Catalytic Amidation of 9-Iodo-*m*-carborane and 2-Iodo-*p*-carborane at a Boron Atom

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The palladium-catalyzed amidation of *B*-iodocarboranes by various amides is described for the first time. The reactions of 2-iodo-1,12-dicarba-*closo*-dodecaborane (2-iodo-*p*-carborane) with acetamide, 2-pyrrolidinone, caprolactam, *p*-methylbenzamide, and 2-phenylacetamide using the system $Pd(dba)_2$/BINAP/NaH (dba = dibenzylideneacetone; BINAP = *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) in dioxane at 100 °C gave 2-*p*-carboranyl derivatives of these amides in good to high yields. Similar reactions of 9-iodo-1,7-dicarba-*closo*-dodecaborane (9-iodo-*m*-carborane) with corresponding amides afforded 9-*m*-carboranyl derivatives in good to high yields. The structures of *N*-(1,12-dicarba-*closo*-dodecaboran-2-yl)pyrrolidin-2-one (**5**), *N*-(1,7-dicarba-*closo*-dodecaboran-9-yl)acetamide (**6**), and *N*-(1,7-dicarba-*closo*-dodecaboran-9-yl)-2-phenylacetamide (**7**) have been established by X-ray diffraction studies.

Introduction

The unique properties of carboranes account for many applications in materials science,[1−4] nonlinear optics,[2,5,6] and medicinal chemistry,[7] especially in boron neutron capture therapy (BNCT). The last method requires the development of new routes to incorporate carborane groups into biologically active compounds. Carborane units can be attached to other molecule either via their C or B atoms. While substitution at the carbon atom in carborane derivatives has been extensively studied,[8] alternative routes involving reactions at the boron center are still a challenge.

Palladium-catalyzed cross-coupling provides a novel route for the introduction of functionality at the boron atoms.[9] However, the study of this palladium-catalyzed boron−carbon bond formation revealed significant differences between the reactivity of C−Hal[10] and carborane B−Hal bonds. Thus, all attempts to detect the formation of a $[C_2H_{11}B_{10}-PdL_2I]$ complex, which could in principle be formed as a result of oxidative addition of the B−I bond to the Pd(0) center, have failed thus far.[11] DFT calculations also indicate that B−I bond reactivity is much lower than the reactivity of an aromatic C−Cl bond.[12]

In comparison with cross-coupling reactions such as the Suzuki and Sonogashira reactions, amination and especially amidation reactions are much more challenging and complicated processes.[13] It is known that even with aryl iodides these reactions require an appropriate choice of base and ligand and

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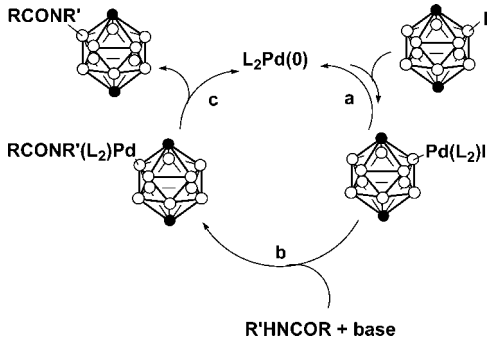
Table 1. Reaction of 2-Iodo-*p*-carborane with Acetamide[a]

entry	base	yield[b] of B−N(**1**), %
1	Cs_2CO_3	10
2	K_3PO_4	16
3	$NaOBu^t$	77
4	NaH	95[c]

[a] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane, 0.15 mmol of acetamide, 0.15 mmol of base, catalyst, 2.5 mol % of $Pd(dba)_2$, 2.5 mol % of BINAP, 1 mL of dioxane, 100 °C, 72 h. [b] Yield determined by ^{11}B NMR. [c] Reaction conditions: 0.1 mmol of 2-iodo-*p*-carborane and catalyst (2.5 mol % of $Pd(dba)_2$, 2.5 mol % of BINAP) were added to 0.14 mmol of acetamide pretreated with 0.12 mmol of NaH in 1 mL of dioxane, 100 °C.

Scheme 1. Proposed Catalytic Cycle for 2-Iodo-*p*-carborane Amidation



are often accompanied by competitive side processes such as reductive dehalogenation.[10] Nevertheless, we have successfully realized the amination of iodo-*p*-carborane (although the reaction is accompanied by unusual hydroxyl derivative formation).[14] This encouraged us to attempt the amidation of carboranes at the boron atom, especially since the products may be expected to possess some interesting properties.

Results and Discussion

Amidation of 2-Iodo-*p*-carborane. It is known that the Pd-catalyzed amidation of aryl halides is more difficult to effect than their amination and that it often requires bulky, electron-rich phosphine ligands and a thorough optimization of reaction conditions.[15] However, in the case of carboranes B−I bond amidation proceeds under the same conditions as amination. Initial attempts using the catalytic system $Pd(dba)_2$/BINAP/$NaOBu^t$/dioxane (100 °C), which we reported earlier for amination, were successful for amidation. Reaction of 2-iodo-*p*-carborane with acetamide as a model reagent afforded the expected coupling product in 77% yield (as determined by ^{11}B NMR) (Table 1, entry 3). However, although a 77% yield usually is quite acceptable, taking in consideration the high cost and limited availability of both *p*-carborane and its iodo derivative, it was necessary to improve the yield of this reaction.

Attempts to change the base and to use bases weaker than t-BuONa, such as Cs_2CO_3 and K_3PO_4, were not successful. These bases are conventionally employed in Pd-catalyzed amidation reactions, but in our case they gave only poor results—10 and 16% product yields, respectively (Table 1, entries 1 and 2). The reason could be that a high concentration of amidate anion is required for realization of the reaction in which equilibrium a is moved to initial compounds (Scheme 1). Otherwise, a side process leading to degradation of catalytic system occurs, and palladium black precipitation is observed under prolonged heating.

Scheme 2. Amidation of 2-Iodo-*p*-carborane

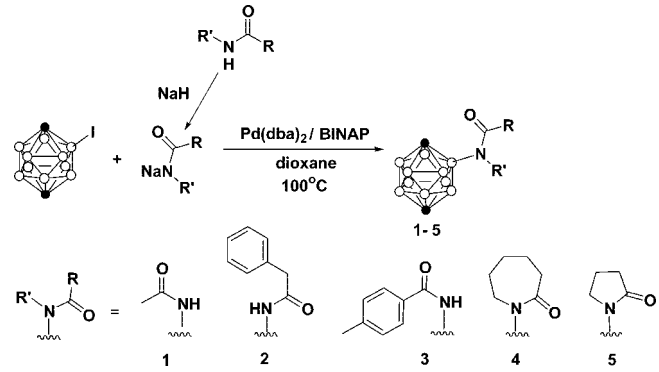
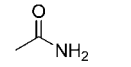
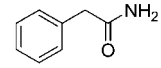
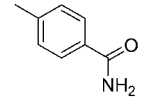


Table 2. Amidation of 2-Iodo-*p*-carborane by Different Amides[a]

entry	amide	product	yield[b] B-N, %
1		**1**	(85)51[c]
2		**2**	(90)73
3		**3**	73
4		**4**	73
5		**5**	(80)51[c]

[a] Reaction conditions: 0.37 mmol of 2-iodo-*p*-carborane and catalyst were added to 0.52 mmol of corresponding amide pretreated with 0.42 mmol of NaH in 3 mL of dioxane, 100 °C, 72 h. [b] Isolated yields. The yield determined by ^{11}B NMR is shown in parentheses. [c] Decreased isolated yields are due to the poor separation of products from dba.

The use of NaH which can fully deprotonate amides results in some formation of the reduced product $C_2H_2B_{10}H_{10}$ in addition to the desired product. However, pretreatment of amides with NaH before the reaction resulted in an almost quantative yield of the product **1** (Table 1, entry 4).

Using these optimized reaction conditions, we have carried out the amidation of 2-iodo-*p*-carborane by different types of amides: aliphatic amides (acetamide, 2-phenylacetamide), aromatic amides (*p*-methylbenzamide), and lactams (caprolactam, pyrrolidin-2-one) (Scheme 2). In all of these reactions high yields of the expected products were obtained. In some cases the isolation of pure compounds was difficult, due to contamination with trace amounts of dba. Consequently, the isolated yield of analytically pure product was significantly lower (50−70%) than the yield determined by NMR spectroscopy (Table 2).

Amidation of 9-Iodo-*m*-carborane. The same protocol used for amidation of 2-iodo-*p*-carborane was employed for amidation

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Scheme 3. Amidation of 9-Iodo-*m*-carborane

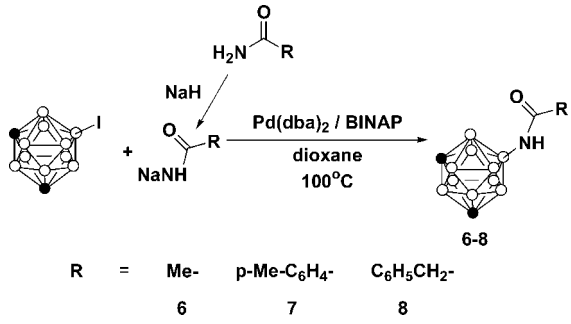
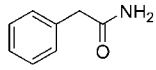
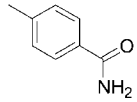


Table 3. Amidation of 9-Iodo-*m*-carborane by Various Amides[a]

entry	amide	product	yield[b] B-N, %
1		**6**	67
2		**7**	63
3		**8**	66

[a] Reaction conditions: 0.37 mmol of 9-iodo-*m*-carborane and catalyst were added to 0.52 mmol of corresponding amide pretreated with 0.42 mmol of NaH in 3 mL of dioxane, 100 °C, 72 h. [b] Isolated yields.

of 9-iodo-*m*-carborane. It is known that 9-iodo-*m*-carborane is less reactive in cross-coupling reactions than 2-iodo-*p*-carborane.[16] Nevertheless, the amidation of 9-iodo-*m*-carborane with acetamide, 2-phenylacetamide, and *p*-methylbenzamide (Scheme 3) afforded practically the same high yields of the products as did the reaction of 2-iodo-*p*-carborane, and pure compounds were isolated in 63−67% yields (Table 3).

Description of the Structures. We have investigated the crystal structures of carboranylamides **5**−**7** obtained in this study. The crystals of compounds **6** and **7** have one and two independent molecules in the unit cell, respectively (Figure 1).

In general, the structures of the central amide fragment are similar. Atoms N(13), C(14), O(15), and C(16) are almost coplanar. The deviation of the atoms from the mean planes is equal to 0.002 Å or **6** and 0.002 and 0.001 Å for the two independent molecules of **7**, respectively. A comparison of bond lengths in these fragments is given in Table 4. It should be noted that the largest variation is observed by the analysis of the relative disposition of the amide fragments and the carborane moiety. Usually for such an analysis the value of the dihedral angle θ is used, which in the present case was chosen as a modulus of the B(12)−B(9)−N(13)−C(14) angle. In the studied compounds the θ angle values are equal to 12.1° for **6** and 108.3 and 65.2° for the two independent molecules of **7**, respectively. It is evident that this fact is caused by the free rotation of the amide fragment around the B(9)−N(13) bond in solution, which leads to the absence of a preferred conformation upon the crystallization and is also the reason for the presence of two independent molecules in the crystal.

The lengths of the B(9)−N(13) bond in the studied compounds vary slightly and are 1.485(2) Å for **6** and 1.472(5) and 1.480(4) Å in the two independent molecules of **7**, respectively. Analysis of the Cambridge Crystallographic Data Base has shown that in the literature only nine monosubstituted carborane derivatives with B−N bonds are described. Among them six are *o*-carborane derivatives, while the other three are *p*-carboranes. For the latter the B−N bond varies in the range of 1.457−1.482 Å, which is in a good agreement with the values found for **6** and **7**.

In the crystal structures of these compounds a main role is played by the H bonds of N−H···O type. In both **6** and **7** they lead to formation of infinite chains along the *a* axis in the case of **6** and the *b* axis in the case of **7**. Such chain formation in the structure of **6** is shown on Figure 2. Both independent molecules of **7** participate in formation of the same chain. Parameters of the H bonds are given in Table 5.

The structure of the third boron-substituted carboranylamide—*N*-(*p*-carboran-2-yl)pyrrolidine-2-one (**5**)—is shown in Figure 3. The unit cell contains two independent molecules. Analysis of their geometries has shown that they have comparable geometrical parameters (see Table 6).

The lengths of B−N bonds are 1.4824(18) and 1.4767(19) Å in the two independent molecules, respectively, in good agreement with the range found for B−N bonds in similar compounds (see above). The five-membered 2-pyrrolidone rings have an envelope conformation. The deviations of the N1, C′(1), C′(2), and C′(4) atoms from the corresponding mean planes are 0.001 and 0.002 Å, respectively. At the same time, C′(3) atoms are shifted from the planes by 0.408 and 0.423 Å, respectively.

It is noteworthy that if one superimposes both independent molecules so that B(2), N(1), and O(1) atoms coincide, then the flaps of the envelope (atoms C′(3)) are pointed in different directions (see Figure 4). At the same time, the atoms of the carborane moieties also do not coincide. This allows us to state that the two independent molecules present in the crystal of **5** differ in the relative conformation of the five-membered rings as well as in the relative disposition of the ring and the carborane moiety.

Conclusion

Using the system Pd(dba)$_2$/BINAP/NaH in dioxane at 100 °C, an amide group was directly introduced at a boron atom of a carborane cage via a nitrogen atom in one step. It is worth noting that the easiness of amidation at the B atom compared to amination is in contrast with the same reactions at the C atom. On the basis of the reaction developed, the convenient one-step method of synthesis of *N*-(9-*m*- and 2-*p*-carboranyl)amides was proposed. *N*-(2-*p*-Carboranyl)amides have not been known until now.[17] Only one *N*-(9-*m*-carboranyl)amide was described by the example of 9-(*N*-formylamino)-*m*-carborane, which was prepared in several steps.[18]

Experimental Section

General Comments. All reactions were performed under argon in oven-dried glassware. Flash chromatography was carried out on

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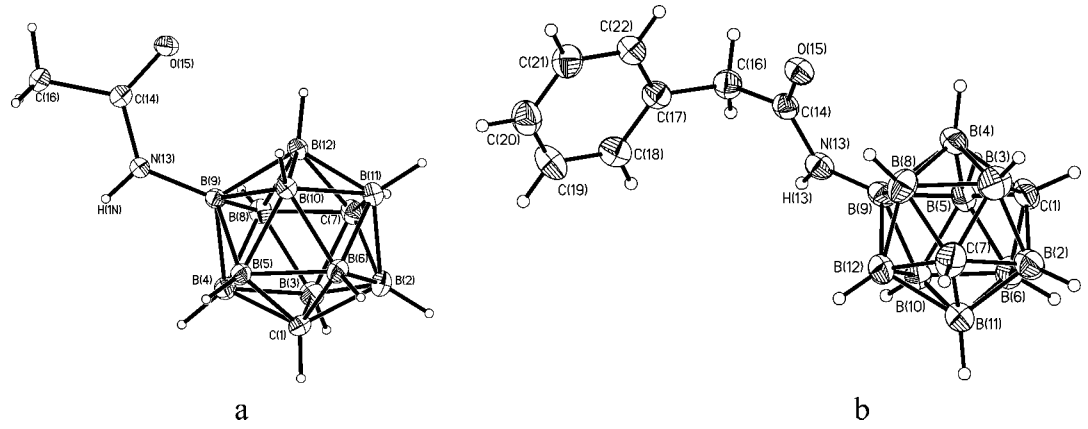

Figure 1. General view of molecules of **6** (a) and one of the independent molecules of **7** (b) in the crystal form. Thermal ellipsoids are shown at the 50% probability level.

Table 4. Selected Bond Lengths (Å) of the Amide Fragment in Crystals of 6 and 7 (for Two Independent Molecules)

	B(9)−N(13)	N(13)−C(14)	C(14)−O(15)	C(14)−C(16)
6	1.485(2)	1.344(2)	1.233(2)	1.507(2)
7	1.472(5)	1.345(4)	1.232(4)	1.529(5)
	1.480(4)	1.344(4)	1.208(4)	1.522(4)

Table 5. Parameters of the H Bonds in Crystals of 6 and 7

	H(13)···O(15) (Å)	N(13)···O(15) (Å)	N(13)−H(13)···O(15) (deg)
6	2.16	2.953(2)	157
7	2.06	2.899(5)	162
	2.22	3.019(4)	153

Merck silica gel 60 (4360 mesh), and Merck silica 60 F254 was used for thin-layer chromatography (TLC). Carborane spots were visualized on TLC by dipping in a 0.5% w/v $PdCl_2$ in 10% concentrated HCl/MeOH solution followed by heating, which gave black spots on a yellow background. All starting amides were recrystallized before use. Dioxane was dried over sodium benzophenone ketyl and distilled under argon prior to use. The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker AMX-400 spectrometer at 400, 100.61, and 128.3 MHz, respectively, from solutions in $CDCl_3$; all shifts are given in units of ppm. ^{11}B chemical shifts were measured relative to $Et_2O \cdot BF_3$ as external reference. Mass spectra were obtained on a Finnigan SSQ-7000 instrument. Elemental analyses were performed in the Microanalytical Laboratory of the INEOS RAS, Moscow, Russia.

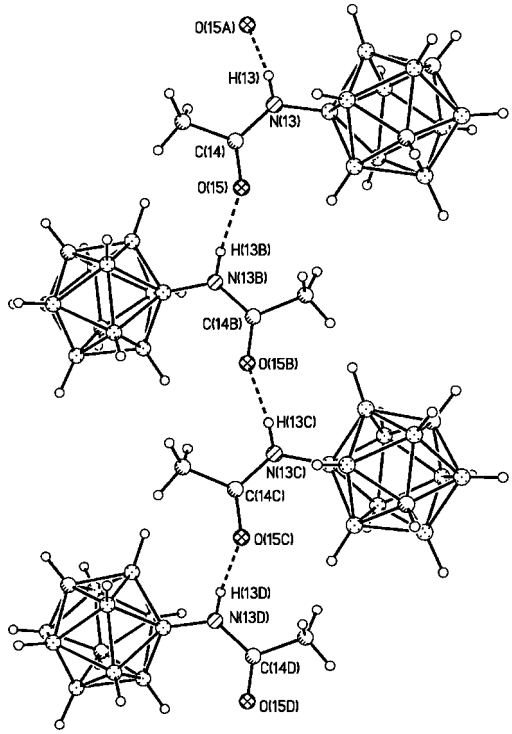

Figure 2. Infinite chains, formed by the N−H···O bonds in the crystal form of **6**.

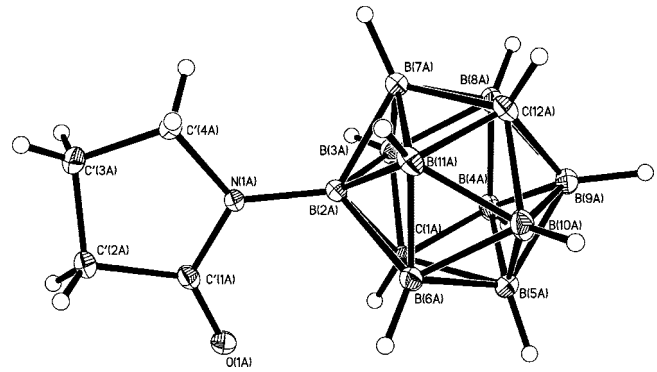

Figure 3. General view of a molecule of **5** in the crystal form. Thermal ellipsoids are shown at the 50% probability level.

Table 6. Selected Bond Lengths (Å) in Two Independent Molecules of 5

B(2)−N(1)	N(1)−C′(1)	N(1)−C′(4)	C′(1)−O(1)
1.4824(18)	1.3647(16)	1.4771(19)	1.2227(16)
1.4767(19)	1.3679(16)	1.4740(19)	1.2318(16)

General Procedure for Amidation Reactions. The amide (0.52 mmol) was added to a suspension of sodium hydride (60% dispersion in mineral oil, used without washing out; 17.4 mg, 0.44 mmol) in dioxane (3 mL). The mixture was stirred at 100 °C for 60 min, and then the corresponding iodocarborane (100 mg, 0.37 mmol), $Pd(dba)_2$ (5.32 mg, 2.5%), and BINAP (5.8 mg, 2.5%) were added to the mixture. Stirring was continued at 100 °C for 72 h. The progress of the reaction was monitored by TLC using chloroform as eluent. Heating was stopped after all iodocarborane was consumed. The resulting mixture was diluted with 5 mL of dichloromethane and filtered through a paper filter. The solvent was carefully removed under vacuum. The crude product was purified by flash chromatography on silica gel using diethyl ether or chloroform as eluent.

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)acetamide (1).** Yield: 51%. Mp: 172−173 °C. ^{11}B NMR: −19.8 (d, 1B, J = 166 Hz), −16.8 (d, 2B, J = 94 Hz), −15.5 (d, 4B, J=160 Hz), −14 (d, 2B, J = 144 Hz), −5.6 (s, 1B). ^1H NMR: 1.3−3.0 (m, 9H, B−H), 2.03 (s, 3H,

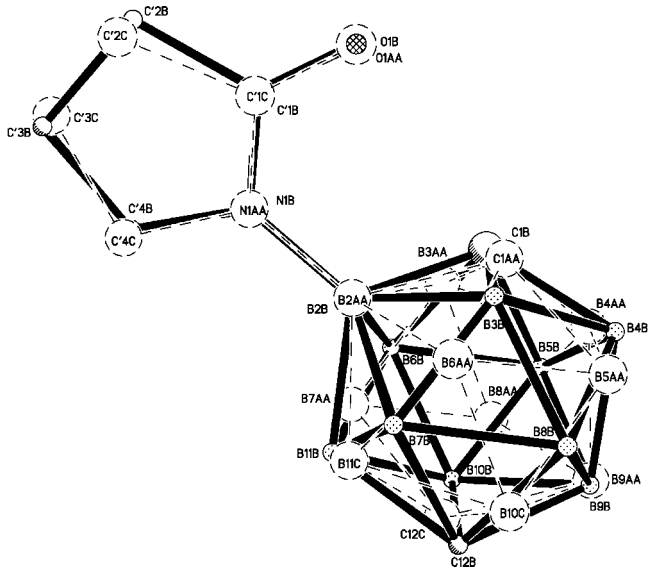

Figure 4. Projection of two independent molecules in the unit cell of **5**, superposed by the atoms B(2), N(1), and O(1).

acetamide CH_3), 2.71 (s, 1H, cage C−H), 3.69 (s, 1H, cage C−H), 5.53 (s, 1H, acetamide NH). ^{13}C NMR: 25.11 (corresponds to Me in AcNH−), 60.51 (cage C), 65.07 (cage C), 173.31 (CO from AcNH−). Anal. Calcd for $C_4H_{15}B_{10}NO$: C, 23.87; H, 7.51; B, 53.71; N, 6.96. Found: C, 23.48; H, 7.56; B, 53.48; N, 6.62.

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)2-phenylacetamide (2).** Yield: 73%. Mp: 155−156 °C. ^{11}B NMR: −19.8 (d, 1B, J = 164 Hz), −16.8 (d, 2B, J = 91 Hz), −15.5 (d, 4B, J = 160 Hz), −14.1 (d, 2B, J = 142 Hz), −5.5 (s, 1B). ^{1}H NMR: 1.4−3.1 (m, 9H, B−H), 2.68 (s, 1H, cage C−H), 3.60 (s, 2H, 2-phenylacetamide CH_2), 3.68 (s,1H, cage C−H), 5.29 (s, 1H, NH), 7.31−7.34 (m, 1H, benzene ring), 7.38−7.41 (m, 2H, benzene ring). ^{13}C NMR: 45.16 (2-phenylacetamide, −NHCO*C*H_2−), 60.58 (carborane cage C), 65.01(carborane cage C), 127.40 (benzene ring C, opposite to −CH_2CONH−), 129.05 (2C, benzene ring), 129.41 (2C, benzene ring), 134.88 (benzene ring C, *C*−CH_2CONH−), 174.05 (CO). Anal. Calcd for $C_{10}H_{19}B_{10}NO$: C, 43.30; H, 6.90; N, 5.05. Found: C, 43.41; H, 6.94; N, 4.89. MS: *m*/*z* (%) 92 (100) ($PhCH_2^{\bullet}$), 156 (3) (NH−$C_2B_{10}H_{11}$), 186 (15) (CONH−$C_2B_{10}H_{11}$), 277 (0.4) $[M]^+$.

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)-*p*-methylbenzamide (3).** Yield: 73%. Mp: 164−165 °C. ^{11}B NMR: −19.7 (d, 1B, J = 155 Hz), −16.7 (d, 2B, J = 96 Hz), −15.4 (d, 4B, J = 159 Hz), −13.9 (d, 2B, J = 141 Hz), −5.1 (s, 1B). ^{1}H NMR: 1.3−3.3 (m, 9H, B−H), 2.42 (s, 3H, *p*-toluamide CH_3), 2.76 (s, 1H, cage C−H), 3.84 (s, 1H, cage C−H), 6.09 (s, 1H, *p*-toluamide NH), 7.25 (d, 2H, J = 8 Hz, *p*-toluamide benzene ring), 7.71 (d, 2H, J = 8 Hz, *p*-toluamide benzene ring). ^{13}C NMR: 21.40 (*p*-methylbenzamide Me), 60.61 (carborane C), 65.25 (carborane C), 127.12 (2C near $CONH_2$ group), 129.19 (2C near CH_3 group), 132.00 (*C*−$CONH_2$), 142.22 (*C*−Me), 169.81 ($CONH_2$). Anal. Calcd for $C_{10}H_{19}B_{10}NO$: C, 43.30; H, 6.90; N, 5.05. Found: C, 43.61; H, 6.97; N, 4.78. MS: *m*/*z* 277 $[M]^+$.

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)caprolactam (4).** Yield: 73%. Mp: 64−65 °C. ^{11}B NMR: −19.7 (d, 1B, J = 167 Hz), −17.1 (d, 2B, J = 123 Hz), −15.7 (d, 2B, J = 120 Hz), −15 (d, 2B, J = 117 Hz), −13.7 (d, 2B, J = 157 Hz), −2.8 (s, 1B). ^{1}H NMR: 1.4−3.1 (m, 9H, B−H), 1.6−1.8 (m, 6H, caprolactam), 2.49−2.56 (m, 2H, caprolactam), 2.71 (s, 1H, cage C−H), 3.71 (s, 2H, caprolactam), 4.41 (s, 1H, cage C−H). ^{13}C NMR: 23.48 (caprolactam C), 28.51 (caprolactam C), 29.35 (caprolactam C), 38.46 (caprolactam C, *C*H_2−CO), 49.56 (caprolactam C, CH_2−N−), 59.39 (carborane cage C), 65.09 (carborane cage C), 180.45 (caprolactam CO). Anal. Calcd for $C_8H_{21}B_{10}NO$: C, 37.63; H, 8.29; B, 42.33; N, 5.48. Found: C, 37.49; H, 8.36; B, 42.49; N, 5.34. MS: *m*/*z* 255 $[M]^+$.

***N*-(1,12-Dicarba-*closo*-dodecaboran-2-yl)pyrrolidin-2-one (5).** Yield: 51%. Mp: 120−121 °C. ^{11}B NMR: −19.4 (d, 1B, J = 168 Hz), −16.6 (d, 2B, J = 159 Hz), −16.2 (d, 2B, J = 162 Hz), −15.4 (d, 2B, J = 170 Hz), −13.9 (d, 2B, J = 159 Hz), −4.9 (s, 1B). ^{1}H

Table 7. Crystal Data and Structure Refinement Details for 5−7

	5	6	7
formula	$C_6H_{17}B_{10}NO$	$C_4H_{15}B_{10}NO$	$C_{10.5}H_{20}B_{10}ClNO$
mol wt	227.31	201.27	319.83
cryst color, habit	colorless, plate	colorless, needle	colorless, prism
cryst size, mm	0.55 × 0.40 × 0.20	0.45 × 0.30 × 0.20	0.23 × 0.17 × 0.14
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	$Pca2_1$	$P2_12_12_1$	$P2_12_12_1$
cell constants			
a, Å	16.7029(8)	8.8115(9)	11.0222(16)
b, Å	7.4094(4)	10.4327(10)	15.039(2)
c, Å	19.8847(9)	12.6598(13)	20.857(3)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
V, Å^3	2460.9(2)	1163.8(2)	3457.4(9)
Z	8	4	8
D_{calcd}, g cm^{-3}	1.227	1.149	1.229
$2\theta_{max}$, deg	54	60	52
abs coeff (Mo Kα), mm^{-1}	0.064	0.060	0.215
no. of rflns collected	30 182	13 313	30 307
completeness	0.993	0.999	0.990
no. of indep rflns	3664 (R_{int} = 0.0243)	1778 (R_{int} = 0.0518)	6746 (R_{int} = 0.0503)
no. of obsd rflns ($I > 2(I)$)	3494	1605	4830
abs structure param	n/a	n/a	−0.01(11)
no. of params	409	193	424
R1 (on F for obsd rflns)	0.0343	0.0394	0.0649
wR2 (on F^2 for all rflns)	0.0956	0.0992	0.1473
weighting scheme			
A	0.051	0.051	0.015
B	0.975	0.5	8.0
F(000)	944	416	1320
GOF	1.039	0.985	0.975
largest diff peak and hole, e Å^{-3}	0.306 and −0.284	0.338 and −0.262	0.275 and −0.456

NMR: 1.3−3.1 (m, 9H, B−H), 2.08 (quintet, 2H, pyrrolidin-2-one), 2.38 (t, 2H, pyrrolidin-2-one), 2,74 (s, 1H, cage C−H), 3.65 (t, 2H, pyrrolidin-2-one), 4.05 (s, 1H, cage C−H). ^{13}C NMR: 19.90 (2-pyrrolidinone C), 32.65 (2-pyrrolidinone C), 50.45 (2-pyrrolidinone C, *C*H_2−NHCO), 60.35 (carborane cage C), 63.69 (carborane cage C), 179.54 (2-pyrrolidinone CO). Anal. Calcd for $C_6H_{17}B_{10}NO$: C, 31.70; H, 7.54; B, 47.56; N, 6.16. Found: C, 31.51; H, 7.79; B, 47.26; N, 5.98. X-ray-quality crystals were obtained by slow diffusion of warm hexane into a hot chloroform solution of **5**. MS: *m*/*z* 227 $[M]^+$.

***N*-(1,7-Dicarba-*closo*-dodecaboran-9-yl)acetamide (6).** Yield: 67%. Mp: 150−151 °C. ^{11}B NMR: −22 (d, 1B, J = 182 Hz), −18.7 (d, 1B, J = 182 Hz), −15.5 (d, 2B, J = 176 Hz), −14 (d, 2B, J = 148 Hz), 11.2 (d, 1B, J = 149 Hz), −7.1 (d, 2B, J = 164 Hz), −0.9 (s, 1B). ^{1}H NMR: 1.3−3.3 (m, 9H, B−H), 2.02 (s, 3H, CH_3), 2.87 (s, 2H, cage C−H), 5.18 (s, 1H, NH). ^{13}C NMR: 25.12 (Me, AcNH−), 51.83 (2C, carborane cage), 172.81 (CO). Anal. Calcd for $C_4H_{15}B_{10}NO$: C, 23.87; H, 7.51; N, 6.96; B,53.71. Found: C, 23.89; H, 7.49; N, 6.69; B, 53.57.

***N*-(1,7-Dicarba-*closo*-dodecaboran-9-yl)-2-phenylacetamide (7).** Yield: 63%. Mp: 85−86 °C. ^{11}B NMR: −22 (d, 1B, J = 180 Hz), −18.7 (d, 1B, J = 182 Hz), −15.5 (d, 2B, J = 174 Hz), −14 (d, 2B, J = 145 Hz), −11.2 (d, 1B, J = 149 Hz), −7.1 (d, 2B, J = 163 Hz), −0.8 (s, 1B). ^{1}H NMR: 1.3−3.3 (m, 9H, B−H), 2.84 (s, 2H, cage C−H), 3.60 (s, 2H, 2-phenylacetamide CH_2), 5.16 (s, 1H, NH), 7.27−7.31 (m, 3H, benzene ring), 7.34−7.38 (m, 2H, benzene ring). ^{13}C NMR: 45.09 (Ph*C*H_2CONH−), 51.84 (carborane cage C), 127.09 (benzene ring C, opposite to −CH_2CONH−), 128.86 (2C, benzene ring), 129.46 (2C, benzene ring), 135.49 (benzene ring C, *C*−CH_2CONH-), 173.61 (CO). Anal. Calcd for $C_{10}H_{19}B_{10}NO$: C, 43.30; H, 6.90; N, 5.05. Found: C, 43.52; H, 6.67; N, 4.79.

***N*-(1,7-Dicarba-*closo*-dodecaboran-9-yl)-*p*-methylbenzamide (8).** Yield: 66%. Mp: 93−94 °C. ^{11}B NMR: −21.9 (d, 1B, J = 180 Hz), −18.6 (d, 1B, J = 182 Hz), −15.4 (d, 2B, J = 173 Hz), −13.8 (d, 2B, J = 148 Hz), −11.1 (d, 1B, J = 150 Hz), −6.9 (d, 2B, J = 162 Hz), −0.4 (s, 1B). ^{1}H NMR: 1.3−3.5 (m, 9H, B−H), 2.38 (s, 3H, *p*-toluamide CH_3), 2.91 (s, 2H, cage C−H), 5.91 (s, 1H, NH), 7.22 (d, 2H, J = 8 Hz), 7.72 (d, 2H, J = 8 Hz). ^{13}C NMR: 21.42 (*C*H_3−C_6H_4−), 51.93 (carborane cage C), 127.22 (2C near $CONH_2$ group), 129.07 (2C near CH_3 group), 132.57 (*C*−$CONH_2$), 141.68 (*C*−Me), 169.46 (*C*ONH_2). Anal. Calcd for $C_{10}H_{19}B_{10}NO$: C, 43.30; H, 6.90; N, 5.05; B, 38.98. Found: C, 43.14; H, 6.91; N, 4.99; B, 38.87.

X-ray Crystal Structure Determination of Compounds 5−7. Crystals of **5**−**7** suitable for X-ray crystal structure determination were grown by slow diffusion of warm hexane into a hot chloroform solution. Crystal data and details of the structure refinement are given in Table 7. Single-crystal X-ray diffraction experiments for **5** and **6** were carried out with a Bruker SMART APEX2 CCD area detector and for **7** with a Bruker SMART 1000 CCD area detector diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å, ω-scans) at 100 K (**5** and **6**) and 120 K (**7**). The 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[19,20] and the semiempirical method SADABS.[21]

The structures were solved by direct methods and refined by full-matrix least squares against F^2 in an anisotropic (for non-hydrogen atoms) approximation. All carborane hydrogen atoms were located from the difference Fourier syntheses; the H(C) atoms were placed in geometrically calculated positions. Some carborane hydrogen atom positions were refined in an isotropic approximation in the riding model with the U_{iso}(H) parameters equal to 1.2[U_{eq}(Xi)], where U(Xi) values are respectively the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. All calculations were performed on an IBM PC/AT computer using SHELXTL software.[22]

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Supporting Information Available: CIF files giving crystallographic data for the structures **5**−**7** (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 **5**−**7** are 693268−693270. These data can be obtained free of charge on application to the CCDC (e-mail deposit@ccdc.cam.ac.uk).

OM800635D

(19) SAINTPlus, Data Reduction and Correction Program, v. 6.01; Bruker AXS, Madison, WI, 1998.
(20) SMART, Bruker Molecular Analysis Research Tool, v. 5.059; Bruker AXS, Madison, WI, 1998.
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