Synthesis, Characterization, and Reactivity of Isocyanato Dicarbaboranes Obtained from *o*-Carborane

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The functionalization of *o*-carborane with (bromoalkyl)phthalimides or propargylphthalimide, their subsequent transformation into isocyanate-substituted *o*-carborane, and their reactivity toward amino- and alcohol-containing molecules are reported. The preparation of these functionalized ureas and carbamates could potentially lead to the utilization of these molecules as suitable precursors for drugs to be used in boron neutron capture therapy (BNCT). The compounds 1-RNHC(O)NH$(CH_2)_n$-1,2-$C_2B_{10}H_{11}$ and 1-ROC(O)NH-1,2-$C_2B_{10}H_{11}$ (n = 1, 2, and 3) were prepared by reaction of 1-O=C=N$(CH_2)_n$-1,2-$C_2B_{10}H_{11}$, (n = 1, 2, and 3) with the corresponding amino- or alcohol-containing substrate. Experimental details and analytical data leading to the identification of the reported compounds are provided. Additionally the X-ray diffraction structures of 1-$C_6H_4(CO)_2NCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**1c**) and 1-$(C_6H_5)_2C$=N-CH_2-1,2-$C_2B_{10}H_{11}$ (**20**) are reported. Compound **1c** crystallizes in the $P\bar{1}$ space group, a = 10.791(1) Å, b = 13.104(1) Å, c = 7.1816(9) Å, α = 97.389(8)°, β = 90.416(5)°, γ = 66.462(6)°, Z = 2, R = 0.0512 for 2140 reflections with $F^2 > 3.0\sigma(F^2)$. Compound **20** crystallizes in the $P2_1/n$ space group, a = 16.5560(7) Å, b = 7.0173(4) Å, c = 16.9750(6) Å, β = 97.932(2)°, Z = 4, R = 0.0843 for 2755 reflections with $F > 4.0\sigma(F)$.

Introduction

The recent report by Teixidor and co-workers, leading to the synthesis and characterization of monolithiated *o*-carborane, according to reactions 1 and 2, has opened a new route for the preparation of new monosubstituted *o*-carborane compounds.

$$1,2\text{-}C_2B_{10}H_{12} + n\text{-BuLi} \rightarrow 1\text{-Li-}1,2\text{-}C_2B_{10}H_{11} + C_4H_{10}\ ^{1} \quad (1)$$

$$1\text{-Li-}1,2\text{-}C_2B_{10}H_{11} + RX \rightarrow 1\text{-R-}1,2\text{-}C_2B_{10}H_{11} + LiX\ ^{1} \quad (2)$$

This method is superior to the previously reported synthetic routes for this type of compound since it precludes the use of monosubstituted alkynes[2] or the preparation of intermediates to block one of the C−H groups in the carborane.[3]

This report prompted us to undertake the preparation of other monosubstituted *o*-carborane compounds. These compounds could be used as potential drugs in boron neutron capture therapy (BNCT). The use of BNCT for cancer therapy as a binary method has been previously summarized by Hawthorne and co-workers.[4] Other potential uses for monosubstituted carboranes are in the area of radiomedical applications since they can be incorporated as immunoconjugates.[5−8]

Recently Soloway and co-workers reported the preparation of (aminoalkyl)carboranes by reactions 3−5.[9]

$$B_{10}H_{12}(CH_3CN)_2 + C_6H_4(CO)_2N(CH_2)_nC{\equiv}CH \rightarrow 1\text{-}C_6H_4(CO)_2N(CH_2)_n\text{-}1,2\text{-}C_2B_{10}H_{11}\ ^{9} \quad (3)$$

$$1\text{-}C_6H_4(CO)_2N(CH_2)_n\text{-}1,2\text{-}C_2B_{10}H_{11} + NaBH_4 + \text{i-PrOH} \rightarrow 1\text{-}C_6H_4(CH_2OH)C(O)NH(CH_2)_n\text{-}1,2\text{-}C_2B_{10}H_{11} \quad (4)$$

$$1\text{-}C_6H_4(CH_2OH)C(O)NH(CH_2)_n\text{-}1,2\text{-}C_2B_{10}H_{11} + HCl + HOAc \rightarrow {}^{+}H_3N(CH_2)_n\text{-}1,2\text{-}C_2B_{10}H_{11} \quad (5)$$

$$n = 1 \text{ or } 3$$

This report also encouraged us to undertake the investigation of monosubstituted *o*-carboranes. We have recently reported the synthesis and characterization of an isocyanatocarborane based on the 7-H_3N-7-$CB_{10}H_{11}$ system.[10]

$$7\text{-}H_3NCB_{10}H_{12} + Cl_2C{=}O \rightarrow [7\text{-}O{=}C{=}N\text{-}7\text{-}CB_{10}H_{12}]^{-} \quad (6)$$

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Given the similarity between 7-H_3N-7-$CB_{10}H_{12}$ and ^+H_3N-$(CH_2)_n$-1,2-$C_2B_{10}H_{11}$, we sought to couple both approaches in order to produce isocyanato carboranes based on the *o*-carborane system.

Experimental Section

All manipulations were carried out using standard high-vacuum or inert atmosphere techniques, when warranted, as described by Shriver.[11]

Materials. *N*-Propargylphthalimide, *N*-(2-bromopropyl)phthalimide, *N*-(3-bromopropyl)phthalimide, *n*-butyllithium (2.0 M in cyclohexane), sodium borohydride, 2-propanol, hydrochloric acid, acetic acid, triphosgene, pyridine, benzene, methylene chloride, benzophenone imine, glycine methyl ester, alanine ethyl ester, phenylalanine methyl ester, 5-aminouracil, adenine, 1-aminoadamantane, 1-(aminopropyl)imidazole, phenethylamine, benzyl alcohol, methanol, *tert*-butyl alcohol, *p*-methoxyphenol, DMSO-d_6, acetone-d_6, CD_3CN, and $CDCl_3$ were purchased form Aldrich. All solvents were dried prior to use. Decaborane-(14) and *o*-carborane were obtained from Strem Chemicals. 1-(Phthalimidomethyl)-1,2-*closo*-dodecaborane (**1a**), (((2-(hydroxymethyl)-benzoyl)amino)methyl)-*o*-carborane (**2a**), and (aminomethyl)-*o*-carborane hydrochloride (**3a**) were prepared according to the literature procedure.[9]

Physical Measurements. The 128.4 MHz boron-11 and 400.0 MHz proton spectra were obtained on a Varian Unity-400 Fourier transform spectrometer. All boron-11 chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2 = 0.0$ ppm with a negative sign indicating an upfield shift. Proton NMR at 200 MHz and carbon-13 NMR at 50.0 MHz were obtained on Varian Gemini-200 Fourier transform spectrometer. Proton chemical shifts and carbon-13 chemical shifts were referenced to TMS = 0.00 ppm with positive values indicating downfield shifts. Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrophotometer and on a Perkin-Elmer 1720 Fourier transform spectrophotometer. Elemental analyses were performed by Desert Analytics, located in Tucson, AZ.

X-ray Crystallography. X-ray intensity data were collected on a Rigaku R-AXIS IIc area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) at a temperature of 295 K for compound **1c** and 235 K for compound **20**. Indexing was performed from a series of 1° oscillations with exposures of 5 and 10 min per frame, respectively. In the case of compound **1c**, a hemisphere of data was collected using 10° oscillations with exposures of 5 min per frame, and for compound **20**, 6° oscillations with exposures of 10 min per frame were used. The crystal to detector distance was 82 mm in both instances. Oscillation images were processed using bioteX,[12] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the teXsan[13] program package for further processing and structure solution on a Silicon Graphics Indigo R4000 computer. Relevant crystallographic data are given in Table 1. The intensity data were corrected for Lorentz and polarization effects but not for absorption.

The structures of compounds **1c** and **20** were solved by direct methods (SIR92).[14] In the case of compound **1c**, refinement was by full-matrix least squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. For compound **20**, the refinement was by full-matrix least squares based on F^2 using SHELXL-93.[15] All reflections were used during refinement (F^2's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + 0.519P^2 + 1.2455P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Positional parameters including displacement parameters, selected bond distances, and bond angles for both compounds are presented in Tables 2−7. Hydrogen atom coordinates and displacement parameters, non-hydrogen atom thermal parameters, and a full listing of interatomic distances and bond angles are available as Supporting Information.

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Table 1. Crystal Data and Structure Refinement for 1-$C_6H_4(CO)_2NCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$ and 1-$(C_6H_5)_2C{=}NCH_2$-1,2-$C_2B_{10}H_{11}$

formula	$C_{13}H_{21}B_{10}NO_2$	$C_{16}H_{23}B_{10}N$
formula weight	331.41	337.45
cryst class	triclinic	monoclinic
a (Å)	10.790(1)	16.5560(7)
b (Å)	13.103(1)	7.0173(4)
c (Å)	7.1816(9)	16.9750(6)
α (deg)	97.389(8)	
β (deg)	90.416(5)	97.932(2)
γ (deg)	66.562(6)	
V (Å^3)	922.1(2)	1953.3(2)
ρ_{calcd} (g cm^{-3})	1.194	1.148
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Z	2	4
μ (cm^{-1})	0.68	0.58
cryst size (mm)	0.40 × 0.28 × 0.15	0.30 × 0.20 × 0.18
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
2θ range (deg)	5.0−50.7	4.84−50.70
hkl collected	+12,±15,±8	+19,±8,±20
no. of rflns measd	6376	14430
no. of unique rflns	3035 (R_{merge} = 0.0371)	3538 (R_{int} = 0.0459)
no. of obsd rflns	2140 ($F^2 > 3.0\sigma(F)^2$)	2755 ($F > 4.0\sigma(F)$)
no. of params	320	289
F(000)	320	704
R	0.0512	0.0843
R_w	0.0608	0.1748
GOF	2.44	1.166
final diff peaks (e/Å^3)	+0.21, −0.22	+0.319, −0.205

Table 2. Refined Positional Parameters for $C_6H_4(CO)_2NCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$

atom	*x*	*y*	*z*	B_{eq}, Å^2 [a]
C1	0.0352(3)	0.7421(2)	0.0084(4)	2.80(6)
C2	0.0507(3)	0.7152(2)	−0.2213(4)	3.62(7)
B3	−0.0191(3)	0.6431(3)	−0.1049(5)	3.47(8)
B4	−0.1152(3)	0.7449(3)	0.0839(5)	3.42(8)
B5	−0.0924(3)	0.8701(3)	0.0740(5)	3.27(8)
B6	0.0181(3)	0.8483(3)	−0.1212(5)	3.49(8)
B7	−0.0844(3)	0.6959(3)	−0.3167(5)	4.40(10)
B8	−0.1953(4)	0.7190(3)	−0.1210(5)	4.00(9)
B9	−0.2398(3)	0.8579(3)	−0.0123(5)	3.80(8)
B10	−0.1571(3)	0.9216(3)	−0.1390(5)	3.44(8)
B11	−0.0605(4)	0.8210(3)	−0.3264(5)	4.25(9)
B12	−0.2211(4)	0.8272(3)	−0.2604(5)	3.95(4)
C13	0.1636(3)	0.7035(3)	0.1211(5)	3.74(8)
C14	0.2177(3)	0.5835(2)	0.1655(5)	3.47(7)
C15	0.3445(3)	0.5632(2)	0.2783(5)	3.47(7)
N16	0.3997(2)	0.4521(2)	0.3405(3)	3.02(5)
C17	0.3705(3)	0.4302(5)	0.5151(4)	3.08(6)
C18	0.4481(2)	0.3082(2)	0.5204(4)	2.62(6)
C19	0.4563(3)	0.2442(3)	0.6598(4)	3.60(7)
C20	0.5418(3)	0.1316(3)	0.6251(5)	3.93(8)
C21	0.6149(3)	0.0864(3)	0.4554(5)	4.35(8)
C22	0.6065(3)	0.1511(3)	0.3154(5)	3.85(8)
C23	0.5213(2)	0.2635(2)	0.3510(4)	2.71(6)
C24	0.4908(3)	0.3523(2)	0.2338(4)	3.06(7)
O1	0.5534(2)	0.3518(2)	0.0763(3)	4.36(5)
O2	0.2976(2)	0.5007(2)	0.6380(3)	4.86(5)

[a] $B_{eq} = {}^8/_3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Synthesis of 1-$(C_6H_4(CO)_2N(CH_2)_n)$-1,2-*closo*-dodecaborane, *n* = 2, 3 (1b,c). At 0 °C, a solution of 2.0 M n-BuLi in cyclohexane (7.00 mmol) was added to a previously prepared solution of *o*-carborane (7.00 mmol) in ethylene glycol dimethyl ether (25.0 mL). After the resulting solution was stirred at 0 °C for 30 min, the solution was allowed to warm up to room temperature and stirred at that temperature for an additional 30 min. After that period of time a solution containing *N*-(2-bromoethyl)phthalimide or *N*-(3-bromopropyl)phthalimide (7.00 mmol) dissolved in 5.0 mL of ethylene glycol dimethyl ether was syringed into the reaction flask, and the resulting reaction mixture was stirred at room temperature for 2 days. The solution was evaporated to

Table 3. Refined Positional Parameters for 1-$(C_6H_5)_2C{=}NCH_2$-1,2-$C_2B_{10}H_{11}$

atom	*x*	*y*	*z*	U_{eq}, Å$^{2\,a}$
C1	0.3200(2)	0.5669(4)	0.5823(2)	0.0463(7)
C2	0.4064(2)	0.4538(4)	0.5950(2)	0.0508(8)
B3	0.4049(3)	0.6748(6)	0.5563(2)	0.0636(10)
B4	0.3343(2)	0.7986(5)	0.6059(2)	0.0566(9)
B5	0.2948(2)	0.6405(6)	0.6703(2)	0.0577(9)
B6	0.3389(3)	0.4146(6)	0.6603(2)	0.0623(10)
B7	0.4845(2)	0.5957(7)	0.6279(3)	0.0743(13)
B8	0.4400(3)	0.8197(7)	0.6382(3)	0.0812(14)
B9	0.3712(2)	0.8011(6)	0.7081(2)	0.0639(11)
B10	0.3739(3)	0.5605(7)	0.7410(2)	0.0777(13)
B11	0.4443(3)	0.4363(7)	0.6917(2)	0.0748(13)
B12	0.4637(3)	0.6715(8)	0.7214(3)	0.0748(13)
C13	0.2548(2)	0.5112(5)	0.5137(2)	0.0705(10)
N14	0.2774(2)	0.3397(4)	0.4734(2)	0.0608(7)
C15	0.2207(2)	0.2263(4)	0.4429(2)	0.0457(7)
C16	0.1326(2)	0.2510(4)	0.4494(2)	0.0449(7)
C17	0.0787(2)	0.3141(5)	0.3854(2)	0.0593(8)
C18	−0.0044(2)	0.3289(5)	0.3929(3)	0.0781(12)
C19	−0.0307(2)	0.2801(5)	0.4635(3)	0.0804(12)
C20	0.0225(2)	0.2208(5)	0.5265(3)	0.0783(11)
C21	0.1031(2)	0.2054(4)	0.5196(2)	0.0594(8)
C22	0.2447(2)	0.0596(4)	0.3972(2)	0.0426(6)
C23	0.3241(2)	0.0373(4)	0.3823(3)	0.0537(8)
C24	0.3459(2)	−0.1167(5)	0.3396(4)	0.0608(8)
C25	0.2886(2)	−0.2487(5)	0.3100(2)	0.0592(8)
C26	0.2094(2)	−0.2276(5)	0.3231(5)	0.0590(8)
C27	0.1873(2)	−0.0752(4)	0.3668(2)	0.0502(7)

^{a} $U_{eq} = {}^1/_3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Table 4. Selected Bond Distances (Å) for $C_6H_4(CO)_2NCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$

O1−C24	1.213(3)	O2−C17	1.213(3)	N16−C15	1.465(4)
N16−C17	1.387(3)	N16−C24	1.388(3)	C1−C2	1.637(4)
C1−C13	1.536(4)	C1−B3	1.737(4)	C1−B4	1.699(4)
C1−B5	1.702(4)	C1−B6	1.721(4)	C2−B3	1.715(4)
C2−B6	1.695(4)	C2−B7	1.702(5)	C2−B11	1.690(5)
C13−C14	1.520(4)	C14−C15	1.533(4)	C17−C18	1.484(4)
C18−C19	1.367(4)	C18−C23	1.381(3)	C19−C20	1.383(4)
C20−C21	1.383(4)	C21−C22	1.377(4)	C22−C23	1.380(4)
C23−C24	1.485(4)	B3−B4	1.773(5)	B3−B7	1.777(5)
B3−B8	1.770(5)	B4−B5	1.764(5)	B4−B8	1.765(5)
B4−B9	1.772(5)	B5−B6	1.766(5)	B5−B9	1.761(5)
B5−B10	1.776(5)	B6−B10	1.758(5)	B6−B11	1.763(5)
B7−B8	1.768(5)	B7−B11	1.768(5)	B7−B12	1.761(5)
B8−B9	1.760(5)	B8−B12	1.770(5)	B9−B10	1.768(5)
B9−B12	1.770(5)	B10−B11	1.762(5)	B10−B12	1.779(5)
B11−B12	1.768(5)				

dryness, and 25.0 mL of distilled water was added to the resulting residue. This solution was stirred at room temperature for 8 h. A white solid precipitated, which was filtered off and recrystallized from methanol. Direct comparison of analytical data of **1a** with that reported in the literature afforded confirmation of the identity for this compound.[9] The $^{11}B\{^1H\}$ NMR of **1a** has not been reported, and it is as follows: δ 1.70 (1B), −0.86 (1B), −5.02 (2B), −7.13 (4B), −8.19 (2B). For **1b**, yield: 3.59 g (81%); mp 140−142 °C; ^1H NMR (DMSO-d_6) δ 2.65 (2H, t, J = 7.9 Hz), 3.68 (2H, t, J = 7.9 Hz), 5.35 (1H, br s, carborane H), 7.85 (4H, br, m); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 34.08 (**C**H_2CH_2), 36.41(CH_2**C**H_2), 64.64 (carborane C), 73.40 (carborane C), 123.86 (aromatic), 131.80 (aromatic), 134.72 (aromatic), 167.63 (C═O), $^{11}B\{^1H\}$ NMR (DMSO-d_6) δ 1.26 (1B), −1.20 (1B), −5.15 (2B), −7.36 (4B), −9.06 (2B); IR (cm^{-1}) 2592 (s), 1768 (m), 1720 (s), 1468 (m), 1448 (w), 1432 (w), 1400 (m), 1380 (m), 1232 (w), 1188 (w), 1148 (w), 1072 (w), 1008 (w), 976 (w), 872 (w), 804 (w), 720 (m), 604 (w), 532 (w). For **1c**: yield, 1.79 g (36%); mp 180−182 °C, ^1H NMR δ 1.92 (2H, m), 2.50 (2H, m), 3.66 (2H, t, J = 6.8 Hz), 4.66 (1H, br s, carborane H), 7.83 (4H, br, m); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 29.10 (**C**$H_2CH_2CH_2$), 35.38 (CH_2**C**H_2CH_2), 37.56 (CH_2CH_2**C**H_2), 63.65 (carborane C), 76.74 (carborane C), 123.78, (aromatic), 133.10 (aromatic), 135.14 (aromatic), 169.22 (C═O); $^{11}B\{^1H\}$ NMR (CD_3-CN) δ 2.02 (1B), −1.07 (1B), −4.65 (2B), −6.57 (4B), −8.00 (2B); IR (cm^{-1}), 2588 (s), 1768 (m), 1716 (s), 1460 (m), 1440 (m), 1400 (m), 1380 (m), 1348 (w), 1192 (w), 1148 (w), 1068 (w), 1048 (w), 828 (m), 724 (m), 628 (w), 532 (w).

Synthesis of (((2-(Hydroxymethyl)benzoyl)amino)alkyl)-*o*-carborane (2a−c). The procedure used for the partial reduction of the phthalimido group was that reported by Soloway and co-workers.[9] The characterization of **2a,** (((2-(hydroxymethyl)benzoyl)amino)methyl)-*o*-carborane, and of **2c**, (((2-hydroxymethyl)benzoyl)amino)propyl)-*o*-carborane, was performed by direct comparison of their ^1H and ^{13}C NMR with those reported in the literature.[9] In the initial report of these compounds, the $^{11}B\{^1H\}$ NMR was not reported; the data is listed here. **2a**: (DMSO-d_6) δ 2.46 (1B), −0.58 (1B), −4.82 (2B), −6.34 (4B), −7.72 (2B), **2c**: (DMSO-d_6) δ 2.16 (1B), −1.03 (1B), −4.60 (2B), −6.48 (4B), −7.96 (2B). For (((2-(hydroxymethyl)benzoyl)amino)-ethyl)-*o*-carborane (**2b**): yield, 2.70 g (83%); mp 121−124 °C, ^1H NMR (DMSO-d_6) δ 2.71 (2H, t, J = 7.7 Hz), 3.56 (2H, m), 4.48 (1H, br s), 4.60 (2H, s), 4.78 (1H, br s, carborane H), 7.46 (4H, m), 8.07 (1H, s); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 36.99 (**C**H_2CH_2), 39.60 (CH_2**C**H_2), 56.94 (**C**H_2OH), 63.92 (carborane C), 74.71 (carborane C), 128.18 (aromatic), 128.63 (aromatic), 130.20 (aromatic), 131.40 (aromatic), 136.04 (aromatic), 141.37 (aromatic), 170.40 (C═O); $^{11}B\{^1H\}$ NMR (DMSO-d_6) δ 1.99 (1B), −0.77 (1B), −4.53 (2B), −6.54 (2B), −8.60 (2B), −9.36 (2B), IR (cm^{-1}), 2564 (s), 2368 (w), 1636 (s), 1600 (w), 1560 (m), 1384 (w), 1332 (w), 1184 (w), 1008 (m), 956 (w), 752 (m).

Synthesis of (Aminoalkyl)-*o*-carborane Hydrochloride (3a−c). The procedure used was similar to that reported by Soloway.[9] Identification of compounds **3a** and **3c** was accomplished by direct comparison of their ^1H and $^{13}C\{^1H\}$ NMR with those reported in the literature.[2] The $^{11}B\{^1H\}$ NMR of these compounds is reported here. **3a**: (DMSO-d_6) δ 1.98 (1B), 0.33 (1B), −5.25 (2B), −11.48 (4B), −13.78 (2B). **3c**: (DMSO-d_6) δ −2.17 (1B), −5.13 (1B), −8.78 (4B), −10.73 (4B). (Aminoethyl)-*o*-carborane hydrochloride (**3b**): ^1H NMR (acetone-d_6) δ 2.71 (2H, m), 2.91 (2H, t, J = 7.9 Hz), 5.50 (1H, br s, carborane H), 8.37 (3H, s); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 33.53 (**C**H_2CH_2), 37.77 (CH_2**C**H_2), 63.11 (carborane C), 72.85 (carborane C); $^{11}B\{^1H\}$ (acetone-d_6) δ 1.46 (1B), −1.24 (1B), −5.26 (4B), −7.40 (4B); IR (cm^{-1}) 2580 (s), 1616 (m), 1584 (m), 1520 (m), 1468 (w), 1328 (w), 1300 (w), 1160 (m), 1124 (m), 1064 (m), 1024 (m), 972 (m), 724 (m).

1-(Isocyanatoalkyl)-1,2-dicarbadodecaborane (4a,b). In a typical reaction, pyridine (12 mmol) in CH_2Cl_2 (8.0 mL) was added dropwise to a suspension of the (aminoalkyl)-*o*-carborane hydrochloride (2 mmol) and triphosgene (0.75 mmol), which had been dissolved in 25.0 mL of CH_2Cl_2. The resulting solution was stirred at room temperature for 2 h. After removal of the solvent *in vacuo*, the resulting residue was extracted with ethyl ether and treated with activated charcoal in order to decolorize the solution. Evaporation of the ethereal solution resulted in the isolation of the sought product.

The direct characterization of 1-(isocyanatomethyl)-*o*-carborane was not possible due to the reactivity of this molecule. All attempts to obtain ^1H, ^{13}C, and ^{11}B NMR as well as IR data failed. The isocyanate carborane was found to be too reactive, and decomposition prevented its characterization. The identity of this compound was inferred from the products obtained upon reaction with amines or alcohols. The ethyl (**4a**) and propyl (**4b**) were more stable, and their analytical data are presented here. For 1-(isocyanatoethyl)-*o*-carborane (**4a**): yield, 0.105 g (98%), oil; ^1H NMR (acetone-d_6) δ 2.70 (2H, t, J = 7.0 Hz), 3.62 (2H, t, J = 7.0 Hz), 4.70 (1H, br s, carborane H); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 38.78 (*C*H_2CH_2), 42.28 (CH_2*C*H_2), 63.25 (carborane C), 74.03 (carborane C), 123.59 (N═C═O); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ 2.32 (1B), −0.57 (1B), −4.53 (2B), −6.65 (4B), −7.94 (2B); IR (cm^{-1}) 3068 (m), 2924 (m), 2856 (sh), 2596 (s), 2276 (s), 1856 (w), 1672 (w), 1552 (w), 1456 (m), 1432 (m), 1364 (m), 1304 (w), 1264 (w), 1240 (w), 1128 (m), 1076 (m), 1048 (sh), 1020 (m), 980 (w), 920 (w), 888 (w), 840 (m), 724 (m). For 1-(isocyanatopropyl)-*o*-carborane (**4b**): yield, 0.306 g (92%), oil; ^1H NMR (CD_3CN) δ 1.78 (2H, m), 2.39 (2H, m), 3.39 (2H, t, J = 6.2 Hz), 4.26 (1H, br s, carborane H); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 31.20 (*C*$H_2CH_2CH_2$), 35.34, (CH_2*C*H_2CH_2), 42.72 (CH_2CH_2*C*H_2), 63.50 (carborane C), 76.49 (carborane C), 123.11 (N═C═O); $^{11}B\{^1H\}$ NMR (CD_3CN) δ 2.22 (1B), 0.97 (1B), −4.55 (2B), −6.40 (4B), −7.85 (2B); IR (cm^{-1}), 3064 (m), 2958 (m), 2593

Table 5. Selected Bond Angles (deg) for $C_6H_4(CO)_2NCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$

C16−N16−C17	124.5(2)	C15−N16−C24	124.3(2)	C17−N16−C24	111.2(2)
C2−C1−C13	118.2(2)	C2−C1−B3	61.0(2)	C2−C1−B4	109.7(2)
C2−C1−B5	109.5(2)	C2−C1−B6	60.6(2)	C13−C1−B3	119.7(2)
C13−C1−B4	123.6(2)	C13−C1−B4	120.1(2)	C13−C1−B6	114.6(2)
B3−C1−B4	62.1(2)	B3−C1−B5	113.6(2)	B3−C1−B6	113.3(2)
B4−C1−B5	62.5(2)	B4−C1−B6	113.4(2)	B5−C1−B6	62.1(2)
C1−C2−B3	62.4(5)	C1−C2−B6	62.2(2)	C1−C2−B7	112.4(2)
C1−C2−B11	112.6(2)	B3−C2−B6	115.9(2)	B3−C2−B7	62.7(2)
B3−C2−B11	115.3(2)	B6−C2−B7	115.0(2)	B6−C2−B11	62.8(2)
B7−C2−B11	62.8(2)	C1−C13−C14	116.8(3)	C13−C14−C15	108.0(3)
N16−C15−C14	112.6(2)	O2−C17−N16	124.6(3)	O2−C17−C18	128.4(3)
N16−C17−C18	106.9(2)	C17−C18−C19	130.6(6)	C17−C18−C23	107.4(2)
C19−C18−C23	122.1(3)	C18−C19−C20	117.2(3)	C19−C20−C21	120.8(3)
C20−C21−C22	121.8(3)	C21−C22−C23	117.1(3)	C18−C23−C22	121.0(3)
C18−C23−C24	108.2(2)	C22−C23−C24	130.8(3)	O1−C24−N16	124.3(3)
O1−C24−C23	129.4(3)	N16−C24−C23	106.3(2)	C1−B3−C2	56.6(2)
C1−B3−B4	57.9(2)	C1−B3−B7	104.3(2)	C1−B3−B8	104.0(2)
C2−B3−B4	102.9(2)	C2−B3−B7	58.3(2)	C2−B3−B8	103.4(2)
B7−B3−B8	59.8(2)	C1−B4−B3	60.0(2)	C1−B4−B5	58.8(2)
C1−B4−B8	105.8(2)	C1−B4−B9	105.0(2)	B3−B4−B5	108.9(2)
B3−B4−B8	60.0(2)	B3−B4−B9	108.0(2)	B5−B4−B8	107.9(3)
B5−B4−B9	59.8(2)	B8−B4−B9	59.7(2)	C1−B5−B4	58.7(2)
C1−B5−B6	59.5(2)	C1−B5−B9	105.4(2)	C1−B5−B10	105.6(2)
B4−B5−B6	108.2(2)	B4−B5−B9	60.3(2)	B4−B5−B10	108.3(3)
B6−B5−B9	107.6(2)	B6−B5−B10	59.5(2)	B9−B5−B10	60.0(2)
C1−B6−C2	57.3(2)	C1−B6−B5	58.4(2)	C1−B6−B10	105.5(2)
C1−B6−B11	105.2(2)	C2−B6−B5	104.0(2)	C2−B6−B10	104.5(3)
C2−B6−B11	58.5(2)	B5−B6−B10	60.5(2)	B5−B6−B11	58.5(2)
B10−B6−B11	60.0(2)	C2−B7−B3	59.0(2)	C2−B7−B8	104.1(3)
C2−B7−B11	58.3(2)	C2−B7−B12	104.4(3)	B3−B7−B8	59.9(2)
B3−B7−B11	108.5(3)	B3−B7−B12	108.8(3)	B8−B7−B11	107.9(3)
B8−B7−B12	108.8(3)	B11−B7−B12	60.1(2)	B3−B8−B4	60.2(2)
B3−B8−B7	60.3(2)	B3−B8−B9	108.7(3)	B3−B8−B12	108.7(3)
B4−B8−B7	108.0(3)	B4−B8−B9	60.3(2)	B4−B8−B12	108.6(3)
B7−B8−B9	107.7(3)	B7−B8−B12	59.7(2)	B9−B8−B12	60.2(2)
B4−B9−B5	59.9(2)	B4−B9−B8	60.0(2)	B4−B9−B10	108.4(2)
B4−B9−B12	108.3(2)	B5−B9−B8	108.2(2)	B5−B9−B10	60.4(2)
B5−B9−B12	60.2(2)	B8−B9−B10	108.6(3)	B8−B9−B12	60.2(2)
B10−B9−B12	60.4(2)	B5−B10−B6	59.9(2)	B5−B10−B9	59.6(2)
B5−B10−B11	107.7(2)	B5−B10−B12	107.7(2)	B6−B10−B9	107.6(2)
B6−B10−B11	60.1(2)	B6−B10−B12	108.1(2)	B9−B10−B11	107.5(2)
B9−B10−B12	59.9(2)	B11−B10−B12	59.9(2)	C2−B11−B6	58.7(2)
C2−B11−B7	58.9(2)	C2−B11−B10	104.6(2)	C2−B11−B12	104.6(3)
B6−B11−B7	108.4(3)	B6−B11−B10	59.9(2)	B6−B11−B12	108.4(3)
B7−B11−B10	108.3(3)	B7−B11−B12	59.7(2)	B10−B11−B12	60.5(2)
B7−B12−B8	60.1(2)	B7−B12−B9	107.5(3)	B7−B12−B10	107.8(3)
B7−B12−B11	60.1(2)	B8−B12−B9	59.6(2)	B8−B12−B10	107.6(3)
B8−B12−B11	107.8(3)	B9−B12−B10	59.7(2)	B9−B12−B11	107.1(3)
B10−B12−B11	59.6(2)				

Table 6. Selected Bond Distances (Å) for 1-$(C_6H_5)_2C{=}NCH_2$-1,2-$C_2B_{10}H_{11}$

N14−C15	1.283(3)	N14−C13	1.458(4)	C1−C13	1.525(4)
C1−C2	1.620(4)	C1−B5	1.689(4)	C1−B4	1.690(4)
C1−B6	1.692(5)	C1−B3	1.710(5)	C2−B7	1.667(5)
C2−B11	1.680(5)	C2−B3	1.683(5)	C2−B6	1.701(5)
C15−C22	1.487(4)	C15−C16	1.489(4)	C16−C17	1.380(4)
C16−C21	1.385(4)	C17−C18	1.403(5)	C18−C19	1.374(5)
C19−C20	1.354(5)	C20−C21	1.360(5)	C22−C23	1.382(4)
C22−C27	1.388(4)	C23−C24	1.377(4)	C24−C25	1.371(4)
C25−C26	1.368(4)	C26−C27	1.379(4)	B3−B7	1.754(6)
B3−B8	1.755(8)	B3−B4	1.761(5)	B4−B5	1.747(5)
B4−B9	1.759(5)	B4−B8	1.767(6)	B5−B10	1.743(6)
B5−B9	1.752(9)	B5−B6	1.763(5)	B6−B10	1.744(6)
B6−B11	1.759(6)	B7−B11	1.752(7)	B7−B12	1.753(6)
B7−B8	1.755(6)	B8−B12	1.753(6)	B8−B9	1.756(6)
B9−B12	1.765(6)	B9−B10	1.777(7)	B10−B12	1.750(7)
B10−B11	1.755(6)	B11−B12	1.742(7)		

(s), 2284 (s), 1452 (m), 1360 (m), 1128 (w), 1052 (w), 1020 (w), 1006 (w), 940 (w), 904 (w), 836 (w), 724 (m).

Synthesis of 1-(Alkylurea)-Substituted 1,2-Dicarbadodecaborane and 1-(Alkylcarbamate)-Substituted 1,2-Dicarbadodecaborane. A CH_3CN solution of 1-(isocyanatoalkyl)-1,2-dicarbadodecaborane (0.5 mmol) was added to a solution containing 0.5 mmol of either the desired amine (in the case of the ureas) or the alcohol (in the case of the carbamates), and the mixture was stirred at room temperature for a period ranging from 2 to 24 h. After removal of the solvent, the product was purified by recrystallization or column chromatography. The analytical data of the alkylureas and alkylcarbamates isolated is listed below.

1-((Adamantylcarbamido)methyl)-*o*-carborane (1-$C_9H_{15}NHC(O)NHCH_2$-1,2-$C_2B_{10}H_{11}$ (5a)): yield, 0.092 g (66%), mp 251−252 °C. Elemental anal. Calcd: C, 47.97; H, 8.63. Found: C, 48.27; H, 8.76. ^{1}H NMR (CD_3CN): δ 1.61 (6H, s), 1.86 (6H, s), 2.20 (3H, s), 3.76 (2H, d, J = 6.7 Hz), 4.91 (1H, br s, carborane H), 5.85 (1H, s), 6.38 (1H, t, J = 6.7 Hz). ^{13}C{^{1}H} NMR (CD_3CN): δ 28.25 (adamantyl), 35.99 (adamantyl), 41.65 (CH_2), 43.85 (adamantyl), 49.53 (adamantyl), 61.90 (carborane C), 78.21 (carborane C), 156.00 (NHC(O)NH). ^{11}B{^{1}H} NMR (CD_3CN): δ 1.44 (1B), −1.53 (1B), −5.53 (4B), −7.29 (2B), −8.22 (2B). IR (cm^{-1}): 3368 (m), 2908 (s), 2852 (m), 2592 (s), 1636 (s), 1560 (s), 1452 (w), 1360 (w), 1296 (m), 1240 (m), 1120 (w), 728 (w).

1-((Adamantylcarbamido)ethyl)-*o*-carborane (1-$C_9H_{15}NHC(O)NHCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (5b)): yield, 0. 134 g (92%); mp 164−166 °C. Elemental Anal. Calcd: C, 49.42; H, 8.85; N, 7.68. Found: C, 48.62; H, 9.29; N, 7.34. ^{1}H NMR (acetone-d_6): δ 1.67 (6H, s), 1.96 (6H, s), 2.09 (3H, s), 2.50 (2H, t, J = 7.0 Hz), 3.26 (2H, m), 4.79 (1H, br s, carborane H), 5.44 (1H, s), 5.65 (1H, t, J = 7.0 Hz). ^{13}C-{^{1}H} NMR (acetone-d_6): δ 30.39 (adamantyl), 37.20 (CH_2CH_2), 38.66 (adamantyl), 39.36 (CH_2CH_2), 43.06 (adamantyl), 51.02 (adamantyl),

Table 7. Selected Bond Angles (deg) for 1-$(C_6H_5)_2C{=}NCH_2$-1,2-$C_2B_{10}H_{11}$

C15−N14−C13	118.7(3)	C13−C1−C2	119.9(2)	C13−C1−B5	121.2(2)
C2−C1−B5	110.8(2)	C13−C1−B4	119.0(3)	C2−C1−B4	110.3(2)
B5−C1−B4	63.2(2)	C13−C1−B6	118.3(3)	C2−C1−B6	61.8(2)
B5−C1−B6	62.9(2)	B4−C1−B6	114.6(2)	C13−C1−B3	115.9(3)
C2−C1−B3	60.6(2)	B5−C1−B3	113.7(2)	B4−C1−B3	62.4(2)
B6−C1−B3	114.4(2)	C1−C2−B7	112.6(3)	C1−C2−B11	111.6(2)
B7−C2−B11	63.1(3)	C1−C2−B3	62.3(2)	B7−C2−B3	63.2(3)
B11−C2−B3	115.6(3)	B3−C2−B6	115.3(2)	N14−C13−C1	111.4(2)
N14−C15−C22	117.7(2)	N14−C15−C16	124.6(2)	C22−C15−C16	117.7(2)
C17−C16−C21	119.0(3)	C17−C16−C15	120.8(3)	C21−C16−C15	120.1(3)
C16−C17−C18	119.2(3)	C19−C18−C17	119.5(3)	C20−C19−C18	121.1(3)
C19−C20−C21	119.7(4)	C20−C21−C16	121.4(3)	C23−C22−C27	118.3(3)
C23−C22−C15	120.9(2)	C27−C22−C15	120.8(2)	C24−C23−C22	120.7(3)
C25−C24−C23	120.3(3)	C26−C25−C24	119.9(3)	C25−C26−C27	120.2(3)
C26−C27−C22	120.7(3)	C2−B3−C1	57.0(2)	C2−B3−B7	58.0(2)
C1−B3−B7	104.2(3)	C2−B3−B8	103.9(3)	C1−B3−B8	104.4(3)
B7−B3−B8	60.0(3)	C2−B3−B4	104.1(2)	C1−B3−B4	58.2(2)
B7−B3−B4	108.1(3)	B8−B3−B4	60.3(2)	C1−B4−B5	58.8(2)
C1−B4−B9	105.2(3)	B5−B4−B9	60.0(2)	C1−B4−B3	59.4(2)
B5−B4−B3	108.4(3)	B9−B4−B3	108.1(3)	C1−B4−B8	104.7(3)
B5−B4−B8	107.4(3)	B9−B4−B8	59.7(2)	B3−B4−B8	59.7(2)
C1−B5−B10	104.7(2)	C1−B5−B4	58.9(2)	B10−B5−B4	108.9(3)
C1−B5−B9	105.5(2)	B10−B5−B9	61.1(3)	B4−B5−B9	60.3(2)
C1−B5−B6	58.6(2)	B10−B5−B6	59.6(2)	B4−B5−B6	108.3(2)
B9−B5−B6	109.0(3)	C1−B6−C2	57.0(2)	C1−B6−B10	104.6(3)
C2−B6−B10	103.9(3)	C1−B6−B11	104.6(3)	C2−B6−B11	58.1(2)
B10−B6−B11	60.1(2)	C1−B6−B5	58.5(2)	C2−B6−B5	103.7(3)
B10−B6−B5	59.6(2)	B11−B6−B5	107.4(3)	C2−B7−B11	58.8(2)
C2−B7−B12	104.1(3)	B11−B7−B12	59.6(3)	C2−B7−B3	58.9(2)
B11−B7−B3	108.5(3)	B12−B7−B3	107.9(3)	C2−B7−B8	104.6(3)
B11−B7−B8	108.0(3)	B12−B7−B8	60.0(3)	B3−B7−B8	60.0(3)
B12−B8−B7	59.9(3)	B12−B8−B3	107.9(3)	B7−B8−B3	60.0(2)
B12−B8−B9	60.4(3)	B7−B8−B9	108.7(4)	B3−B8−B9	108.5(3)
B12−B8−B4	107.6(3)	B7−B8−B4	107.8(3)	B3−B8−B4	60.0(2)
B9−B8−B4	59.2(2)	B5−B9−B8	107.7(3)	B5−B9−B4	59.7(2)
B8−B9−B4	60.4(2)	B5−B9−B12	106.6(3)	B8−B9−B12	59.7(3)
B4−B9−B12	107.4(3)	B5−B9−B10	59.2(2)	B8−B9−B10	107.0(3)
B4−B9−B10	106.9(3)	B12−B9−B10	59.2(3)	B5−B10−B6	60.8(2)
B5−B10−B12	107.7(3)	B6−B10−B12	108.1(3)	B5−B10−B11	108.5(3)
B6−B10−B11	60.4(3)	B12−B10−B11	59.6(3)	B5−B10−B9	59.7(2)
B6−B10−B9	108.7(3)	B12−B10−B9	60.1(3)	B11−B10−B9	108.1(3)
C2−B11−B12	104.0(3)	C2−B11−B7	58.1(2)	B12−B11−B7	60.2(3)
C2−B11−B10	104.3(3)	B12−B11−B10	60.0(3)	B7−B11−B10	108.2(3)
C2−B11−B6	59.2(2)	B12−B11−B6	107.8(3)	B7−B11−B6	108.3(3)
B10−B11−B6	59.5(2)	B11−B12−B10	60.4(3)	B11−B12−B7	60.2(3)
B10−B12−B7	108.4(3)	B11−B12−B8	108.5(3)	B10−B12−B8	108.4(3)
B7−B12−B8	60.1(3)	B11−B12−B9	109.2(3)	B10−B12−B9	60.7(3)
B7−B12−B9	108.4(3)	B8−B12−B9	59.9(3)		

63.27 (carborane C), 75.05 (carborane C), 157.94 (NHC(O)NH). $^{11}B\{^1H\}$ NMR: δ 2.08 (1B), −0.84, (1B), −4.53 (2B), −6.60 (4B), −7.80 (2B). IR (cm^{-1}): 3360 (m), 3060 (w), 2908 (s), 2852 (m), 2592 (s), 1704 (m), 1636 (s), 1564 (s), 1464 (m), 1360 (w), 1286 (m), 1248 (w), 1092 (w), 936 (w), 724 (m).

1-((Adenylcarbamido)methyl)-*o*-carborane (1-$C_5H_3N_4NHC(O)NHCH_2$-1,2-$C_2B_{10}H_{11}$ (6)): yield, 0.067 g (50%); mp 275−278 °C; ^1H NMR (DMSO-d_6) δ 4.31 (2H, d, J = 6.4 Hz), 5.24 (1H, br s, carborane H), 7.29 (2H, s), 8.25 (1H, s), 8.65 (1H, s), 9.48 (1H, t, J = 6.4 Hz); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 44.27 (CH_2), 62.20 (carborane C), 75.55 (carborane C), 119.24 (adenyl), 138.65 (adenyl), 147.82 (adenyl), 149.15 (adenyl), 153.48 (adenyl), 156.70 (NHC(O)NH); $^{11}B\{^1H\}$ NMR (DMSO-d_6) δ −1.53 (1B), −1.32 (1B), −5.51 (4B), −7.004 (2B), −12.37 (2B); IR (cm^{-1}) 3380 (m), 3188 (m), 2592 (s), 1728 (s), 1656 (s), 1564 (s), 1504 (w), 1472 (m), 1420 (w), 1364 (w), 1336 (m), 1284 (m), 1252 (m), 1204 (m), 1124 (w), 1020 (w), 990 (w), 796 (w), 732 (m), 644 (m), 504 (w).

1-((5′-Uracinylcarbamido)methyl)-*o*-carborane (1-$C_4H_3N_2O_2NHC(O)NHCH_2$-1,2-$C_2B_{10}H_{11}$ (7)): yield, 0.095 g (62%); mp > 350 °C. Elemental Anal. Calcd: C, 29.44; H, 5.56; N, 17.17. Found: C, 29.46; H, 5.39; N, 17.17. ^1H NMR (DMSO-d_6) δ 3.87 (2H, d, J = 5.5 Hz), 5.03 (1H, br s, carborane H), 7.39 (1H, t, J = 7.0 Hz), 7.81 (1H, d, J = 4.5 Hz), 8.03 (1H, s), 10.52 (1H, d, J = 4.0 Hz), 11.45 (1H, s). $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 43.73 (CH_2), 61.90 (carborane C), 77.05 (carborane C), 114.32 (uracinyl), 125.11 (uracinyl), 149.29 (uracinyl), 154.26 (uracinyl), 160.78 (NHC(O)NH). $^{11}B\{^1H\}$ NMR (DMSO-d_6) δ 1.39 (1B), −1.34 (1B), −5.30 (4B), −7.58 (4B). IR (cm^{-1}): 3356 (m), 2596 (s), 1728 (m), 1704 (s), 1656 (s), 1572 (s), 1480 (w), 1420 (w), 1356 (w), 1228 (m), 1004 (w), 756 (w), 724 (w), 552 (w).

1-((Carbomethoxymethyl)carbamido)methyl)-*o*-carborane (1-$CH_3OOCCH_2NHC(O)NHCH_2$-1,2-$C_2B_{10}H_{11}$ (8a)): yield, 0.088 g (77%); mp 164−166 °C; ^1H NMR (DMSO-d_6) δ 3.67 (3H, s), 3.91 (2H, d, J = 5.9 Hz), 3.99 (2H, d, J = 6.8 Hz), 4.54 (1H, br s, carborane H), 6.21 (1H, unresolved triplet), 6.72 (1H, unresolved triplet); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 42.53 (CH_2), 46.02 (CH_2), 52.12 (OCH_3), 61.75 (carborane C), 78.50 (carborane C), 158.75 (NHC(O)NH), 172.00 (C=O); $^{11}B\{^1H\}$ NMR (DMSO-d_6) δ 2.57 (1B), −0.68 (1B), −4.99 (2B), −6.51 (2B), −7.79 (4B); IR (cm^{-1}) 3360 (s), 3064 (m), 2956 (m), 2592 (s), 1752 (s), 1640 (s), 1572 (s), 1440 (m), 1424 (sh), 1408 (w), 1372 (m), 1284 (w), 1212 (s), 1184 (sh), 1120 (m), 1076 (w), 1020 (m), 980 (w), 824 (w), 776 (w), 728 (m), 660 (m), 516 (w).

1-(((Carbomethoxymethl)carbamido)ethyl)-*o*-carborane (1-$CH_3OOCCH_2NHC(O)NHCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (8b)): yield, 0.105 g (98%); mp 76−79 °C; ^1H NMR (acetone-d_6) δ 2.56 (2H, t, J = 7.6 Hz), 3.32 (2H, m), 3.69 (3H, s), 3.88 (2H, d, J = 6.0 Hz), 4.75 (1H, br s, carborane H), 6.21 (2H, m); $^{13}C\{^1H\}$ NMR (acetone-d_6), δ 38.44 (CH_2CH_2), 40.05 (CH_2CH_2), 42.54 (CH_2), 52.28 (OCH_3), 63.49 (carborane C), 75.14 (carborane C), 159.18 (NHC(O)NH), 172.56 (C=O); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ 2.11 (1B), −0.82 (1B), −4.56

(2B), −6.55 (4B), −7.99 (2B); IR (cm^{-1}) 3368 (m), 3001 (w), 2989 (w), 2952 (s), 1744 (s), 1640 (s), 1568 (s), 1436 (m), 1350 (w), 1216 (m), 920 (w).

1-(((1-Carbethoxyethyl)carbamido)ethyl)-*o*-carborane (1-CH_3-$CH_2OOCCH(CH_3)NHC(O)NH$-CH_2CH_2)-1,2-$C_2B_{10}H_{11}$ (9)): yield, 0.118 g (89%); liquid; ^1H NMR (acetone-d_6) δ 1.21 (3H, t, J = 7.1 Hz), 1.28 (3H, d, J = 7.0 Hz), 2.53 (2H, t, J = 7.0 Hz), 3.30 (2H, m), 4.14 (2H, q, J = 7.1 Hz), 4.28 (1H, m), 4.74 (1H, br s, carborane H), 5.97 (1H, d, J = 3.5 Hz), 6.07 (1H, d, J = 5.1 Hz); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 14.31 (**C**H_3CH_2O), 18.53 (CH_3), 38.15 (*C*H_2CH_2), 39.51 (CH_2CH_2), 49.41 (CH), 61.19 (CH_3CH_2O), 63.10 (carborane C), 74.77 (carborane C), 158.20 (NHC(O)NH), 174.24 (C═O); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ 2.11 (1B), −0.87 (1B), −4.59 (2B), −6.55 (4B), −7.99 (2B), IR (cm^{-1}), 3364 (m), 3060 (m), 2984 (m), 2592 (s), 1732 (s), 1636 (s), 1564 (s), 1452 (m), 1376 (w), 1196 (m), 1124 (m), 1056 (w), 1020 (m), 724 (m).

1-(((1-Carbomethoxy-2-phenylethyl)carbamido)ethylurea)-*o*-carborane (1-$CH_3OOCCH(CH_2C_6H_5)NHC(O)NHCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (10)): yield, 0.117 g (75%); mp 97−100 °C; ^1H NMR (acetone-d_6) δ 2.49 (2H, t, J = 7.4 Hz), 3.03 (2H, m), 3.26 (2H, m), 4.46 (2H, m), 6.03 (2H, unresolved triplet), 7.75 (5H, m); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 38.25 (*C*H_2CH_2), 38.94 (CH_2CH_2), 39.65 (CH), 52.23 (CH_2), 55.11 (OCH_3), 63.26 (carborane C), 75.03 (carborane C), 127.51 (aromatic), 129.21 (aromatic), 130.23 (aromatic), 137.98 (aromatic), 158.19 (NHC(O)NH), 173.66 (C═O); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ 2.15 (1B), −0.82 (1B), −4.56 (2B), −6.58 (4B), −7.90 (2B); IR (cm^{-1}) 3360 (m), 3060 (m), 3028 (sh), 2958 (m), 2592 (s), 1740 (s), 1636 (s), 1564 (s), 1496 (w), 1466 (m), 1430 (m), 1356 (m), 1264 (w), 1212 (m), 1180 (w), 1100 (m), 1076 (w), 1020 (m), 936 (w), 724 (m), 700 (m).

1-((3′-Pyridinylcarbamido)ethyl)-*o*-carborane (1-$C_5H_5NNHC(O)$-$NHCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (11)): yield, 0.068 g (99%), mp 155−156 °C; ^1H NMR (acetone-d_6) δ 2.60 (2H, t, J = 7.3 Hz), 3.08 (1H, s), 3.40 (2H, m), 4.77 (1H, br s, carborane H), 6.15 (1H, unresolved triplet), 7.24 (1H, dd, J_{AX} = 4.3 Hz, J_{BX} = 3.7 Hz), 7.99 (1H, m), 8.15 (1H, m), 8.33 (1H, s), 8.55 (1H, d, J = 2.5 Hz); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 38.03 (*C*H_2CH_2), 39.76 (CH_2CH_2), 63.63 (carborane C), 75.00 (carborane C), 124.23 (pyridine), 125.82 (pyridine), 138.03 (pyridine), 141.03 (pyridine), 143.75 (pyridine), 155.98 (NHC(O)NH); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ 2.11 (1B), −0.89 (1B), −4.60 (2B), −6.67 (4B), −8.08 (2B), IR (cm^{-1}), 3348 (m), 3036 (w), 2584 (s), 1684 (m), 1660 (m), 1588 (w), 1556 (s), 1476 (m), 1420 (m), 1324 (w), 1260 (w), 1124 (w), 1020 (w), 800 (w), 724 (w), 704 (w).

***N,N′*-Bis(*o*-carboran-1-ylethyl)urea (1,2-$C_2B_{10}H_{11}$-1-$CH_2CH_2NH)_2$-C═O (12)):** yield, 0.072 g (80%); mp 166−168 °C; ^1H NMR (DMSO-d_6) δ 2.52 (4H, t, J = 7.1 Hz), 3.27 (4H, m, J_{AX} = 6.0 Hz, J_{BX} = 7.1 Hz), 4.75 (2H, br s, carborane H), 5.84 (2H, unresolved triplet); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 38.37 (*C*H_2CH_2), 39.74 (CH_2CH_2), 63.35 (carborane C), 75.00 (carborane C), 158.59 (NHC(O)NH); $^{11}B\{^1H\}$ NMR (DMSO-d_6) δ 2.03 (1B), −0.93 (1B), −4.63 (2B), −6.56 (4B), −8.11 (2B), IR (cm^{-1}), 3364 (m), 3060 (m), 2940 (w), 2588 (s), 1748 (w), 1636 (s), 1568 (s), 1436 (m), 1376 (w), 1292 (w), 1264 (m), 1128 (w), 1072 (w), 1020 (w), 1004 (sh), 724 (m), 640 (w).

1-(((1′-Imidazolylpropyl)carbamido)propyl)-*o*-carborane (1-$C_3H_3N_2CH_2CH_2CH_2NHC(O)NHCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (13)): yield, 0.101 g (100%); oil; ^1H NMR (acetone-d_6) δ 1.67 (2H, m), 1.92 (2H, t, J = 6.7 Hz), 3.11 (4H, m), 3.37 (2H, m), 4.06 (2H, t, J = 6.8 Hz), 4.86 (1H, br s, carborane H), 6.02 (2H, m), 6.95 (1H, d, J = 1.5 Hz), 7.14 (1H, d, J = 1.5 Hz), 7.63 (1H, s); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 31.20 (*C*$H_2CH_2CH_2$), 32.77 (*C*$H_2CH_2CH_2$), 35.66 ($CH_2CH_2CH_2$), 37.54 ($CH_2CH_2CH_2$), 39.56 ($CH_2CH_2CH_2$), 44.74 ($CH_2CH_2CH_2$), 64.38 (carborane C), 77.02 (carborane C), 120.00 (imidazole), 129.33 (imidazole), 138.21 (imidazole), 159.47 (NHC(O)NH); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ −2.06 (1B), −4.80 (2B), −6.37 (4B), −12.06 (1B), −13.28 (1B), −16.87 (1B); IR (cm^{-1}) 3324 (s), 3112 (m), 2940 (m), 2872 (sh), 2582 (s), 1652 (s), 1568 (s), 1512 (m), 1452 (m), 1372 (w), 1252 (m), 1108 (m), 1080 (m), 1020 (m), 916 (m), 820 (m), 724 (m), 664 (m), 624 (w).

1-((Phenethylcarbamido)propyl)-*o*-carborane (1-$C_6H_5CH_2CH_2$-$NHC(O)NHCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (14)): yield, 0.099 g (100%), oil, ^1H NMR (acetone, d_6), δ 1.65 (2H, m), 2.36 (2H, t, J = 7.1 Hz), 2.75 (2H, t, J = 7.4 Hz), 3.10 (2H, m), 3.33 (2H, m), 4.71 (1H, br s, carborane H), 5.67 (1H, unresolved triplet), 5.82 (1H, unresolved triplet), 7.27 (5H, m); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 31.31 (*C*H_2CH_2), 35.68 (*C*$H_2CH_2CH_2$), 37.28 (CH_2CH_2), 39.47 ($CH_2CH_2CH_2$), 42.24 ($CH_2CH_2CH_2$), 63.33 (carborane C), 77.03 (carborane C), 125.85 (aromatic), 129.18 (aromatic), 129.57 (aromatic), 140.69 (aromatic), 159.18 (NHC(O)NH); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ 2.18 (1B), −1.01 (1B), −4.58 (2B), −6.43 (4B), −7.89 (2B); IR (cm^{-1}) 3320 (m), 3068 (m), 3028 (m), 2932 (m), 2864 (m), 2592 (s), 1632 (s), 1572 (s), 1496 (m), 1452 (m), 1364 (w), 1256 (m), 1108 (w), 1064 (w), 1020 (w), 748 (w), 724 (m), 700 (m), 456 (s).

1-((Carbobenzoxyamino)methyl)-*o*-carborane (1-$C_6H_5CH_2OC$-$(O)NHCH_2$-1,2-$C_2B_{10}H_{11}$ (15)): yield, 0.093 g (38%); oil; ^1H NMR ($CDCl_3$) δ 3.87 (2H, d, J = 6.8 Hz), 5.13 (2H, s), 5.48 (2H, s, carborane H and NH signals overlap), 7.38 (5H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 46.22 (CH_2), 59.78 (CH_2O), 67.69 (carborane C), 74.91 (carborane C), 128.62 (aromatic), 128.62 (aromatic), 135.48 (aromatic), 156.47 (NHC(O)OCH_2); $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ −1.79 (1B), −5.17 (1B), −9.72 (2B), −11.90 (2B), −12.82 (4B); IR (cm^{-1}) 3328 (m), 3064 (m), 2956 (w), 2588 (s), 1716 (s), 1520 (m), 1456 (m), 1428 (w), 1368 (w), 1256 (m), 1164 (w), 1112 (w), 1080 (w), 1020 (w), 976 (w), 908 (w), 824 (w), 776 (w), 728 (m), 696 (m).

1-((Carbomethoxyamino)ethyl)-*o*-carborane (1-$CH_3OC(O)NH$-CH_2CH_2-1,2- $C_2B_{10}H_{11}$ (16)): yield, 0.098 g (98%); mp 64−66 °C; ^1H NMR (acetone-d_6) δ 2.56 (2H, t, J = 8.0 Hz), 3.30 (2H, m), 3.57 (3H, s), 4.77 (1H, br s, carborane H), 6.41 (1H, br s); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 37.48 (*C*H_2CH_2), 40.47 (CH_2CH_2), 51.99(CH_3O), 63.35 (carborane C), 74.55 (carborane C), 157.57 (NHC(O)OCH_3); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ 2.15 (1B), −0.83 (1B), −4.58 (2B), −6.65 (4B), −8.05 (2B); IR (cm^{-1}) 3456 (m), 3408 (m), 3044 (m), 2952 (w), 2600 (s), 1716 (s), 1548 (m), 1524 (m), 1456 (w), 1388 (w), 1308 (w), 1256 (m), 1192 (w), 1144 (w), 1104 (w), 1048 (w), 1024 (m), 920 (w), 776 (m), 724 (m), 560 (w), 504 (w), 476 (w).

1-(((*tert*-Butoxycarbonyl)amino)ethyl)-*o*-carborane (1-$(CH_3)_3COC$-$(O)NHCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (17)): yield, 0.109 g (99%); mp 84−86 °C; ^1H NMR (acetone-d_6) δ 1.19 (9H, s), 2.51 (2H, t, J = 7.2 Hz), 3.29 (2H, m, J_{AX} = 7.5 Hz, J_{BX} = 6.7 Hz), 4.77 (1H, br s, carborane H), 5.91 (1H, unresolved triplet); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 31.37 (C(*C*$H_3)_3$, 38.21 (*C* H_2CH_2), 39.63, (CH_2CH_2), 63.21 (carborane C), 68.18 (O*C*$(CH_3)_3$), 74.86 (carborane C), 158.15 (NHC(O)OC$(CH_3)_3$); $^{11}B\{^1H\}$ NMR (acetone-d_6) δ 2.05 (1B), −0.92 (1B), −4.63 (2B), −6.55 (4B), −8.11 (2B); IR (cm^{-1}) 3436 (m), 2976 (m), 2580 (s), 1632 (s), 1572 (s), 1448 (w), 1364 (w), 1288 (w), 1172 (w), 1020 (w), 908 (w), 724 (m).

1-(Carbomethoxyamino)propyl)-*o* -carborane (1-$CH_3OC(O)$-$NHCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (18)): yield, 0.090 g (99%); ^1H NMR ($CDCl_3$) δ 1.72 (2H, m), 2.40 (2H, m), 3.12 (2H, t, J = 6.9 Hz), 3.56 (3H, s), 4.68 (1H, br s, carborane H), 6.31 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 35.63 (*C*$H_2CH_2CH_2$), 39.57 ($CH_2CH_2CH_2$), 40.53 (CH_2-CH_2CH_2), 51.85 (CH_3O), 63.40 (carborane C), 76.89 (carborane C), 157.79 (NHC(O)OCH_3), $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ 2.11 (1B), −1.09 (1B), −4.63 (2B), −6.54 (2B), −8.02 (4B).

1-((((*p*-Methoxyphenoxy)carbonyl)amino)propylcarbamate)-*o*-carborane ($CH_3OC_6H_4OC(O)NHCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (19)): yield, 0.52 g (55%), mp 91−93 °C, ^1H NMR ($CDCl_3$) δ 1.69 (2H, m), 2.22 (2H, m), 3.19 (2H, m), 3.57 (1H, br s, carborane H), 3.79 (3H, s), 5.26 (1H, unresolved triplet), 6.89 (2H, m), 6.99 (2H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 29.60 (*C*$H_2CH_2CH_2$), 34.90 ($CH_2CH_2CH_2$), 39.97 ($CH_2CH_2CH_2$), 55.22 (CH_3O), 61.20 (carborane C), 74.44 (carborane C), 114.23 (aromatic), 122.23 (aromatic), 144.18 (aromatic), 155.27 (aromatic), 156.90 (NHC(O)C_6H_4); $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ −2.42 (1B), −5.81 (1B), −9.42 (4B), −11.80 (4B); IR (cm^{-1}) 3366 (m), 3056 (w), 2940 (w), 2592 (s), 1732 (s), 1612 (w), 1540 (m), 1504 (s), 1464 (m), 1300 (w), 1248 (m), 1204 (s), 1180 (sh), 1100 (w), 1036 (m), 828 (w), 724 (w).

Synthesis of 1-(($C_6H_5)_2C$═NCH_2)-1,2-$C_2B_{10}H_{11}$ (20)). In a typical reaction, a solution containing 0.199 g (1.10 mmol) of benzophenone imine, dissolved in 1 mL of dichloromethane, was added dropwise to 0.210 g (1.00 mmol) of **3a** dissolved in 5 mL of dichloromethane. The resulting reaction mixture was stirred at room temperature for 12 h. The solution was then filtered, removing NH_4Cl, which is formed as a byproduct of the reaction. The dichloromethane was removed *in vacuo*, leaving crude product, which was dissolved in ethyl ether and filtered once more. The ether was evaporated and the residue recrystallized

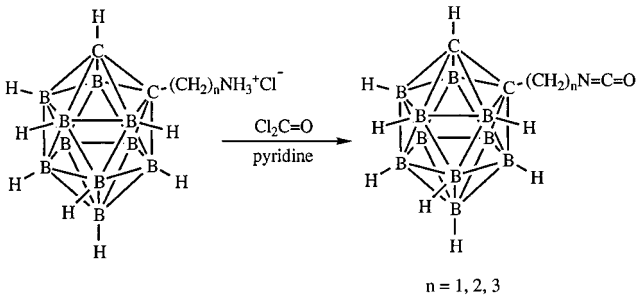

Figure 1. Synthesis of isocyanato dicarbaboranes.

from pentane. This resulted in the formation of **20**: yield, 0.273 g (81%); white crystals; ^{1}H NMR ($CDCl_3$) δ 3.09 (2H, s), 4.44 (1H, br s, carborane H), 7.09 (2H, m), 7.50 (8 H, m); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 56.80 (CH_2), 57.97 (carborane C), 74.60 (carborane C), 127.11 (aromatic), 128.31 (aromatic), 128.60 (aromatic), 129.04 (aromatic), 129.33 (aromatic), 131.08 (aromatic), 135.60 (aromatic), 138.36 (aromatic), 170.71 (C=N); ^{11}B{^{1}H} NMR ($CDCl_3$) δ −3.16 (1B), −5.41 (1B), −9.26 (2B), −11.39 (2B), −13.06 (4B). Confirmation of the structure of this compound was obtained by single-crystal X-ray diffraction.

Results and Discussion

The general synthetic strategy for the preparation of the starting materials used to prepare the reported alkylureas and alkylcarbamates relied on the combination of the methods developed by Teixidor[1] and Soloway.[9] The commercially available (bromoalkyl)phthalimides were coupled in ethylene glycol dimethyl ether in the presence of freshly prepared monolithiated *o*-carborane. This reaction resulted in the incorporation of the alkylphthalimide via formation of a carbon−carbon bond by displacement of the Li^+ ion. The reaction was successful when the employed alkylphthalimide was either ethyl- or propylphthalimide. For the preparation of the methylphthalimide this approach did not work. The synthesis of this derivative was performed by the reported method of Soloway and co-workers.[9] The preparation of the carborane-substituted amines relied on the reported method of Soloway and co-workers. These compounds were isolated as the hydrochloride salts.

The synthetic pathway leading to the preparation of the isocyanato carboranes, 1-(isocyanatoethyl)-1,2-dicarbadodecaborane (**4a**) and 1-(isocyanatopropyl)-1,2-dicarbadodecaborane (**4b**), is shown in Figure 1. The methodology is analogous to that recently reported by this laboratory.[10] The conversion of the precursor carborane amines into these compounds resulted in isolation of the products in 98% and 92% yield, respectively. The chemical structures of the isocyanato carboranes was established by IR spectroscopy and ^{1}H, ^{11}B, and ^{13} C NMR. Selected compounds, such as 1-(phthalimidopropyl)-1,2-dicarbadodecaborane (**1c**), in which an X-ray single-crystal structure was obtained, or 1-((adamantylcarbamido)ethyl)-*o*-carborane (**5b**), in which elemental analysis was used, also allowed the identification of compounds **4a** and **4b**.

The identity of the related isocyanato carborane 1-O=C=N-1,2-$C_2B_{10}H_{11}$, was inferred from the products obtained in its reactions with amines and alcohols. The elemental analysis of two of those compounds, **5a** and **7** clearly indicated that this compound had to be present in order to obtain **5a** and **7**. The identity of this compound was also inferred by the derivatization of its immediate precursor, (**3a**), with benzophenone imine, resulting in the formation of 1-$(C_6H_5)_2$C=NHCH$_2$-1,2-$C_2B_{10}H_{11}$ (**20**) in 81% yield. A single-crystal X-ray diffraction study of this compound unequivocally established its structure. In order to execute reactions with this compound, it has to be freshly prepared and the corresponding substrate added, to prevent extensive decomposition of this reactive molecule.

The relative importance of these isocyanato carboranes lies in the fact that it allows for the introduction of substrates bearing amine or alcohol functionalities, resulting in the formation of the corresponding ureas or carbamates, respectively. This methodology, although not investigated as part of this study, has the potential application of incorporating carborane moieties into relevant biomolecules for use in BNCT. Indeed, there is precedent in the scientific literature for this type of approach. For example, the boranes $Na(CH_3)_3NB_{10}H_8NCO$[16,17] and $NaB_{12}H_{11}NCO$[16] and the carborane $RC_2B_{10}H_9NCO$[18] (where R = H, CH_3) have been found to be reactive toward either simple amines or monoclonal antibodies.

Compounds related to those synthesized as part of this study that also have been investigated include 2-*O*′-(*o*-carboran-1-ylmethyl)uridine,[19] which has been shown to have a significant uptake by glioma cells,[20] and carboranylalanine.[21] The carboranylalanine system has been derivatized into other amino acids, hydantoins, and barbiturates.[22] Studies leading to the synthesis of carborane-containing ether lipids, diols, phosphate ether, nitroimidazole, nucleosides, and carbohydrates have been reported.[23] The unifying theme of all of these seemingly unrelated compounds is the versatility of the *o*-carborane system. We sought to study this system in order to exploit its versatility. The immediate need of suitable compounds for use in BNCT has been stressed in some of the studies cited. Our study hopes to address some of those needs.

The reaction sequence used for the synthesis of the reported alkylureas and alkylcarbamates (**5a**−**19**) is shown in Figure 2. The reaction of any of the reported isocyanato *o*-carboranes (1-O=C=N$(CH_2)_n$-1,2-$C_2B_{10}H_{11}$, n =1, 2, or 3) resulted in the formation of either a carborane-containing urea or carbamate in moderate to excellent yield.

Simple amines, such as 1-aminoadamantane, 3-aminopyridine, 1-(aminopropyl)imidazole, and phenethylamine, were found

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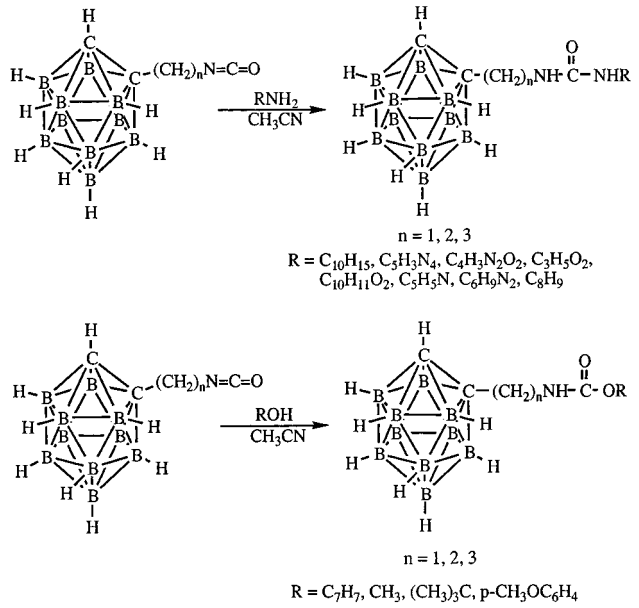

Figure 2. Synthesis of *o*-carborane ureas and carbamates.

to react cleanly with the isocyanate-containing carboranes. The yield obtained from these reactions ranged from 66% to quantitative. The identities of these compounds were established by their ^{1}H, ^{11}B, and ^{13}C NMR data. In the case of the aminoadamantane-containing ureas, **5a** and **5b**, elemental analysis also supported the proposed formulation of these compounds.

It was also our interest to investigate the reaction of these isocyanato carboranes with amino-containing biomolecules. To this effect, these compounds were reacted with adenine, 5-aminouracil, glycine methyl ester, alanine ethyl ester, and phenylalanine methyl ester. All of the reactions proceeded to form a single compound. The isolated yield of the compounds synthesized ranged from 50% in the adenine reaction to a maximum of 98% for glycine methyl ester. For the 5-aminouracil compound (**7**), an elemental analysis confirmed the proposed formulation for this compound. The ^{1}H, ^{11}B, and ^{13}C NMR data, as well as the IR spectrum of these compounds, provided further confirmation of their identity.

During the course of the preparation of the isocyanato carboranes it was found that if care was not taken in performing the additions of triphosgene to the precursor amine, in addition to the sought isocyanate, a second compound was also formed. On the basis of the ^{1}H, ^{11}B, and ^{13}C NMR data, the identity of this compound was established as the symmetrical urea. Obviously if there is unreacted amino carborane present during the formation of the isocyanato carborane, it will proceed to react with the excess amine. To test this hypothesis, half of the usual amount of triphosgene was added slowly to 1-(isocyanatoethyl)-1,2-dicarbadodecarborane (**4a**). The result of this reaction was the symmetrical urea **12** in 80% yield. The ^{13}C NMR data showed only four peaks, indicative of the dimerization of **4a**. Furthermore, the ^{1}H NMR spectrum was also very simple.

In order to overcome the formation of the symmetrical ureas during the preparation of the isocyanato carboranes, the starting amino carborane was always present as the hydrochloride salt, which was mixed with triphosgene in methylene chloride, which formed a suspension. To this suspension was slowly added pyridine dissolved in methylene chloride. This resulted in the deprotonation of the hydrochloride salt, which would react with the present triphosgene, and the resulting isocyanate would dissolve in the solution, preventing it from reacting with the insoluble amine hydrochloride salt.

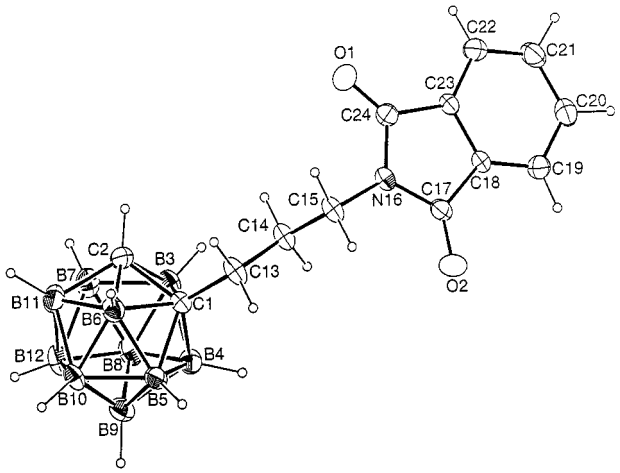

Figure 3. ORTEP drawing of 1-$C_6H_4(CO)_2NCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**1c**) with 30% probability thermal ellipsoids.

Another type of reaction of interest was that of the isocyanate carboranes with alcohols. We have previously found that $[7O{=}C{=}N\text{-}7\text{-}CB_{10}H_{12}]^-$ was unreactive toward alcohols. The reasons for this unreactivity are not completely clear, but the close proximity of the isocyanate group to the carborane cage could somehow deactivate the isocyanate group. The preparation of *o*-carborane isocyanates having a methylene spacer of one, two, or three units should render the isocyanate active once more. To test this hypothesis, the reaction of these compounds with benzyl alcohol, methanol, *tert*-butyl alcohol and *p*-methoxyphenol was studied. The results obtained indicated that these compounds were active toward alcohols, resulting in the formation of the corresponding carbamate in yields ranging from 38% to 99%. The alcohols that reacted the least were those that contained a phenyl group: benzyl alcohol (38%) and *p*-methoxyphenol (55%). A plausible explanation is the lower nucleophilicity of these compounds due to their increased acidity, when compared to aliphatic alcohols.

The characterization of **1c** and **20** was accomplished by X-ray diffraction methods. The X-ray study of **1c** and **20** was undertaken to unambiguously establish the structures of these compounds. This fact allowed for the establishment of the structures of compounds derived from these molecules. The reactions performed on **1c** dealt with the transformation of the exopolyhedral group, and it should not be expected that the *o*-carborane cage be affected by them. Similarly, the derivatization of **3a** into **20** clearly established the structure not only of **3a** but also of the compounds derived from **3a**. The ORTEP plots for both of these compounds are shown in Figures 3 and 4.

Compounds **1c** and **20** are further examples of the relatively few structurally characterized compounds in the family of monosubstituted *o*-carboranes. Other examples of this type of compound include *o*-(1,2-dicarba-*closo*-dodecaboran-1-yl) methyl cholesterol[24] and 4,4′-bis(*closo*-1,2-$C_2B_{10}H_{11}$-1-yl)biphenyl.[25] The interatomic distances on compounds **1c** and **20** fall within normal values for this type of compound. The bond between the polyhedral carbon (C1) and the exopolyhedral carbon atom (C13) was found to be 1.536(4) and 1.525(4) Å for **1c** and **20**, respectively. These values are comparable to those found on *o*-(1,2-dicarba-*closo*-dodecaboran-1-yl) methyl chloresterol[24] and

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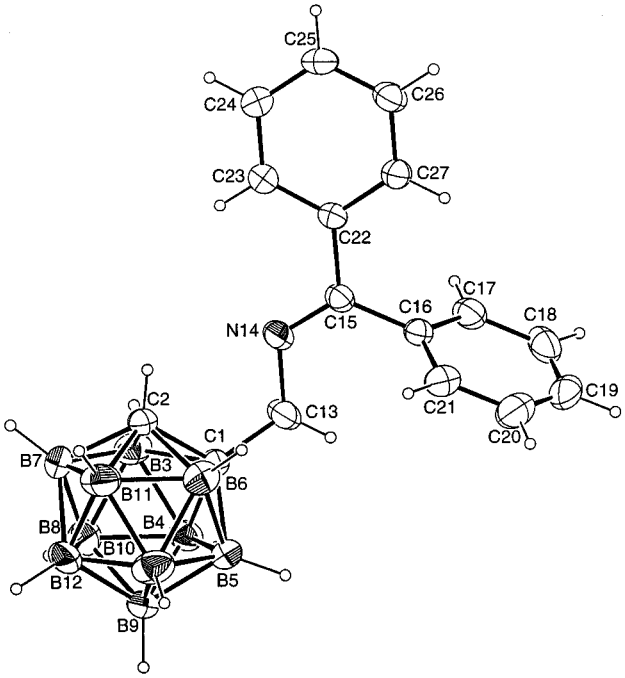

Figure 4. ORTEP drawing of 1-(C_6H_5)C═NCH_2-1,2-$C_2B_{10}H_{11}$ (**20**) with 30% probability thermal ellipsoids.

4,4′-bis(*closo*-1,2-$C_2B_{10}H_{11}$-1-yl)biphenyl.[25] The interatomic distances between C1 and C2 in these compounds are 1.637(4) and 1.620(4) Å, respectively. These distances are the shortest interatomic distances within the icosahedron, which agrees with previous observations in similar systems.[24,25]

Clearly these molecules can be used for the efficient synthesis of compounds in which a stable urea or carbamate linkage is desirable. The presence of such a group could result in the enhanced stability of the compound. This is evidenced by the fact that no special precautions have to be taken in the storage of the compounds prepared. All of the ureas and carbamates isolated are stable for an indefinite period of time. The ^{1}H, ^{11}B, and ^{13}C NMR taken on selected samples after extended periods of time showed no appreciable decomposition of the compounds.

In summary, the results presented here demonstrate that the synthesis of these new isocyanato carboranes can be performed in a simple and efficient way. The reactivity of these compounds with amines and alcohols was studied and found to result in the formation of the corresponding ureas and carbamates. The nature of the amino- or alcohol-containing substrate seems to be unimportant, since simple amines, amino acids, and purine bases, as well as aliphatic alcohols and aromatic alcohols, were found to react cleanly with these isocyanato carboranes. We will continue to study the reactivity of these and other related molecules in order to synthesize suitable compounds that might be used in BNCT technology. The results of these investigations will be reported in the future.

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Supporting Information Available: Tables of bond angles, bond distances (including those to hydrogen atoms), anisotropic temperature factors, and hydrogen atom coordinates for compounds **1c** and **20** (13 pages). Ordering information is given on any current masthead page.

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