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Syntheses and structural characterization of *o*-carboranylamides with direct cage–amide bond†

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Reactions of lithio-*o*-carborane with isocyanates under various conditions were studied, and the structural features of the resulting carboranylamides are described. The reactions of *o*-carborane (*o*-$C_2B_{10}H_{12}$), *n*-BuLi (two equiv.) and two equiv. of (substituted) phenylisocyanate, pentylisocyanate and *p*-ethylphenylthioisocyanate in diethyl ether, respectively, led, after workup, to the corresponding mono-substituted carboranylamide **2a–g** and carboranylthioamide **5** in low to moderate yields, and only with RNCO (R = Ph, *m*-$MeOC_6H_4$, pentyl) could disubstituted products **3a–c** be isolated. The reaction with phenylisocyanate afforded the mono-amide and di-amide products in a ratio of approximately 1 : 2, whereas in the other two reactions the ratios are approximately 4 : 1 and 3 : 2, respectively. In tetrahydrofuran all the reactions attempted with RNCO (R = Ph, *p*-IC_6H_4, *m*-NCC_6H_4 and pentyl) gave more monoamide products than those in diethyl ether. With phenylisocyanate no diamide product was isolated and with pentylisocyanate the ratio between monoamide and diamide is approximately 3.5 : 1. The new carboranylamides were characterized by means of elemental analyses, IR and NMR spectroscopy and mass spectrometry, as well as single-crystal X-ray diffraction analyses of **2a–f**, **3a** and **5**.

Introduction

Polyhedral carborane cluster compounds have been widely studied because of their three-dimensional aromatic structures and unique physical and chemical properties.[1] Among the most studied carborane systems are the icosahedral 1,2-dicarba-*closo*-dodecaborane(12) ($C_2B_{10}H_{12}$, *o*-carborane (**1**)) and its *m*- and *p*-isomers (Fig. 1). Due mainly to the diverse potential applications in biomedical, catalysis and materials sciences, the syntheses and properties of functionalized carboranes have become an increasingly important subfield. To that end the reactions of carborane–metal species with small unsaturated molecules (aldehyde, ketone, alkene, alkyne, carbodiimide, and so on) have proven a straightforward and effective way.[2–5]

The structure of amide is pervasive in proteins and peptides, and is an important fragment in organic medicines. The carborane-substituted amides or carboranylamides have great potential in medicinal chemistry such as the boron neutron capture therapy (BNCT) of tumors and the boron neutron capture synovectomy (BNCS)[6,7] of rheumatoid. Although there are a number of papers concerning such carboranylamide compounds, there has been a relatively small portion of such compounds in which the carborane skeleton and the amide moieties are directly linked at the cage carbon[8,9] or boron[10,11] atom. Moreover, there has been much less work on the crystallographic studies of such carboranylamide species (some of which belong to carborane carbamoyl compounds such as carboranylcarbamates derived from C- or B-aminocarboranes).

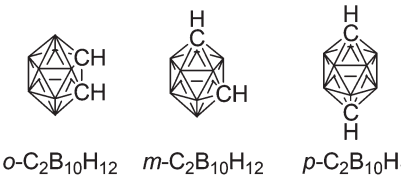

Fig. 1 Structures of *o*-, *m*-, and *p*-carborane isomers (unmarked vertices are BH).

The general approach to amide compounds is the condensation reaction of amine and carboxylic acid or its derivatives, which also applies to the synthesis of carboranylamides (reactions of carboranyl acid halides and amines (or ammonia) or, carboranylamine and carboxylic acid halides).[1] The reaction of lithiocarborane with amino-substituted acid chloride ($Me_2NC(O)Cl$) also led to the formation of the corresponding carboranylamide.[12] Recently a new synthesis of carboranylamides has be reported by transition metal catalysis. For instance, Bregadze and Beletskaya *et al.*[13] developed the

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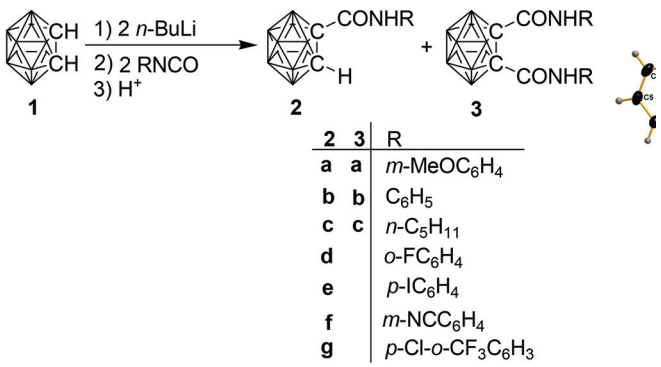
palladium catalyzed cross coupling of B-iodinated *m*- and *p*-carboranes with sodium amidates which afforded the corresponding carboranylamide products. Llop *et al.*[14] reported some *m*-carboranylamides *via* palladium catalyzed reactions of C-iodinated carborane with amine and CO.

Another straightforward route to amide is the reaction of organolithium and isocyanates. In this direction, Zakharkin *et al.*[8b] reported that *o*-(RC)(CLi)$B_{10}H_{10}$ (R = Me, Ph) react with phenylisocyanate and phenylthioisocyanate, respectively, to give the corresponding carboranylamide and -thioamide products. Wade *et al.*[9c] studied similar reactions of $Li_2C_2B_{10}H_{10}$ and phenylisocyanate and methylisocyanate, respectively, and obtained the corresponding disubstituted carboranylamides. To further explore the reactions of lithiocarboranes with different isocyanates and the detailed structures of the carboranylamides with direct cage–amide bond(s), we have investigated the reactions of lithio-*o*-carboranes with (substituted) phenylisocyanates, pentylisocyanate and *p*-ethyl-phenylthioisocyanate under various conditions, in which it was found that the solvent effect (diethyl ether and THF) and steric effect of isocyanates influence the product distribution (monoamide and/or diamide) and the yields. The isolation, spectral characterization and crystal structures of these carboranylamides are reported herein.

Results and discussion

Syntheses and spectral characterization

Wade *et al.*[9c] reacted $Li_2C_2B_{10}H_{10}$ with two equivalents of RNCO and obtained the corresponding carboranyl diamide products (yields 77%, R = Ph; 65%, R = Me), and characterized them by IR and MS methods. We studied the corresponding reaction of *o*-carborane (**1**), *n*-BuLi and 3-methoxyphenylisocyanate (in a ratio of = 1 : 2 : 2 or 1 : 2.2 : 2.2) and isolated, after workup, the corresponding monoamide **2a** and diamide **3a** (Scheme 1, Table 1), but with **2a** as the major product, which is different from Wade's results.[9c] Compounds **2a** and **3a** were characterized by IR and NMR spectroscopy and mass spectrometry, as well as single-crystal X-ray analyses (see below).



Scheme 1 Reactions of lithiocarborane with isocyanates.

Table 1 The amounts of reactants and product distribution in the reactions of lithiocarborane and isocyanates[a]

Entry	R	**1**/mmol	*n*-BuLi/mmol	RNCO/mmol	Isolated yield/% **2**	Isolated yield/% **3**
1	*m*-$MeOC_6H_4$	0.99	2.20	2.11	55.4	14.6
2[b]	*m*-$MeOC_6H_4$	1.00	1.10	1.09	61.1	—
3	C_6H_5	1.01	2.02	2.09	26.7	59.0
4[c]	C_6H_5	1.01	2.15	2.27	81.6	—
5	*n*-C_5H_{11}	0.99	2.20	2.15	58.5	38.7
6[c]	*n*-C_5H_{11}	1.03	2.20	2.18	70.5	20.8
7	*o*-FC_6H_4	1.00	2.05	2.13	58.6	—
8[d]	*p*-IC_6H_4	1.01	2.20	2.15	10.4	—
9[c]	*p*-IC_6H_4	0.42	0.88	0.86	65.3	—
10[e]	*m*-NCC_6H_4	1.01	2.20	2.19	17.5	—
11[c]	*m*-NCC_6H_4	1.02	2.20	2.20	64.4	—
12	*p*-Cl-*o*-$CF_3C_6H_3$	1.01	2.20	2.12	23.3	—
13[c]	*p*-Cl-*o*-$CF_3C_6H_3$	1.01	2.20	2.07	65.8	—

[a] Unless otherwise stated, diethyl ether was used as the solvent, the yields are isolated ones based on the amount of **1**. [b] The reaction mixture was cooled by liq. N_2, then warmed to room temperature. [c] THF was used as the solvent. [d] *p*-IC_6H_4NCO was added as a solid, toluene as the solvent. [e] *m*-NCC_6H_4NCO was added as a solid.

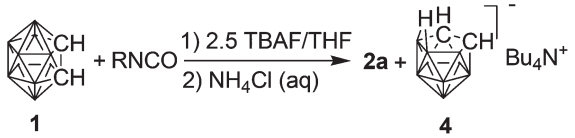
To understand our results on 3-methoxyphenylisocyanate, we repeated the same reaction as Wade *et al.*[9c] of dilithiocarborane with two equiv. of phenylisocyanate in diethyl ether under reflux, and obtained the corresponding diamide **3b** as the major product, together with a relatively small amount of the monoamide **2b**[8a,e] (Scheme 1, Table 1). Compounds **2b** and **3b** were characterized by IR, NMR and MS, as well as single-crystal X-ray analysis of **2b** (see below).

Comparing with Wade's results, the reactions were carried out under almost the same conditions and 3-methoxyphenylisocyanate has only one more 3-OMe substituent on the phenyl ring, but the product distribution is different. This difference may be attributed to the presence of the electron-donating 3-OMe group, which results in slightly lower electrophilicity of the isocyanate, meanwhile the steric effect of the carboranyl skeleton and the isocyanate compound may also play a role in such transformations, leading to monoamide as the major product.

As the monoamide is the major product in the reaction with 3-methoxyphenylisocyanate, we carried out a similar reaction to Planas *et al.*[15] ($LiC_2B_{10}H_{11}$ and pyridylaldehyde form carboranylalcohol at low temperature) by reacting $LiC_2B_{10}H_{11}$ with 3-methoxyphenylisocyanate in a 1 : 1 ratio (Scheme 2 and entry 2 in Table 1). Under such conditions, compound **2a** was obtained in a yield of 61%, without any diamide **3a** isolated.

In order to further optimize the reaction conditions, we tried the reaction of **1** and 3-methoxyphenylisocyanate in the presence of tetrabutylammonium fluoride (TBAF) at room temperature, and **2a** was isolated only in a low yield (6.5%) with the discovery of the starting carborane **1**. Moreover, elevated temperature did not improve the yield of **2a**, leading instead to the deboronation product $[Bu_4N][C_2B_9H_{12}]$[16] (**4**) (Scheme 3). Comparing the results with those of Yamamoto *et al.*,[17] who reported that in the presence of TBAF, **1** and

Scheme 2 Reaction of $LiC_2B_{10}H_{11}$ with one equiv. of 3-methoxyphenylisocyanate.

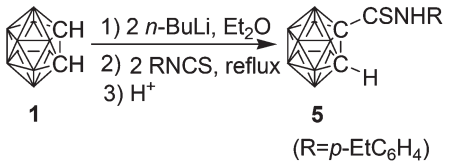


Scheme 3 Reaction of **1**, 3-methoxyphenylisocyanate with TBAF.

aldehyde/ketone produced the corresponding carboranylalcohols, it suggests that due to the weaker electrophilicity of the isocyanate function than the aldehyde/ketone, the addition of lithiocarborane to isocyanate is sluggish, leading to *nido*-carborane **4** *via* deboronation instead.

To extend the scope and limitations of this type of reaction, we carried out similar reactions of dilithiocarborane $Li_2C_2B_{10}H_{11}$ with two equivalents of pentylisocyanate, and isolated the corresponding monoamide **2c** and diamide **3c**, with the former as the major product (Scheme 2, Table 1), which is again different with Wade *et al.*'s results on methylisocyanate, presumably the different steric effect between methyl and pentyl groups plays some role. It is apparent that there is a subtle substituent effect in these seemingly straightforward transformations. We then studied the same reactions with substituted phenylisocyanates (with electron-withdrawing groups 2-F, 4-I, 3-CN, 4-Cl-2-CF_3 on the benzene ring) from which only monoamides were isolated, however, the corresponding yields were only from medium (**2d**) to low (**2e–g**) (Scheme 1, Table 1), although in principle phenylisocyanates with electron-withdrawing groups on the phenyl ring should exhibit better activity towards organolithium than those with electron-donating groups. Apart from the isolation of **2e–g**, some unidentified solid products were obtained at the bottom of the preparative TLC plates which by ^{11}B-NMR were tentatively assigned to be deboronated species. Compounds **2c–g** were characterized by IR and NMR spectroscopy and mass spectrometry, and the solid-state structures have been established by single-crystal X-ray diffraction analyses of **2c–f** (see below).

Most probably the low yields of compounds **2e–g** is because RNCO (R = *p*-IC_6H_4, *m*-NCC_6H_4) are not soluble in diethyl ether or toluene. We then carried out the same reactions in the more polar solvent tetrahydrofuran (THF) in which the two isocyanates are soluble. The yields of compound **2e–g** are much better that those from the reactions in diethyl ether (Table 1). In the case of *p*-Cl-*o*-$CF_3C_6H_4NCO$, the yield is also increased (Table 1). Moreover, when we repeated the same reactions of phenylisocyanate and pentylisocyanate in THF, respectively, the solvent effect is more apparent. With phenylisocyanate, the monoamide product was isolated in 70.5% and 81.6% (two runs), whereas no diamide product was obtained, which is



Scheme 4 Reaction of dilithiocarborane with 4-ethylphenylthioisocyanate.

remarkably different to that in diethyl ether (Table 1). In the case of pentylisocyanate, more monoamide and somewhat less diamide were isolated. These results may probably be attributed to the better solubility of both the isocyanates and lithiocarborane in THF and steric reason of the isocyanates. In THF all the reactions attempted gave more monoamide products than the corresponding diamide (if any).

It was described by Teixidor *et al.*[18] that the monolithio-*o*-carborane species in different ethereal solvents (diethyl ether, dimethoxyethane and THF) show different reactivity towards S/Se and halogen-containing reagents, one of the main reason being the different property of contact ion pairs of solvated lithiocarboranes. In the present case of phenylisocyanate, similarly the different property of the contact ion pairs of solvated dilithiocarborane species (with THF or diethyl ether) may play a major role.

Apart from the reactions with isocyanates, we also investigated a similar reaction with 4-ethylphenylthioisocyanate (in a ratio of 1 : 2.2 : 2.2) and obtained the corresponding monothioamide product **5** in good yield (Scheme 4). Compound **5** was characterized by IR, NMR and EI-MS, and its crystal structure has been determined by X-ray diffraction (see below).

X-ray structures of 2a–f, 3a and 5

Colorless crystals of compounds **2a–f** and **3a** were obtained by solvent (diethyl ether) evaporation, and yellow crystals of compound **5** were grown in a solution of hexane–dichloromethane (4/1, v/v) at room temperature. The corresponding crystal data and refinement parameters are shown in Tables 2 (**2a–b**, **3a**), 4 (**2c–e**) and 6 (**2f**, **5**), respectively. Selected bond lengths and bond angles are listed in Tables 3, 5 and 7, and the related hydrogen bond information is given in Table S1.†

In the structure (Fig. 2) of compound **2a**, the carbonyl carbon of the amide moiety is directly attached to the cage carbon with the C2–C3 bond length of 1.526(3) Å, showing that it is essentially a single bond. The amide part and the phenyl ring are coplanar (torsion angles of both O2–C3–N1–C4 and C3–N1–C4–C5 are 0.000(1)°) and the molecule is symmetric about the plane passing through C1, C2 and the amide moiety. The intramolecular O2···H1A (2.51 Å) and O2···H5 (2.28 Å) interactions fix the orientation of the amide fragment respective to the carborane cage. The cage C1–C2 bond length is 1.631(3) Å, essentially the same as that in *o*-carborane (**1**, 1.629(6) Å[19]), probably due to the conjugation effect of the amide moiety that balances the steric hindrance of the amide substituent which usually makes the cage carbon–carbon bond somewhat longer than that in **1**. There exists

Table 2 Crystal data and structure refinement parameters of **2a**, **3a** and **2b**

	2a	**3a**	**2b**
Empirical formula	$C_{10}H_{19}B_{10}NO_2$	$C_{18}H_{26}B_{10}N_2O_4$	$C_9H_{17}B_{10}NO$
Formula weight	293.36	442.51	263.34
Temperature/K	293.15	293.15	293.15
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Cmca*	$P2_1/c$	$P\bar{1}$
a/Å	7.2645(7)	10.9013(10)	7.1110(7)
b/Å	21.8580(13)	15.5194(10)	9.6524(8)
c/Å	20.1778(15)	14.2472(10)	12.4183(8)
α/°	90.00	90.00	104.922(6)
β/°	90.00	98.225(7)	104.856(7)
γ/°	90.00	90.00	103.257(8)
Volume/Å^3	3204.0(4)	2385.6(3)	755.24(11)
Z	8	4	2
ρ_{calc}/mg mm^{-3}	1.216	1.232	1.158
m/mm^{-1}	0.069	0.077	0.062
F(000)	1216.0	920.0	272.0
Crystal size/mm^3	0.42 × 0.41 × 0.32	0.56 × 0.43 × 0.034	0.43 × 0.22 × 0.18
2*Θ* range for data collection	5.5 to 52.74°	5.14 to 52.74°	6.24 to 52.74°
Index ranges	$-8 \le h \le 7$ $-27 \le k \le 27$ $-17 \le l \le 25$	$-13 \le h \le 13$ $-17 \le k \le 19$ $-17 \le l \le 17$	$-8 \le h \le 8$ $-12 \le k \le 12$ $-15 \le l \le 15$
Reflections collected	5366	14 790	7825
Independent reflections	1753 [*R*(int) = 0.0475]	4877 [*R*(int) = 0.0635]	3071 [*R*(int) = 0.0401]
Data/restraints/parameters	1753/0/127	4877/0/309	3071/0/190
Goodness-of-fit on F^2	1.060	1.036	1.031
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0556 wR_2 = 0.1479	R_1 = 0.0704 wR_2 = 0.1693	R_1 = 0.0590 wR_2 = 0.1537
Final *R* indexes [all data]	R_1 = 0.0688 wR_2 = 0.1613	R_1 = 0.1235 wR_2 = 0.2088	R_1 = 0.0935 wR_2 = 0.1761
Largest diff. peak/hole/e Å^{-3}	0.26/−0.27	0.37/−0.23	0.22/−0.19

Table 3 Selected bond lengths (Å) and bond angles (°) in **2a**, **3a** and **2b**

2a			
C(1)–C(2)	1.631(3)	C(2)–B(5)	1.699(3)
C(2)–C(3)	1.526(3)	C(2)–B(3)	1.729(2)
C(3)–O(2)	1.204(3)	C(1)–B(3)	1.716(2)
C(3)–N(1)	1.343(3)	C(1)–B(4)	1.689(3)
C(4)–N(1)	1.418(3)		
C(3)–C(2)–C(1)	113.55(18)	O(2)–C(3)–N(1)	126.5(2)
B(5)–C(2)–C(3)	124.97(14)	C(3)–N(1)–C(4)	128.2(2)
B(3)–C(2)–C(3)	114.88(11)	C(1)–C(2)–B(3)	61.35(9)
O(2)–C(3)–C(2)	119.9(2)	C(1)–C(2)–B(5)	110.43(14)
N(1)–C(3)–C(2)	113.68(19)		
3a			
C(1)–C(10)	1.659(3)	C(11)–N(2)	1.329(3)
C(2)–C(1)	1.532(3)	N(2)–C(12)	1.428(3)
C(2)–O(1)	1.214(3)	C(1)–B(1)	1.686(4)
C(2)–N(1)	1.334(3)	C(1)–B(2)	1.725(4)
C(3)–N(1)	1.431(3)	C(1)–B(5)	1.733(4)
C(10)–C(11)	1.523(4)	C(1)–B(6)	1.699(4)
C(11)–O(3)	1.214(3)		
C(1)–C(10)–C(11)	114.6(2)	C(10)–C(11)–O(3)	118.8(3)
C(2)–C(1)–C(10)	120.8(2)	N(2)–C(11)–O(3)	124.2(3)
C(1)–C(2)–N(1)	115.9(2)	C(11)–N(2)–C(12)	126.0(2)
N(1)–C(2)–O(1)	124.5(2)	B(1)–C(1)–C(10)	110.9(2)
C(1)–C(2)–O(1)	119.2(2)	B(1)–C(1)–B(6)	63.2(2)
C(3)–N(1)–C(2)	124.1(2)	B(1)–C(1)–B(2)	62.20(19)
C(10)–C(11)–N(2)	116.8(2)		
2b			
C(1)–C(10)	1.659(3)	C(11)–N(2)	1.329(3)
C(2)–C(1)	1.532(3)	N(2)–C(12)	1.428(3)
C(2)–O(1)	1.214(3)	C(1)–B(1)	1.686(4)
C(2)–N(1)	1.334(3)	C(1)–B(2)	1.725(4)
C(3)–N(1)	1.431(3)	C(1)–B(5)	1.733(4)
C(10)–C(11)	1.523(4)	C(1)–B(6)	1.699(4)
C(11)–O(3)	1.214(3)		
C(1)–C(10)–C(11)	114.6(2)	C(10)–C(11)–O(3)	118.8(3)
C(2)–C(1)–C(10)	120.8(2)	N(2)–C(11)–O(3)	124.2(3)
C(1)–C(2)–N(1)	115.9(2)	C(11)–N(2)–C(12)	126.0(2)
N(1)–C(2)–O(1)	124.5(2)	B(1)–C(1)–C(10)	110.9(2)
C(1)–C(2)–O(1)	119.2(2)	B(1)–C(1)–B(6)	63.2(2)
C(3)–N(1)–C(2)	124.1(2)	B(1)–C(1)–B(2)	62.20(19)
C(10)–C(11)–N(2)	116.8(2)		

intermolecular C–H···O hydrogen bonds that link the molecules of **2a** into a one-dimensional chain structure (Fig. S12, Table S1†).

In the structure (Fig. 3) of the diamide **3a**, the C2–C1 and C10–C11 bond lengths are found to be 1.532(3) and 1.523(4) Å, respectively. Because of the steric effect of the amide groups, the cage C1–C10 bond length is 1.659(3) Å, slightly longer than those in **1** and **2a**. The two amide moieties are not as planar as that in the structure of **2a**, with the torsion angles C3–N1–C2–O1 and C12–N2–C11–O3 being 3.9(5)° and −8.1(5)°, respectively. The dihedral angles between the two amide moieties is 80.1(2)°, and those between O3–C11–N2–C12/phenyl and between O1–C2–N1–C3/phenyl are 20.0(1)° and 46.6(1)°, respectively. In crystal of **3a** there are intramolecular C–H···O and intermolecular C–H···O and N–H···O hydrogen bond interactions, and the latter link the molecules of **3a** into a one-dimensional chain structure (Fig. S13, Table S1†).

In the structure (Fig. 4) of compound **2b**, the C2–C3 bond length is 1.525(3) Å. The amide moiety is essentially planar (torsion angle O2–C3–N1–C4 = 7.1(3)°) and also coplanar both cage carbon atoms, and this plane and that of the phenyl ring have a dihedral angle of 17.9(8)°. The cage C1–C2 bond length is 1.624(2) Å, essentially the same as those in *o*-carborane and **2a**, but slightly shorter than that in **3a**. Similar to that in the structure of **2a**, the intramolecular O1···H1A (2.54 Å) and O1···H5 (2.32 Å) interactions fix the relative orientations of the amide fragment and the carborane cage, a feature also found in other monoamide structures herein. In the solid state there exist intermolecular C–H···O hydrogen bonds linking the molecules of **2b** into a dimeric structure (Fig. S14, Table S1†).

In the structure (Fig. 5) of compound **2c** with a pentyl group, the C2–C3 bond length is found to be 1.519(3) Å and the cage C1–C2 bond length is 1.626(3) Å, respectively, the latter being essentially the same as those in *o*-carborane and **2a,b**. The amide moiety is essentially planar (torsion angle O1–C3–N1–C4 is −3.8(4)°). Similar to those in the structures of **2a,b**, the intramolecular O1···H1A (2.55 Å) and O1···H4A (2.48 Å) interactions are present . In crystal of **2c** the intermolecular N–H···O hydrogen bonds interaction link the molecules of **2c** into a one-dimensional chain (Fig. S15, Table S1†).

Compounds **2d–f** have monoamide structures and electron-withdrawing substituents (*o*-F (**2d**), *p*-I (**2e**) and *m*-CN (**2f**)) on

Table 4 Crystal data and structure refinement parameters of **2c–e**

	2c	2d	2e
Empirical formula	$C_8H_{23}B_{10}NO$	$C_9H_{16}B_{10}FNO$	$C_9H_{16}B_{10}INO$
Formula weight	257.37	281.33	389.23
Temperature/K	293.15	293.15	293.15
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/n$
a/Å	11.6375(6)	6.735(2)	7.2249(2)
b/Å	10.1626(6)	11.253(4)	22.8107(10)
c/Å	27.496(2)	11.649(4)	10.5504(4)
α/°	90.00	114.63(3)	90.00
β/°	90.00	90.84(3)	109.334(4)
γ/°	90.00	106.42(3)	90.00
Volume/Å^3	3251.8(3)	760.9(4)	1640.71(11)
Z	8	2	4
ρ_{calc}/mg mm^{-3}	1.051	1.228	1.576
m/mm^{-1}	0.055	0.074	1.941
F(000)	1088.0	288.0	752.0
Crystal size/mm^3	0.38 × 0.36 × 0.23	0.38 × 0.32 × 0.28	0.41 × 0.36 × 0.15
2*Θ* range for data collection	6.1 to 52.74°	6.38 to 52.74°	6.28 to 52.74°
Index ranges	$-13 \le h \le 14$ $-12 \le k \le 12$ $-33 \le l \le 34$	$-8 \le h \le 8$ $-13 \le k \le 14$ $-14 \le l \le 14$	$-9 \le h \le 9$ $-28 \le k \le 28$ $-13 \le l \le 13$
Reflections collected	10 775	7806	19 725
Independent reflections	3326 [*R*(int) = 0.0500]	3110 [*R*(int) = 0.0485]	3340 [*R*(int) = 0.0394]
Data/restraints/parameters	3326/0/182	3110/0/199	3340/0/199
Goodness-of-fit on F^2	1.044	1.077	1.044
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0744 wR_2 = 0.2061	R_1 = 0.0623 wR_2 = 0.1672	R_1 = 0.0340 wR_2 = 0.0744
Final *R* indexes [all data]	R_1 = 0.1169 wR_2 = 0.2380	R_1 = 0.0986 wR_2 = 0.2001	R_1 = 0.0456 wR_2 = 0.0806
Largest diff. peak/hole/e Å^{-3}	0.39/−0.22	0.20/−0.21	0.53/−0.88

Table 5 Selected bond lengths (Å) and bond angles (°) in **2c–e**

2c			
C(1)–C(2)	1.626(3)	C(4)–N(1)	1.452(3)
C(2)–C(3)	1.519(3)	C(1)–B(3)	1.700(4)
C(3)–O(1)	1.222(3)	C(2)–B(3)	1.719(4)
C(3)–N(1)	1.321(3)	C(2)–B(4)	1.702(3)
C(1)–C(2)–C(3)	115.22(17)	C(3)–N(1)–C(4)	123.1(2)
C(2)–C(3)–O(1)	119.6(2)	C(1)–C(2)–B(3)	61.01(15)
C(2)–C(3)–N(1)	114.73(19)	C(1)–C(2)–B(4)	110.47(17)
N(1)–C(3)–O(1)	125.6(2)	C(1)–C(2)–B(5)	110.91(18)
2d			
C(1)–C(2)	1.624(3)	C(4)–N(1)	1.419(3)
C(2)–C(3)	1.533(3)	C(1)–B(4)	1.708(4)
C(3)–O(1)	1.212(3)	C(2)–B(4)	1.716(4)
C(3)–N(1)	1.327(3)	C(2)–B(5)	1.700(3)
C(1)–C(2)–C(3)	114.17(17)	C(3)–N(1)–C(4)	127.57(19)
C(2)–C(3)–O(1)	121.0(2)	C(1)–C(2)–B(4)	61.43(15)
C(2)–C(3)–N(1)	113.66(19)	C(1)–C(2)–B(5)	111.15(17)
N(1)–C(3)–O(1)	125.3(2)	C(1)–C(2)–B(6)	110.97(17)
2e			
C(1)–C(2)	1.624(4)	C(4)–N(1)	1.416(3)
C(2)–C(3)	1.725(5)	C(1)–B(3)	1.710(5)
C(3)–O(1)	1.208(4)	C(2)–B(3)	1.725(5)
C(3)–N(1)	1.336(4)	C(2)–B(11)	1.696(4)
C(1)–C(2)–C(3)	114.1(2)	C(3)–N(1)–C(4)	127.7(3)
C(2)–C(3)–O(1)	119.8(3)	C(1)–C(2)–B(6)	61.5(2)
C(2)–C(3)–N(1)	114.7(3)	C(1)–C(2)–B(11)	111.3(2)
N(1)–C(3)–O(1)	125.4(3)	B(7)–C(2)–B(11)	62.6(2)

Table 6 Crystal data and structure refinement parameters of **2f** and **5**

	2f	5
Empirical formula	$C_{10}H_{16}B_{10}N_2O$	$C_{11}H_{21}B_{10}NS$
Formula weight	288.35	307.45
Temperature/K	293.15	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a/Å	7.1169(6)	11.4931(16)
b/Å	8.6634(5)	18.880(2)
c/Å	25.2552(15)	8.6737(10)
α/°	90.00	90.00
β/°	90.00	110.802(13)
γ/°	90.00	90.00
Volume/Å^3	1557.14(19)	1759.4(4)
Z	4	4
ρ_{calc}/mg mm^{-3}	1.230	1.161
m/mm^{-1}	0.068	0.172
F(000)	592.0	640.0
Crystal size/mm^3	0.38 × 0.34 × 0.12	0.42 × 0.26 × 0.23
2*Θ* range for data collection	5.94 to 52.74°	6.62 to 52.74°
Index ranges	$-8 \le h \le 5$ $-6 \le k \le 10$ $-31 \le l \le 31$	$-14 \le h \le 14$ $-23 \le k \le 22$ $-10 \le l \le 10$
Reflections collected	5365	9305
Independent reflections	3104 [*R*(int) = 0.0429]	3591 [*R*(int) = 0.0419]
Data/restraints/parameters	3104/0/208	3591/0/209
Goodness-of-fit on F^2	1.028	1.036
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0606 wR_2 = 0.1135	R_1 = 0.0601 wR_2 = 0.1508
Final *R* indexes [all data]	R_1 = 0.1019 wR_2 = 0.1320	R_1 = 0.0939 wR_2 = 0.1812
Largest diff. peak/hole/e Å^{-3}	0.16/−0.17	0.23/−0.20

the phenyl rings (Fig. 6–8, respectively). Different from all other structures in this paper molecules of compound **2f** crystallize in the chiral space group ($P2_12_12_1$). The corresponding cage carbon–carbon bonds in **2d–f** are found to be similar (1.624(3), 1.624(4) and 1.639(3) Å, respectively), also similar to those in **1** and the above monoamides, suggesting that the amide groups have no significant influence on the geometries of the icosahedra. The amide moieties in the structures of **2d–f** are essentially planar (torsion angles O1–C3–N1–C4 are 4.5(4), 8.5(6), −1.7(5)°, respectively). The fluorine atom in **2d** participates in intramolecular N–H···F hydrogen bond interaction, and the intermolecular C–H···O hydrogen bonds link the molecules of **2d** into a dimer (Fig. S16, Table S1†). There is no significant intermolecular hydrogen bond interaction in the structure of **2e**, but intramolecular C–H···O one exists (Fig. 7, Table S1†). The molecules of **2f** are linked together by intermolecular N–H···N hydrogen bond interactions to form a one-dimensional chain structure (Fig. S17, Table S1†).

In the structure (Fig. 9) of compound **5**, the carborane skeleton is directly linked to the thioamide moiety with the C2–C3 bond length of 1.519(3) Å. The cage carbon–carbon bond is found to be 1.641(3) Å, similar to those in **1** and the monoamide **2a–f**. The thioamide moiety is essentially planar (torsion angle S1–C3–N1–C4 6.6(4)°). Interestingly, in crystal of **5** there exists intramolecular C–H···S hydrogen bond and weak

Table 7 Selected bond lengths (Å) and bond angles (°) in **2f** and **5**

2f			
C(1)–C(2)	1.639(3)	C(4)–N(1)	1.423(3)
C(2)–C(3)	1.525(3)	C(1)–B(3)	1.699(5)
C(3)–O(1)	1.191(3)	C(2)–B(6)	1.711(5)
C(3)–N(1)	1.347(3)	C(2)–B(11)	1.696(4)
C(1)–C(2)–C(3)	113.7(2)	C(3)–N(1)–C(4)	127.2(2)
C(2)–C(3)–O(1)	120.3(2)	C(8)–C(10)–N(2)	178.9(3)
C(2)–C(3)–N(1)	114.0(2)	C(1)–C(2)–B(6)	113.4(2)
N(1)–C(3)–O(1)	125.7(3)	C(1)–C(2)–B(11)	123.9(2)
5			
C(1)–C(2)	1.641(3)	C(4)–N(1)	1.434(3)
C(2)–C(3)	1.519(3)	C(2)–B(4)	1.701(3)
C(3)–S(1)	1.635(2)	C(2)–B(6)	1.731(3)
C(3)–N(1)	1.327(3)		
C(1)–C(2)–C(3)	116.95(19)	C(3)–N(1)–C(4)	125.3(2)
C(2)–C(3)–S(1)	121.13(18)	C(1)–C(2)–B(6)	60.85(15)
C(2)–C(3)–N(1)	113.2(2)	C(1)–C(2)–B(4)	109.76(19)
N(1)–C(3)–S(1)	125.66(18)		

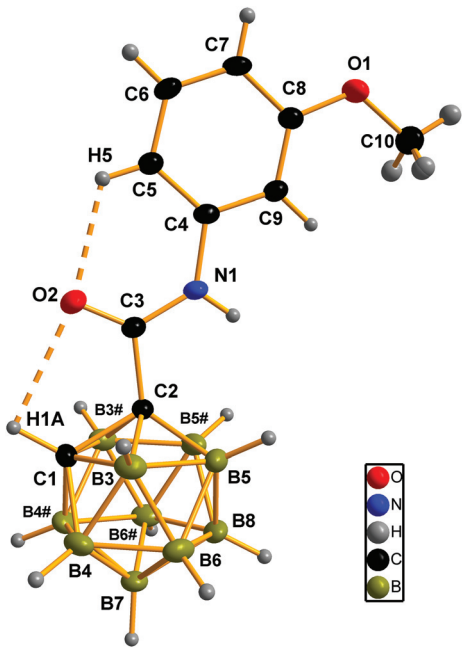


Fig. 2 Molecular structure of compound **2a** with numbering scheme, the ellipsoids are drawn at the 30% probability.

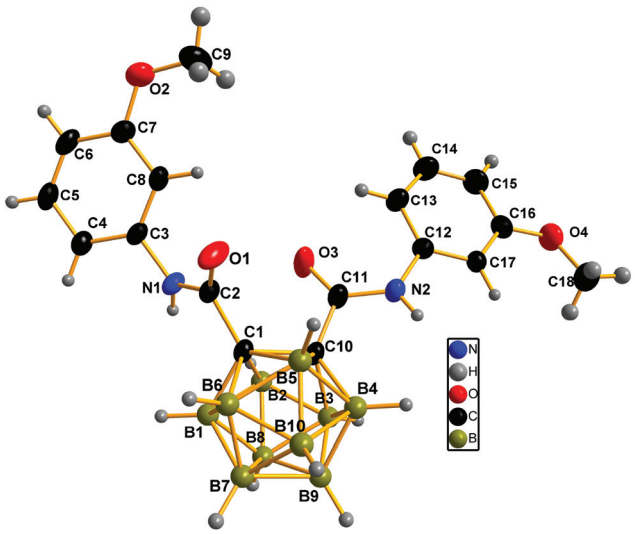


Fig. 3 Molecular structure of compound **3a** with numbering scheme, the ellipsoids are drawn at the 30% probability.

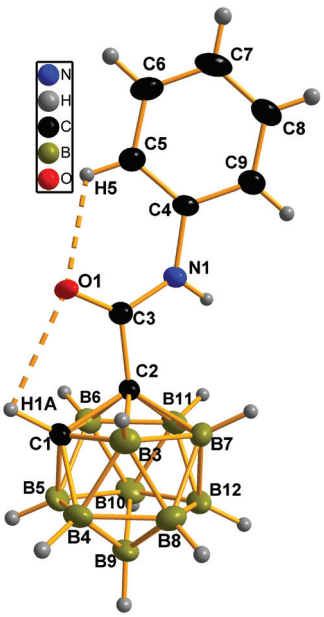


Fig. 4 Molecular structure of compound **2b** with numbering scheme, the ellipsoids are drawn at the 30% probability.

N–H···H–B dihydrogen bond (Table S1†), which fix the orientation of the thioamide moiety relative to the carborane cage. The H1···H4 distance is found to be 2.21 Å, lying in the range of the reported values (typically 1.7–2.2) for X–H···H–B (X = C, N, O, S) dihydrogen bonds.[20] Additionally, the cage C–H peak (4.97 ppm) in the ^{1}H NMR of **5** indicates the presence of intramolecular C–H···S bond in solution, similar to that with C–H···N intramolecular bond in solution.[20h]

Experimental section

General

All reactions were carried out under dry Ar using standard Schlenk techniques. The solvents diethyl ether, toluene and THF were dried over sodium/benzophenone and distilled under nitrogen prior to use. Other analytically pure reagents were commercially available. IR spectra were recorded in the range 400–4000 cm^{-1} on a Perkin Elmer Spectrum RX I spectrometer using KBr pellets. NMR analyses were performed on a Bruker Avance 400 III MHz spectrometer with tetramethylsilane (TMS) and the deuterated solvent as internal standard (^{1}H) and BF_3·OEt_2 as external standard (^{11}B). Melting points were measured with a SGW X-4 apparatus and are not corrected. The mass spectra were recorded on an Agilent 5973N MSD (low resolution) and Agilent 6890-Micromass GCT (GC-MS, high resolution) instruments. Elemental analyses

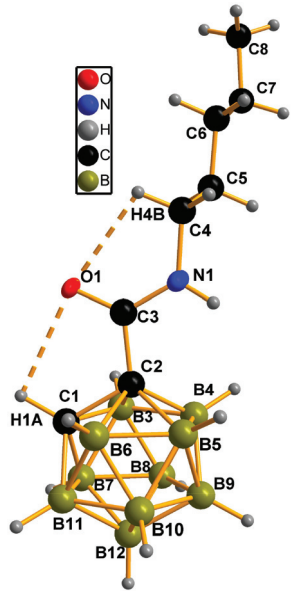


Fig. 5 Molecular structure of compound **2c** with numbering scheme, the ellipsoids are drawn at the 20% probability.

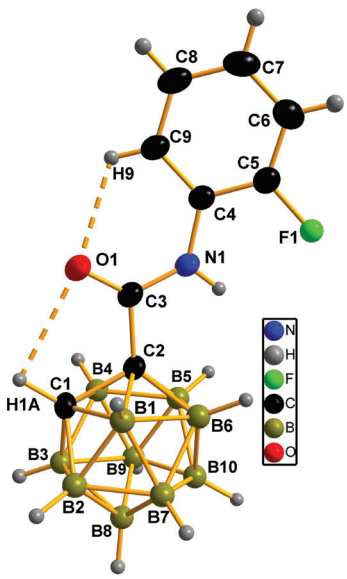


Fig. 6 Molecular structure of compound **2d** with numbering scheme, the ellipsoids are drawn at the 30% probability.

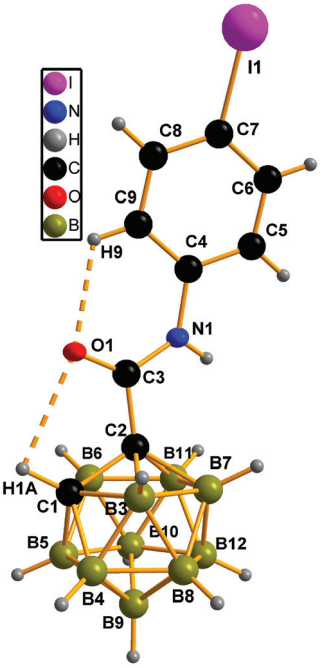


Fig. 7 Molecular structure of compound **2e** with numbering scheme, the ellipsoids are drawn at the 50% probability.

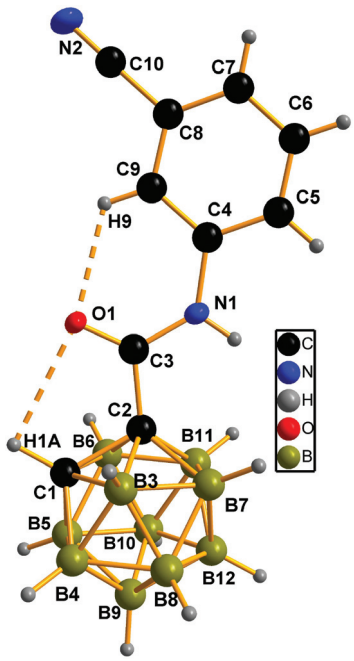


Fig. 8 Molecular structure of compound **2f** with numbering scheme, the ellipsoids are drawn at the 30% probability.

were performed on an Elementar Vario EL III instrument (Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences).

Reaction of dilithiocarborane with two equiv. of 3-methoxyphenylisocyanate

A portion of *n*-BuLi (2.2 m in *n*-hexane, 1.0 mL, 2.20 mmol) was added dropwise to a solution of *o*-carborane (143 mg, 0.99 mmol) in diethyl ether (30 mL) at 0 °C. The resulting colorless precipitate was stirred for 30 min at 0 °C and 30 min at room temperature. It was cooled to 0 °C and a solution of 3-methoxyphenylisocyanate (315 mg, 2.11 mmol) in diethyl ether (10 mL) was added. On addition the precipitate disappeared and the reaction mixture became light yellow. It was

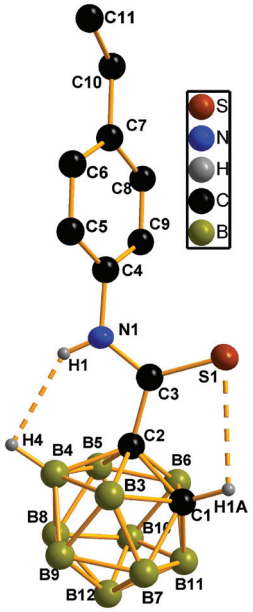


Fig. 9 Molecular structure of compound **5** with numbering scheme (only the hydrogen atoms involved in hydrogen bonds are shown), the ellipsoids are drawn at the 30% probability.

heated at reflux for 5 h during which a white precipitate appeared. After cooling to room temperature the reaction mixture was quenched with dilute HCl and then neutralized with aqueous NaOH. The organic phase was separated and the water phase extracted with diethyl ether (3 × 10 mL). The organic portions were combined, dried (anhydrous $MgSO_4$) and concentrated *in vacuo*. The resulting light yellow solid residue was further purified by preparative TLC on silica gel. Elution with *n*-hexane–dichloromethane (1/2, v/v) gave **2a** (161 mg, 55.4%) and **3a** (64 mg, 14.6%) as colorless solids.

2a: R_f = 0.62; m.p. 161–164 °C; IR (KBr): ν = 3410, 3068, 2936, 2838, 2632, 2596, 2555, 1714, 1685, 1609, 1543, 1496, 1460, 1419, 1265, 1040, 827, 782, 727, 718, 683 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 291.3 K): δ = −3.2 (2B), −8.6 (2B), −11.6 (2B), −13.1 (4B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 291.2 K): δ = 7.57 (s, 1H, NH), 7.27 (t, 1H, J = 8.0 Hz, ArH), 7.14 (m, 1H, ArH), 6.94 (dd, 1H, J = 8.0, 2.0 Hz, ArH), 6.76 (dd, 1H, J = 8.0, 2.0 Hz, ArH), 4.35 (s, 1H, $C_{cage}H$), 3.81 (s, 3H, OCH_3), 1.6–3.3 (br, 10H, BH) ppm; EI-MS (70 eV) m/z (%): 293 $[M]^+$ (100), 278 $[M - CH_3]^+$ (2), 261 $[M - OCH_3 - H]^+$ (6), 141 $[C_2B_{10}H_9]^+$ (12); HRMS (EI): calcd for $C_{10}H_{19}B_{10}NO_2$ $[M]^+$ 295.2346, found 295.2422; Calcd (%) for $C_{10}H_{19}B_{10}NO_2$: C 40.65, H 6.49, N 4.74%; found: C 41.14, H 6.55, N 4.74%.

3a: R_f = 0.15; m.p. 146–152 °C; IR (KBr): ν = 3414, 3353, 2933, 2590, 1693, 1609, 1537, 1494, 1453, 1425, 1235, 1042, 846, 779, 721, 683 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 290.9 K): δ = −1.7 (4B), −9.0 (3B), −10.3 (3B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 291.1 K): δ = 7.81 (s, 2H, NH), 7.24 (t, 2H, J = 8.4 Hz, ArH), 7.15 (m, 2H, ArH), 6.95 (dd, 2H, J = 8.0, 1.2 Hz, ArH), 6.74 (dd, 2H, J = 8.0, 2.0 Hz, ArH), 3.79 (s, 6H, OCH_3), 1.8–3.3 (br, 10H, BH) ppm; EI-MS (70 eV) m/z (%): 442 $[M]^+$ (10), 294 $[M - C_7H_8NO + H]^+$ (15), 123 $[MeOC_6H_4NH_2]^+$ (100).

Reaction of lithiocarborane with one equiv. of 3-methoxyphenylisocyanate at low temp

A portion of *n*-BuLi (2.2 m in *n*-hexane, 0.44 mL, 0.97 mmol) was added dropwise to a solution of *o*-carborane (145 mg, 1.00 mmol) in diethyl ether (20 mL) pre-cooled with liq. N_2. The resulting colorless precipitate was stirred at low temperature for 1 h and a solution of 3-methoxyphenylisocyanate (162 mg, 1.09 mmol) in diethyl ether (10 mL) was added. On addition the precipitate disappeared and the reaction mixture became colorless. It was stirred for 4 h and then at room temperature for 11 h during which the solution became yellow. After quenching with dilute HCl and neutralization with aqueous NaOH, the organic phase was separated and the water phase extracted with diethyl ether (3 × 10 mL). The organic portions were combined, dried (anhydrous $NaSO_4$) and concentrated *in vacuo*. The light yellow solid residue was further purified by preparative TLC on silica gel. Elution with *n*-hexane–dichloromethane (1/2, v/v) gave **2a** (179 mg, 61.1%) as a colorless solid.

Reaction of *o*-carborane with one equiv. of 3-methoxyphenylisocyanate and TBAF

To a solution of *o*-carborane (101 mg, 0.70 mmol) in THF (30 mL) at room temperature was added a solution of 3-methoxyphenylisocyanate (104 mg, 0.70 mmol) in THF (10 mL). To the resulting solution TBAF in THF (1.7 mL, 1 mol L^{-1}, 1.7 mmol) was added which resulted in a light yellow solution. It was stirred for 10 min at room temperature and heated at 70 °C for 50 min. After cooling to room temperature the reaction mixture was quenched with saturated NH_4Cl solution. The organic phase was separated and the water phase extracted with diethyl ether (3 × 10 mL). The organic portions were combined, dried (anhydrous $MgSO_4$) and concentrated *in vacuo*. The light yellow solid residue was dissolved with ethyl acetate (5 mL) and diethyl ether (30 mL), the resulting white solid was filtered and washed with ether and water, and dried to give compound **4**[16] as a white solid (149 mg, 56.6%). From the filtrate, a small amount of **2a** (10 mg, 4.9%) was isolated by preparative TLC on silica gel (eluent: *n*-hexane–dichloromethane (1/2, v/v)). Compound **4** was identified by a comparison of the IR and NMR data with those reported.[16] X-ray analysis of **4**: formula $C_{18}H_{48}B_9N$ (M.W. 375.86), triclinic, space group $P\bar{1}$; cell parameters a = 10.851(3), b = 10.875(3), c = 12.556(2) Å; α = 75.596(17), β = 84.333(17), γ = 67.11(2)°.

Reaction of dilithiocarborane with two equiv. of phenylisocyanate in Et_2O

Similar procedures were used to those for compound **2a**. *o*-Carborane (146 mg, 1.01 mmol), *n*-BuLi (2.2 m in *n*-hexane, 0.92 mL, 2.02 mmol), phenylisocyanate (249 mg, 2.09 mmol). Compounds **2b**[8a,e] (71 mg, 26.7%) and **3b**[9c] (228 mg, 59.0%) were obtained as colorless solids after TLC separation (eluent: *n*-hexane–dichloromethane (2/1, v/v)).

2b: R_f = 0.58; m.p. 127–128 °C; IR (KBr): ν = 3409, 3066, 2591, 2554, 1699, 1605, 1532, 1444, 1314, 1248, 1138, 1014, 751 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 293.4 K): δ = −3.2 (2B), −8.5 (2B), −11.7 (2B), −13.1 (4B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 293.4 K): δ = 7.59 (s, 1H, NH), 7.45 (d, 2H, J = 8.0 Hz, ArH), 7.38 (t, J = 7.8 Hz, 2H, ArH), 7.22 (t, 1H, J = 7.4 Hz, ArH), 4.36 (s, 1H, $C_{cage}H$), 1.6–3.3 (br, 10H, BH) ppm; EI-MS (70 eV) m/z (%): 263 $[M]^+$ (100), 141 $[C_2B_{10}H_9]^+$ (24); Calcd (%) for $C_9H_{17}B_{10}NO$: C 40.72, H 6.46, N 5.28%; found: C 41.18, H 6.51, N 5.25%.

3b: R_f = 0.16; m.p. 168–170 °C; IR (KBr): ν = 3395, 3341, 2578, 1697, 1597, 1514, 1443, 1314, 1242, 1114, 740, 691 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 293.6 K): δ = −2.0 (4B), −9.2 (3B), −10.8 (3B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 293.5 K): δ = 7.84 (s, 2H, NH), 7.45 (d, 4H, J = 8.0 Hz, ArH), 7.35 (t, 4H, J = 8.0 Hz, ArH), 7.19 (t, 2H, J = 7.4 Hz, ArH), 1.8–3.5 (br, 10H, BH) ppm.

Reaction of dilithiocarborane with two equiv. of phenylisocyanate in THF

Similar procedures to those for compound **2a**, except that the reaction was carried out in dry THF (25–30 mL). *o*-Carborane (147 mg, 1.02 mmol), *n*-BuLi (2.2 M in hexane, 1.0 mL, 2.20 mmol), phenylisocyanate (253 mg, 2.12 mmol) in THF (10 mL). The reaction mixture was heated at 40 °C for 5.5 h, and the light yellow crude product was further purified by TLC separation (eluent: *n*-hexane–dichloromethane (2/1, v/v) to give compound **2b** (190 mg, 70.5%). Another run was with *o*-carborane (146 mg, 1.01 mmol), *n*-BuLi (newly obtained, 2.5 M in hexane, 0.86 mL, 2.15 mmol), phenylisocyanate (270 mg, 2.27 mmol) in THF (10 mL), **2b** (218 mg, 81.6%) was obtained after workup.

Reaction of dilithiocarborane with two equiv. of pentylisocyanate in Et_2O

Similar procedures were used to those for compound **2a**. *o*-Carborane (143 mg, 0.99 mmol), *n*-BuLi (2.2 m in *n*-hexane, 1.0 mL, 2.20 mmol), pentylisocyanate (243 mg, 2.15 mmol). The white crude product was further purified by column chromatography (eluent: petroleum ether (b.p. 30–60 °C)–dichloromethane (1/1, v/v)) to give compounds **2c** (149 mg, 58.5%) and **3c** (142 mg, 38.7%) as colorless solids.

2c: m.p. 79–81 °C; IR (KBr): ν = 3346, 3080, 2934, 2859, 2605, 2586, 2552, 1674, 1543, 1458, 1274, 1018, 721 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 294.6 K): δ = −3.5 (2B), −8.8 (2B), −12.0 (2B), −13.3 (4B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 294.7 K): δ = 5.98 (s, 1H, NH), 4.29 (s, 1H, $C_{cage}H$), 3.27 (q, J = 6.7 Hz, 2H, NCH_2), 1.6–3.2 (br, 10H, BH), 1.52 (quint, 2H, J = 7.2 Hz, NCH_2CH_2), 1.22–1.38 (m, 4H, $CH_2CH_2CH_3$), 0.90 (t, 3H, J = 7.0 Hz, CH_3) ppm; EI-MS (70 eV) m/z (%): 257 $[M]^+$ (5), 242 $[M - CH_3]^+$ (3), 228 $[M - C_2H_5]^+$ (10), 214 $[M - C_3H_7]^+$ (43), 201 $[M - C_4H_8]^+$ (100), 188 $[M - C_5H_9]^+$ (12), 171 $[M - C_5H_{11}NH]^+$ (46), 142 $[M - C_6H_{13}NO]^+$ (32), 114 $[C_5H_{11}NHCO]^+$ (34); Calcd (%). for $C_8H_{23}B_{10}NO$: C 37.35, H 8.95, N 5.40%; found: C 37.30, H 8.95, N 5.42%.

3c: m.p. 99–102 °C; IR (KBr): ν = 3322, 2950, 2931, 2877, 2858, 2597, 1676, 1535, 1433, 1266, 721 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 293.4 K): δ = −2.6 (4B), −9.8 (2B), −11.1 (4B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 293.4 K): δ = 6.18 (s, 2H, NH), 3.26 (q, 4H, J = 6.8 Hz, NCH_2), 1.7–3.1 (br, 10H, BH), 1.53 (quint, 4H, J = 7.2 Hz, NCH_2CH_2), 1.25–1.33 (m, 8H, $CH_2CH_2CH_3$), 0.90 (t, 6H, J = 7.0 Hz, CH_3) ppm; EI-MS (70 eV) m/z (%): 370 $[M]^+$ (4), 341 $[M - C_2H_5]^+$ (2), 328 $[M - C_3H_6]^+$ (2), 315 $[M - C_4H_7]^+$ (7), 284 $[M - C_5H_{11}NH]^+$ (24), 256 $[M - C_5H_{11}NHCO]^+$ (4), 242 $[M - C_5H_{11}NHCO - CH_2]^+$ (3), 214 $[M - C_5H_{11}NHCO - C_3H_6]^+$ (16), 201 $[M - C_5H_{11}NHCO - C_4H_8]^+$ (6), 185 $[M - C_5H_{11}NHCO - C_5H_{12}]^+$ (4), 171 $[M - C_5H_{11}NHCO - C_5H_{11}N]^+$ (9), 141 $[C_2B_{10}H_9]^+$ (9), 114 $[C_5H_{11}NHCO]^+$ (27), 86 $[C_5H_{11}NH]^+$ (100); Calcd (%) for $C_{14}H_{34}B_{10}N_2O_2$: C 45.38, H 9.25, N 7.56%; found: C 45.56, H 9.38, N 7.16%.

Reaction of dilithiocarborane with two equiv. of pentylisocyanate in THF

Similar procedures to those for compound **2a**, except that the reaction was carried out in dry THF (30 mL). *o*-Carborane (148 mg, 1.03 mmol), *n*-BuLi (2.5 M in hexane, 0.88 mL, 2.20 mmol), pentylisocyanate (246 mg, 2.18 mmol) in THF (10 mL). The reaction mixture was heated at 40 °C for 4.5 h, and the light yellow crude product was further purified by TLC separation (eluent: petroleum ether (b.p. 30–60 °C)–dichloromethane (1/1, v/v) to give compound **2c** (186 mg, 70.5%) and **3c** (79 mg, 20.8%).

Reaction of dilithiocarborane with two equiv. of 2-fluorophenylisocyanate

Similar procedures were used to those for compound **2a**. *o*-Carborane (142 mg, 0.98 mmol), *n*-BuLi (2.2 m in *n*-hexane, 1.0 mL, 2.20 mmol), 2-fluorophenylisocyanate (308 mg, 2.25 mmol). The orange red oily crude product was further purified by TLC separation (eluent: *n*-hexane–dichloromethane (4/1, v/v) to give compound **2d** (153 mg, 55.5%) as a colorless solid. **2d**: R_f = 0.43; m.p. 106–110 °C; IR (KBr): ν = 3427, 3062, 2621, 2583, 1709, 1623, 1540, 1481, 1457, 1322, 1261, 1239, 1190, 1017, 823, 755, 723 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 291.7 K): δ = −3.1 (2B), −8.5 (2B), −11.7 (2B), −13.1 (4B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 291.6 K): δ = 8.06–8.11 (m, 1H, ArH), 7.94 (s, 1H, NH), 7.14–7.18 (m, 3H, ArH), 4.35 (s, 1H, $C_{cage}H$), 1.7–3.3 (br, 10H, BH) ppm; EI-MS (70 eV) m/z (%): 281 $[M]^+$ (100), 261 $[M - HF]^+$ (4), 171 $[M - NHC_6H_4F]^+$ (10), 141 $[C_2B_{10}H_9]^+$ (10); HRMS (EI) calcd for $C_9H_{16}B_{10}NOF$: $[M]^+$ 283.2146, found 283.2198; Calcd (%) for $C_9H_{16}B_{10}NOF$: C 38.13, H 5.69, N 4.94%; found: C 38.29, H 5.87, N 4.70%.

Reaction of dilithiocarborane with two equiv. of 4-iodophenylisocyanate

Similar procedures to those for compound **2a**, except that the reaction was carried out in dry THF (30 mL). *o*-Carborane (61 mg, 0.42 mmol), *n*-BuLi (2.2 M in hexane, 0.4 mL, 0.88 mmol), 4-iodophenylisocyanate (210 mg, 0.86 mmol). The reaction mixture was heated at 40 °C for 5.5 h and the light yellow crude product was further purified by TLC separation

(eluent: *n*-hexane–dichloromethane (2/1, v/v) to give compound **2e** (107 mg, 65.3%) as a colorless solid. **2e**: R_f = 0.67; m.p. 144–147 °C; IR (KBr): ν = 3318, 3044, 2573, 1703, 1597, 1524, 1489, 1393, 1314, 1239, 930, 812, 731 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 294.0 K): δ = −3.2 (2B), −8.5 (2B), −11.5 (2B), −13.0 (4B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 293.8 K): δ = 7.68 (d, 2H, J = 8.8 Hz, ArH), 7.56 (s, 1H, NH), 7.23 (d, 2H, J = 8.8 Hz, ArH), 4.34 (s, 1H, $C_{cage}H$), 1.6–3.1 (br, 10H, BH) ppm; EI-MS (70 eV) m/z (%): 389 $[M]^+$ (65), 262 $[M - I]^+$ (7), 171 $[M - IC_6H_4NH]^+$ (17), 142 $[C_2B_{10}H_{10}]^+$ (100); Calcd (%) for $C_9H_{16}B_{10}NOI$: C 27.61, H 4.12, N 3.58%; found: C 27.74, H 4.18, N 3.52%.

Reaction of dilithiocarborane with two equiv. of 3-cyanophenylisocyanate

Similar procedures to those for compound **2e**. *o*-Carborane (148 mg, 1.02 mmol), *n*-BuLi (2.2 M in hexane, 1.0 mL, 2.20 mmol), 3-cyanophenylisocyanate (317 mg, 2.20 mmol). The light yellow crude product was further purified by TLC separation (eluent: *n*-hexane–dichloromethane (1/3, v/v) to give compound **2f** (186 mg, 64.4%) as a colorless solid. **2f**: R_f = 0.76; m.p. 246–247 °C; IR (KBr): ν = 3333, 3069, 2613, 2593, 2232, 1705, 1588, 1549, 1430, 1295, 1247, 1129, 1017, 938, 792 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 294.1 K): δ = −3.1 (2B), −8.4 (2B), −11.8 (2B), −13.1 (4B) ppm: ^1H NMR (400.1 MHz, $CDCl_3$, 294.0 K): δ = 7.92 (m, 1H, ArH), 7.69 (s, 1H, NH), 7.63 (dt, 1H, J = 2.6, 6.8 Hz, ArH), 7.52–7.49 (m, 2H, ArH), 4.35 (s, 1H, $C_{cage}H$), 1.6–3.1 (br, 10H, BH) ppm; EI-MS (70 eV) m/z (%): 288 $[M]^+$ (100), 261 $[M - CN + H]^+$ (10), 171 $[M - NC\ C_6H_4NH]^+$ (41), 141 $[C_2B_{10}H_9]^+$ (57); Calcd (%) for $C_{10}H_{16}B_{10}N_2O$: C 41.35, H 5.56, N 9.65%; found: C 41.98, H 5.63, N 9.61%.

Reaction of dilithiocarborane with two equiv. of 4-chloro-3-trifluoromethylphenyl-isocyanate

Similar procedures to those for compound **2e**. *o*-Carborane (145 mg, 1.01 mmol), *n*-BuLi (2.2 M in hexane, 1.0 mL, 2.20 mmol), 4-chloro-2-trifluoromethylphenylisocyanate (459 mg, 2.07 mmol) in THF (10 mL). The light yellow crude product was further purified by TLC separation (eluent: *n*-hexane–dichloromethane (2/1, v/v) to give compound **2g** (242 mg, 65.8%) as a colorless solid. **2g**: R_f = 0.61; m.p. 83–85 °C; IR (KBr): ν = 3296, 3073, 2589, 1692, 1519, 1506, 1413, 1308, 1129, 1055, 816, 723 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 294.1 K): δ = −2.9 (2B), −8.5 (2B), −11.7 (2B), −13.0 (4B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 294.1 K): δ = 8.02 (s, 1H, NH), 7.98 (d, 1H, J = 8.8 Hz, ArH), 7.65 (d, 1H, J = 2.0 Hz, ArH), 7.57 (dd, 1H, J = 2.4, 8.8 Hz, ArH), 4.30 (s, 1H, $C_{cage}H$), 1.6–3.3 (br, 10H, BH) ppm; EI-MS (70 eV) m/z (%): 366 $[M]^+$ (83), 296 $[M - CF_3]^+$ (13), 171 $[M - NHC_6H_3CF_3Cl]^+$ (70), 141 $[C_2B_{10}H_9]^+$ (100); Calcd (%) for $C_{10}H_{15}B_{10}NOF_3Cl$: C 32.68, H 4.12, N 3.81%; found: C 33.82, H 4.26, N 3.79%.

Reaction of dilithiocarborane with two equiv. of 4-ethylphenylthioisocyanate

Similar procedures were used to those for compound **2a**. *o*-Carborane (148 mg, 1.03 mmol), *n*-BuLi (2.2 m in *n*-hexane, 1.0 mL, 2.20 mmol), 4-ethylphenylthioisocyanate (343 mg, 2.10 mmol). The yellow oily crude product was further purified by TLC separation (eluent: *n*-hexane–dichloromethane (4/1, v/v) to give compound **5** (239 mg, 75.4%) as a yellow solid. **5**: R_f = 0.62; m.p. 69–71 °C; IR (KBr): ν = 3322, 3045, 2963, 2928, 2598, 1512, 1491, 1367, 1127, 1014, 930, 731 cm^{-1}; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 292.6 K): δ = −3.5 (2B), −8.8 (2B), −10.4 (2B), −12.9 (4B) ppm; ^1H NMR (400.1 MHz, $CDCl_3$, 292.5 K): δ = 9.06 (s, 1H, NH), 7.50 (d, 2H, J = 8.4 Hz, ArH), 7.26 (d, 2H, J = 8.4 Hz, ArH), 4.97 (s, 1H, $C_{cage}H$), 2.67 (q, 2H, J = 7.6 Hz, CH_2), 1.6–3.4 (br, 10H, BH), 1.24 (t, 3H, J = 7.6 Hz, CH_3) ppm; EI-MS (70 eV) m/z (%): 307 $[M]^+$ (32), 138 $[PhNHCS + 3H]^+$ (100); Calcd (%) for $C_{11}H_{21}B_{10}NS$: C 42.69, H 6.84, N 4.53%; found: C 43.04, H 7.00, N 4.38%.

Crystal structure determination

Suitable crystals were selected and mounted on an Oxford Gemini E diffractometer for data collection (graphite-monochromated MoK_α radiation (λ = 0.71073 Å), ω scan mode) at 293(2) K. The structures were solved at the interface of Olex2[21] using Superflip[22] and Shelxs[23] and expanded using Fourier difference techniques with the Shelxtl-97[23] program package. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were placed in geometric positions and refined isotropically. CCDC 937467, 952824, 950184, 937468, 958414, 958415, 937469 and 963492 contain the information of **2a–f**, **3a** and **5**, respectively.

Conclusions

It is clear from the present work that both the substituent and the solvent have an effect on the product (monoamide and/or diamide) distribution and the corresponding yields. In most of the reactions of dilithiocarborane with two equiv. of isocyanates in diethyl ether or THF only carboranyl monoamide products or more monoamide than the corresponding diamide product (in the cases of 3-methoxyphenylisocyanate and pentylisocyanate) are isolated. The only exception is found in the case of phenylisocyanate, in which the product distribution of monoamide and diamide is opposite in diethyl ether and in THF. Similar to the corresponding monolithio-*o*-carborane system,[18] it is apparent that ethereal solvents also play an important role in the dilithio-*o*-carborane system, which merits further detailed investigation, both experimentally and theoretically.

The structural studies of the carboranylamide compounds show that the amide moieties do not have significant influence on the directly linked cage structure due to the electron delocalization of the amide fragments. In both the monoamide and diamide structures, the amide moieties are essentially planar and the carbonyl oxygen atoms participate in intramolecular

and/or intermolecular hydrogen interactions of different type. Moreover, in the monoamide structures, the C_{cage}–H···O interactions have helped to fix the orientation of the amide moieties with respect to the carborane cage. In the monoamide compounds **2a,b,d** and the thioamide **5** the C_{cage}–H groups participate in intermolecular C–H···O (**2a,b,d**) or intramolecular C–H···S (**5**) hydrogen bond interactions. In the monoamides **2e** and **5** there is no intermolecular weak interactions, whereas in other structures intermolecular hydrogen bonds of different type link the molecules into dimeric (**2b,d**) or one-dimensional chain structures (**2a,c,f** and **3a**).

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