed in geometrically calculated positions. All hydrogen atom positions were refined in isotropic approximation in a riding model with the U_{iso}(H) parameters equal to $1.2U_{eq}$(Ci), where U(Ci) are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. All calculations were performed on an IBM PC/AT using the SHELXTL software.[32] Crystallographic data and refinement parameters for compounds are presented in Table 8.

Acknowledgment. Financial support by the Russian Foundation for Basic Researches (Grant No. 05-03-32359) is gratefully acknowledged.

Supporting Information Available: Crystallographic data for the structures **1**, **2**, **4**, and **5** (atomic coordinates, bond lengths, bond angles, and thermal parameters). This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited at the Cambridge Crystallographic Data Centre (CCDC). Deposition numbers for the structures **1**, **2**, **4**, and **5** are 615616, 615615, 615617, and 629064 correspondingly. These data can be obtained free of charge on application to the CCDC (e-mail deposit@ccdc.cam.ac.uk).

OM0611756

(29) *SAINTPlus*, Data Reduction and Correction Program v. 6.01; Bruker AXS: Madison, WI, 1998.
(30) *SMART*, Bruker Molecular Analysis Research Tool, v. 5.059; Bruker AXS: Madison, WI, 1998.
(31) Sheldrick G. M. *SADABS* v.2.01, Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998.
(32) Sheldrick G. M. *SHELXTL-97*, Version 5.10; Bruker AXS Inc.: Madison, WI, 1997.