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Nucleophilic addition reactions to the ethylnitrilium derivative of *nido*-carborane 10-EtC≡N-7,8-$C_2B_9H_{11}$†

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Alkylnitrilium derivatives of *nido*-carborane 10-RC≡N-7,8-$C_2B_9H_{11}$ (R = Me, Et) have been prepared by the reaction of the parent anion [7,8-$C_2B_9H_{12}$]$^-$ with mercury(II) chloride in mixtures of the corresponding nitriles and benzene. Hydrolysis of 10-EtC≡N-7,8-$C_2B_9H_{11}$ resulted in iminol 10-EtC(OH)=HN-7,8-$C_2B_9H_{11}$ which on treatment with a base gave the corresponding amide 10-EtC(=O)HN-7,8-$C_2B_9H_{11}$. The reactions of 10-EtC≡N-7,8-$C_2B_9H_{11}$ with alcohols and thiols were found to give stable imidates and thioimidates 10-EtC(XR)=HN-7,8-$C_2B_9H_{11}$ (X = O, R = Me, Et, iPr, Bu; X = S, R = Et, Bu, Hx) as mixtures of *E*- and *Z*-isomers that were successfully separated by column chromatography. The crystal molecular structures of *E*-10-EtC(OR)=HN-7,8-$C_2B_9H_{11}$ (R = Et, i-Pr, Bu) and *Z*-10-EtC(SEt)=HN-7,8-$C_2B_9H_{11}$ were determined by single crystal X-ray diffraction.

1. Introduction

Since its discovery 7,8-dicarba-*nido*-undecaborate anion (*nido*-carborane) and its derivatives for many years have attracted attention as unusual three-dimensional π-ligands[1,2] as well as water-solubilizing boron moieties in design of potential drugs for boron neutron capture therapy of cancer.[3,4] In both cases modification of the carborane cage at carbon atoms of the parent 1,2-dicarba-*closo*-dodecaborane (*ortho*-carborane) followed by transformation to *nido*-carborane is widely used. Modification of the carborane ligand at boron atoms in metallacarboranes is used mainly to introduce the so-called "charge-compensating" substituents decreasing the ligand charge[5] or to protect the most reactive positions of metallacarborane complexes in highly aggressive media (*i.e.*, derivatives of cobalt bis(dicarbollide) used in processing of high-level nuclear wastes).[6] Modification of *nido*-carborane through its oxonium,[7] sulfonium[8] and ammonium[9] derivatives was proposed recently for the synthesis of carborane derivatives for medical applications, whereas other types of its modification have received much less attention.[10–13]

Electrophile induced nucleophilic substitution (EINS) is considered as one of the main mechanisms of substitution of hydrogen atoms in polyhedral boron hydrides. The key step of this mechanism is formation of the so-called transient "quasi-borinium cation", which is subjected to subsequent nucleophilic attack.[14] These quasi-borinium cations are strong Lewis acids[15] which are capable of activating C–H bonds in aromatics[16] and C–X (X = Cl, Br) bonds in halogenalkanes.[17] In the presence of organonitriles they give the corresponding nitrilium derivatives.[18,19] The reactivity of these compounds in some way resembles those of the transition metal nitrile complexes. Transition metal mediated addition reactions of various nucleophiles to coordinated nitriles are well known.[20–23] It was demonstrated earlier that similar to transition metal nitrile complexes the nitrilium derivatives of *closo*-decaborate $[B_{10}H_{10}]^{2-}$,[24] *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$,[25] and cobalt bis(dicarbollide) [3,3′-Co(1,2-$C_2B_9H_{11})_2$]$^-$[19] anions easily undergo hydrolysis into the corresponding amides. Some time later numerous addition and cycloaddition reactions of various nucleophiles (alcohols,[26] amines,[27] hydrazine derivatives,[28] oximes,[29] nitrones,[30] azide,[31] CH acids[32]) to the triple C≡N bonds of nitrilium derivatives of *closo*-decaborate were reported demonstrating high potential of this type of reaction for modification of other polyhedral boron hydrides. At the same time, the electronic effects in the series of polyhedral boron hydrides differ significantly,[33] which leads to differences in the reactivity of their derivatives.[34] Therefore a study of reactivity of nitrilium derivatives of other polyhedral boron hydrides is important.

In this contribution we describe synthesis of a 10-propionitrilium derivative of *nido*-carborane [10-EtC≡N-*nido*-7,8-$C_2B_9H_{11}$] and its reactions with water, alcohols, mercaptans and amines.

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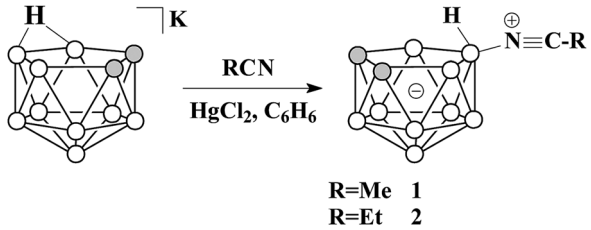


Scheme 1 Synthesis of methyl- and ethylnitrilium derivatives of *nido*-carborane.

2. Results and discussion

The first nitrilium derivative of *nido*-carborane [10-MeC≡N-7,8-$C_2B_9H_{11}$] was obtained by the reaction of (Me_4N)[7,8-$C_2B_9H_{12}$] with $AlCl_3$ in acetonitrile in the presence of acetone.[11a] However, in our hands, the yield of the target product after a troublesome isolation and purification procedure did not exceed 60%. Therefore, we decided to apply for this goal the same approach which was used earlier for preparation of the oxonium derivatives of *nido*-carborane, namely, the reactions of *nido*-carborane with $HgCl_2$ in the appropriate solvents.[7a,35,36] We found out that the reactions of the potassium salt of the 7,8-dicarba-*nido*-undecaborate anion K[7,8-$C_2B_9H_{12}$] with mercury(II) chloride in boiling benzene–acetonitrile/propionitrile mixtures result in the corresponding symmetrically substituted organonitrilium derivatives 10-RC≡N-7,8-$C_2B_9H_{11}$ (R = Me (**1**), Et (**2**)) in nearly quantitative yield (Scheme 1).

The ^{11}B NMR spectra of **1** and **2** in (acetone-d_6 and $CDCl_3$, correspondently) demonstrate characteristic patterns 2:2:1:2:1:1 that agree well with the planar symmetry of the symmetrically substituted *nido*-carborane cage with the singlet of the B(10) atom approx. at −25 and −29 ppm, respectively. In the ^{13}C NMR spectra the signals of the –N^+≡C– carbon atom are observed at 114.0 and 112.9 ppm. The IR spectra of **1** and **2** contain characteristic absorption bands of a nitrilium group at 2351 and 2345 cm^{-1}.

To study reactivity of the nitrilium derivatives of *nido*-carborane in the reactions of nucleophilic addition to a polarized C≡N triple bond we chose the propionitrilium derivative **2** due to better visibility of the ethyl group in ^{1}H NMR spectra. Addition of water (hydrolysis) is the simplest example of a nucleophilic addition reaction. The hydrolysis of **2** in a boiling mixture of acetonitrile and water results in the corresponding protonated iminol 10-EtC(OH)=NH-7,8-$C_2B_9H_{11}$ (**3**) that on treatment with triethylamine produces amide (Et_3NH)[10-EtC(O)NH-7,8-$C_2B_9H_{11}$] (**4**) (Scheme 2). In the ^{1}H NMR spectra we observed the sequential high-field shift of the CH_2 group signal (from 2.71 ppm for **2** to 2.65 ppm for **3** and then to 2.20 ppm for **4**). At the same time the ^{13}C NMR spectra exhibit the low-field shift of the signals of the α-carbon atom (182.5 ppm for **3** and 177.3 ppm for **4**). The IR spectra of **3** and **4** demonstrate the absence of the nitrilium group absorption band. The IR spectrum of **3** contains absorption bands of OH (3613 cm^{-1}) and NH (3336 and 3188 cm^{-1}) groups, as well as a characteristic band of the N=C stretching at 1645 cm^{-1}. The IR spectrum of **4** demonstrates the absorption bands of NH (3401 cm^{-1}) and C=O groups (1616 cm^{-1}).

It should be noted that no evidence of *E*/*Z* isomerism was found in the case of protonated iminol **3** probably due to fast iminol protonated amide–iminol tautomeric equilibrium.

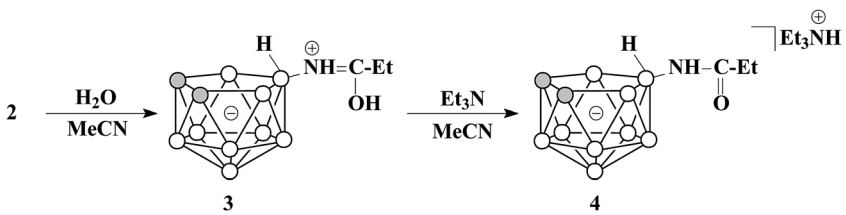
The reactions of **2** with alcohols (methanol, ethanol, isopropanol and butanol) under reflux conditions resulted in the corresponding imidates 10-EtC(OR)=NH-7,8-$C_2B_9H_{11}$ (R = Me (**5**), Et (**6**), i-Pr (**7**), Bu (**8**)). The reactions proceed also at room temperature and their completion requires much more time. In contrast with hydrolysis, the addition of alcohols to the polarized triple bond of **2** was found to produce mixtures of *E* and *Z* isomers with a slight excess of *E*-isomers, which can be separated by column chromatography on silica (Scheme 3).

On standing in solution, both *E* and *Z* isomers were found to demonstrate a tendency to mutual isomerization. This tendency is strongly noticeable for the methoxy derivatives **5a** and **5b** however it sharply decreases with the length of the alkyl chain.

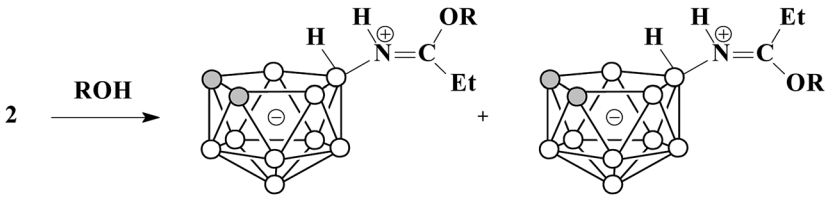
The assignment of the *E* and *Z* isomers was performed using single crystal X-ray diffraction. The structures of *E* isomers **6a**, **7a** and **8a** are presented in Fig. 1. In all derivatives the oxygen atom is directed outwards from the carborane cage; the lengths of the B(10)–N(1) bonds equal 1.530 Å, the lengths of the N(1)–C(1) bonds are in the range 1.286–1.299 Å, the C(1)–O(1) bonds are significantly shorter than the O(1)–C(4) bonds (1.307–1.322 Å and 1.457–1.475 Å, respectively) suggesting partial delocalization of the positive charge in the imidate fragment.

Unfortunately, all our attempts to obtain suitable crystals of the *Z*-isomers for X-ray diffraction studies failed. It should be noted that in the case of imidates based on the *closo*-decaborate anion, only crystals of *E*-isomers suitable for X-ray diffraction were obtained, although formation of mixtures of *E* and *Z* isomers was reported.[26]

The *E* and *Z* isomers of **5–8** significantly differ spectrally. The biggest difference is observed in the ^{1}H NMR spectra.



Scheme 2 Synthesis of iminol and amide derived from the ethylnitrilium derivative of *nido*-carborane.



Scheme 3 Nucleophilic addition of alcohols to the ethylnitrilium derivative of *nido*-carborane.

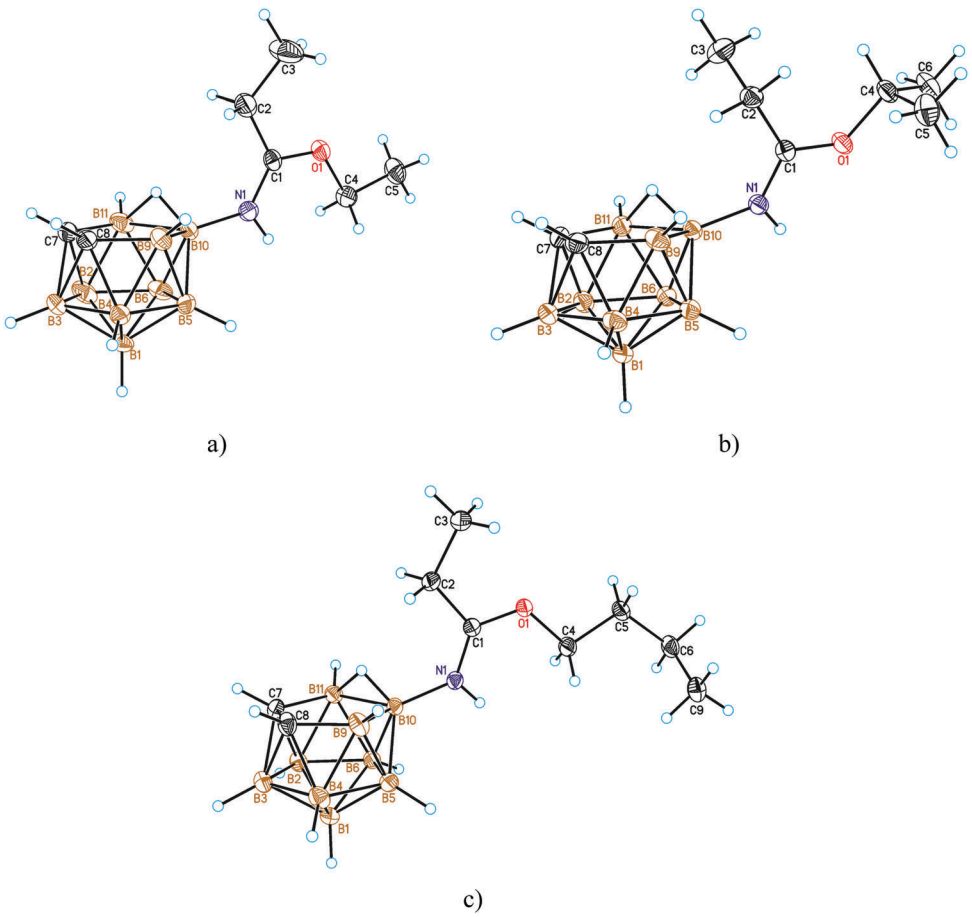


Fig. 1 General view of the structures **6a** (a), **7a** (b) and **8a** (c) with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

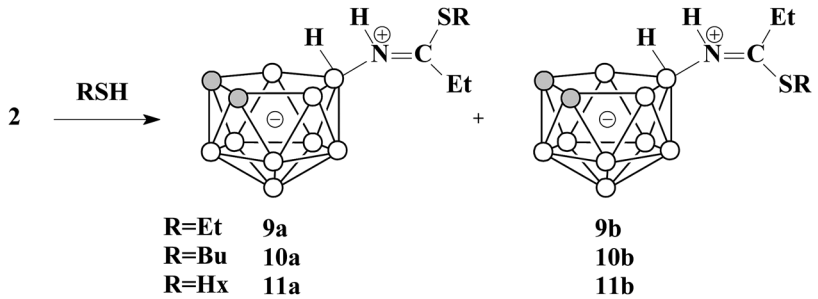
In general, the ^{1}H NMR spectral patterns of the *Z*-isomers are "wider" than those of the *E*-isomers: the signal of the =COCH_2R group in the spectra of *Z*-isomers is low-field shifted by 0.19–0.36 ppm, whereas the signals of the =CCH_2Me groups are high-field shifted by 0.25–0.45 ppm relatively to those for *E*-isomers (Table 1). At the same time, the signals of the NH and B(10)H groups in the spectra of *Z*-isomers are low-field shifted by 0.25–0.53 ppm and high-field shifted by ~0.3 ppm relative to those for *E*-isomers.

In the ^{13}C NMR spectra the signal of the –NH=C– carbon is observed at 180–182 ppm and it is slightly low-field shifted by 0.4–1.0 ppm for the *Z*-isomers relative to that for the *E*-isomer. In the ^{11}B NMR spectra the signal of the B(10) atom was found to be the most sensitive to *E*/*Z* isomerism. It is low-field shifted by 1.2–1.7 ppm for the *Z*-isomers in comparison with that for the *E*-isomers. The difference of other signals in the ^{11}B NMR spectra of *E* and *Z*-isomers is not significant.

The IR spectra of imidates **5–8** demonstrate the N–H and C=N stretching bands in the ranges 3400–3200 and 1636–1618 cm^{-1}, respectively, as well as the B–H stretching bands in the range 2546–2499 cm^{-1}.

Table 1 Selected signals in ^{1}H NMR spectra of *E*- and *Z*-imidates 10-EtC(OR)═NH-7,8-$C_2B_9H_{11}$

	$CDCl_3$, δ, ppm				
Compound	═CCH_2Me	═CCH$_2$CH_3	–OCH_2R	CH_{carb}	Other signals
E-10-EtC(OMe)HN-7,8-$C_2B_9H_{11}$ **5a**	3.20	1.35	4.22	1.98	—
Z-10-EtC(OMe)HN-7,8-$C_2B_9H_{11}$ **5b**	2.95	1.33	4.41	1.89	—
E-10-EtC(OEt)HN-7,8-$C_2B_9H_{11}$ **6a**	3.15	1.38	4.21	2.09	1.54 (OCH$_2$CH_3)
Z-10-EtC(OEt)HN-7,8-$C_2B_9H_{11}$ **6b**	2.70	1.32	4.53	2.05	1.65 (OCH$_2$CH_3)
E-10-EtC(OiPr)HN-7,8-$C_2B_9H_{11}$ **7a**	3.11	1.36	4.70	2.10	1.46 (OCH(CH_3)$_2$), 1.44 (OCH(CH_3)$_2$)
Z-10-EtC(OiPr)HN-7,8-$C_2B_9H_{11}$ **7b**	2.71	1.32	5.02	2.04	1.59 (OCH(CH_3)$_2$), 1.58 (OCH(CH_3)$_2$)
E-10-EtC(OBu)HN-7,8-$C_2B_9H_{11}$ **8a**	3.15	1.39	4.10	2.08	1.86 (OCH$_2$CH_2CH$_2$CH$_3$), 1.48 (OCH$_2$CH$_2$CH_2CH$_3$), 1.01 (OCH$_2$CH$_2$CH$_2$CH_3)
Z-10-EtC(OBu)HN-7,8-$C_2B_9H_{11}$ **8b**	2.72	1.31	4.46	2.04	1.96 (OCH$_2$CH_2CH$_2$CH$_3$), 1.62 (OCH$_2$CH$_2$CH_2CH$_3$), 1.05 (OCH$_2$CH$_2$CH$_2$CH_3)



Scheme 4 Nucleophilic addition of thiols to the ethylnitrilium derivative of *nido*-carborane.

The addition of thiols to activated nitriles is much less studied than the alcohol addition.[22,37] The reactions of **2** with thiols (ethylthiol, butylthiol, hexylthiol) proceed much faster, approx. 20 min at ambient temperature, resulting in the corresponding imidates 10-EtC(SR)═NH-7,8-$C_2B_9H_{11}$ (R = Et (**9**), Bu (**10**), Hx (**11**)). Like the addition of alcohols, the addition of thiols to the polarized triple bond of **2** produces mixtures of *E* and *Z* isomers, which can be separated by column chromatography on silica (Scheme 4).

As in the case of the imidates **5–8**, the assignment of the *E* and *Z* isomers in thioimidates was performed using single crystal X-ray diffraction studies. Unlikely to the imidates, the structure of *Z*-isomer **9b** was determined (Fig. 2). The sulfur atom is turned towards the open pentagonal face of the *nido*-carborane cage; the length of the B(10)–N(1) and N(1)–C(1) bonds are 1.528 and 1.309 Å, respectively, the C(1)–S(1) bond is significantly shorter than the S(1)–C(4) bonds (1.719 and 1.818 Å, respectively) suggesting partial delocalization of the positive charge in the thioimidate fragment.

In contrast to the ^{1}H NMR spectra of imidates **5–8**, the difference in chemical shifts of the corresponding signals in the spectra of *E*- and *Z*-isomers of thioimidates **9–11** is practically negligible (Table 2).

Taking into account the acidic character of the *endo*-proton in *nido*-carborane derivatives,[38] the significant difference in the ^{1}H NMR spectra of the *E*- and *Z*-isomers of imidates **5–8** and its practical absence in the spectra of thioimidates **9–11** could be explained by formation of intramolecular hydrogen B–H···O bonds in the *Z*-isomers of the imidates and failure of sulfur atoms to form such bonds in the thioimidates (Scheme 5).

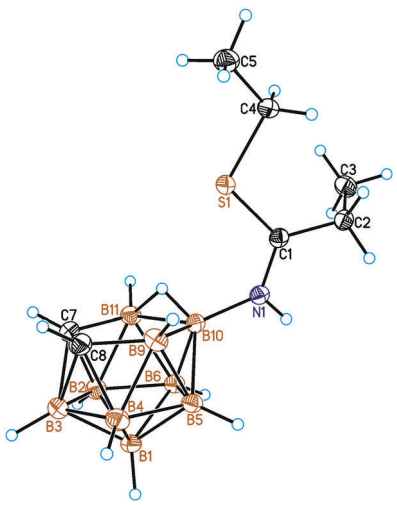


Fig. 2 General view of the structure **9b** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

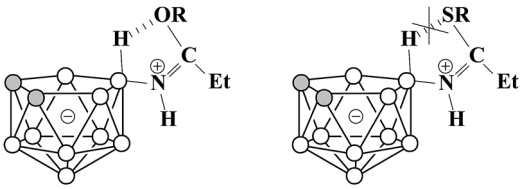
The IR spectra of thioimidates **9–11** showed the N–H stretching bands in the range 3400–3200 cm^{-1}, while the C═N stretching appeared in the range 1580–1559 cm^{-1} at lower values compared to those found for imidates **5–8** (1636–1618 cm^{-1}).

3. Conclusions

Reactions of *nido*-carborane [7,8-$C_2B_9H_{12}$]$^-$ with alkylnitriles in the presence of mercury(II) chloride produce symmetrically

Table 2 Selected signals in ^{1}H NMR spectra of *E*- and *Z*-thioimidates 10-EtC(SR)═NH-7,8-$C_2B_9H_{11}$

Compound	$CDCl_3$, δ, ppm				
	═CCH_2Me	═CCH$_2$CH_3	–SCH_2R	CH_{carb}	Other signals
E-10-EtC(SEt)HN-7,8-$C_2B_9H_{11}$ **9a** (in acetone-d_6)	3.20	1.47	2.86	1.99	1.26 (SCH$_2$CH_3)
Z-10-EtC(SEt)HN-7,8-$C_2B_9H_{11}$ **9b**	3.24	1.56	2.88	2.14	1.33 (SCH$_2$CH_3)
E-10-EtC(SBu)HN-7,8-$C_2B_9H_{11}$ **10a**	3.20	1.47	2.86	2.09	1.72 (SCH$_2$CH_2CH$_2$CH$_3$), 1.49 (SCH$_2$CH$_2$CH_2CH$_3$), 0.98 (SCH$_2$CH$_2$CH$_2$CH_3)
Z-10-EtC(SBu)HN-7,8-$C_2B_9H_{11}$ **10b**	3.18	1.32	2.87	2.14	1.82 (SCH$_2$CH_2CH$_2$CH$_3$), 1.58 (SCH$_2$CH$_2$CH_2CH$_3$), 1.04 (SCH$_2$CH$_2$CH$_2$CH_3)
E-10-EtC(SHx)HN-7,8-$C_2B_9H_{11}$ **11a**	3.21	1.46	2.86	2.11	1.73 (SCH$_2$CH_2(CH$_2$)$_3$CH$_3$), 1.44 (S(CH$_2$)$_2$CH_2(CH$_2$)$_2$CH$_3$), 1.33 (S(CH$_2$)$_3$CH_2CH_2CH$_3$), 0.92 (S(CH$_2$)$_5$CH_3)
Z-10-EtC(SHx)HN-7,8-$C_2B_9H_{11}$ **11b**	3.17	1.32	2.87	2.14	1.86 (SCH$_2$CH_2(CH$_2$)$_3$CH$_3$), 1.54 (S(CH$_2$)$_2$CH_2(CH$_2$)$_2$CH$_3$), 1.38 (S(CH$_2$)$_3$CH_2CH_2CH$_3$), 0.95 (S(CH$_2$)$_5$CH_3)



Scheme 5 The proposed formation of intramolecular hydrogen B–H···O bonds in the *Z*-isomers of the imidates.

substituted alkylnitrilium derivatives 10-RC≡N-7,8-$C_2B_9H_{11}$ (R = Me, Et). Hydrolysis of 10-EtC≡N-7,8-$C_2B_9H_{11}$ results in the corresponding *N*-protonated iminol 10-EtC(OH)═HN-7,8-$C_2B_9H_{11}$ which on treatment with a base gives amide 10-EtC(═O)HN-7,8-$C_2B_9H_{11}$. The reactions of 10-EtC≡N-7,8-$C_2B_9H_{11}$ with alcohols were found to give stable imidates 10-EtC(OR)═HN-7,8-$C_2B_9H_{11}$ (R = Me, Et, iPr, Bu) as mixtures of *E*- and *Z*-isomers, which can be separated by column chromatography. Significant difference in the ^{1}H NMR spectra of *E*- and *Z*-isomers of the imidates can be explained by formation of intramolecular B–H···O hydrogen bonds in *Z*-isomers. Crystal molecular structures of *E*-10-EtC(OR)═HN-7,8-$C_2B_9H_{11}$ (R = Et, i-Pr, Bu) were determined by single crystal X-ray diffraction. The reactions of 10-EtC≡N-7,8-$C_2B_9H_{11}$ with thiols produce thioimidates 10-EtC(SR)═HN-7,8-$C_2B_9H_{11}$ (R = Et, Bu, Hx) as mixtures of *E*- and *Z*-isomers, which can be separated by column chromatography. The absence of any noticeable difference in the ^{1}H NMR spectra of *E*- and *Z*-isomers suggests failure of intramolecular hydrogen bonding in *Z*-isomers of thioimidates. The absence of intramolecular hydrogen bonding in *Z*-isomers of thioimidates in the solid state was supported by an X-ray structure of *Z*-10-EtC(OEt)═HN-7,8-$C_2B_9H_{11}$. In summary, nucleophilic addition reactions to a highly polarized triple bond of alkylnitrilium derivatives of *nido*-carborane can be considered as a very promising method for the synthesis of substituted derivatives of 7,8-dicarba-*nido*-carborane.

4. Experimental

The potassium salt of 7,8-dicarba-*nido*-caborane was prepared according to the literature procedure.[39] Acetonitrile, methanol, ethanol, isopropanol and butanol were dried using standard procedures.[40] All reactions were carried out in air. The reaction progress was monitored by thin-layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5% $PdCl_2$ in 1% HCl in aq. MeOH (1 : 10). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B) and 100.0 MHz (^{13}C) were recorded with a Bruker Avance-400 spectrometer. The residual signal of the NMR solvent relative to tetramethylsilane was taken as the internal reference for ^{1}H and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced using $BF_3{\cdot}Et_2O$ as an external standard. Infrared spectra were recorded on an IR Prestige-21 (SHIMADZU) instrument. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were carried out in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from *m*/*z* 50 to *m*/*z* 3000; external or internal calibration was carried out with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile (flow rate 3 ml min^{-1}). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

4.1. Synthesis of 10-MeCN-7,8-$C_2B_9H_{11}$ (1)

The potassium salt of 7,8-dicarba-*nido*-caborane (0.15 g, 0.87 mmol) and mercury(II) chloride (0.24 g, 0.87 mmol) in a mixture of benzene (3 ml) and acetonitrile (3 ml) was heated under reflux for about 4 h. After cooling to room temperature, the solution was decanted, and the residue was washed with benzene. The washings were combined with the solution and evaporated under reduced pressure to give 0.13 g (86%) of a white product. ^{1}H NMR (acetone-d_6, ppm): δ 2.44 (s, 3H, CH_3), 1.87 (s, 2H, CH_{carb}), 2.3–(−0.5) (br s, 8H, B*H*), −1.0 (br s, 1H, B*H*B). ^{11}B NMR (acetone-d_6, ppm): δ −10.3 (d, J = 128 Hz, 2B), −16.1 (d, J = 134 Hz, 2B), −20.3 (d, J = 167 Hz, 1B), −22.6 (d, J = 150 Hz, 2B), −25.3 (s, 1B), −39.2 (d, J = 145 Hz, 1B). IR (film, cm^{-1}): 2949 (br, ν_{C-H}), 2923 (br, ν_{C-H}), 2544 (br, ν_{B-H}), 2351 ($\nu_{N\equiv C}$).

4.2. Synthesis of 10-EtCN-7,8-$C_2B_9H_{11}$ (2)

The procedure was analogous to that described for synthesis of **1**, using potassium salt of 7,8-dicarba-*nido*-caborane

(0.30 g, 1.74 mmol) and mercury(II) chloride (0.48 g, 1.74 mmol) in a mixture of benzene (8 ml) and propionitrile (8 ml) to give 0.32 g (98%) of a white product. ^{1}H NMR ($CDCl_3$, ppm): δ 3.02 (q, 2H, J = 7.5 Hz, CH_2), 2.14 (s, 2H, CH_{carb}), 1.54 (t, 3H, J = 7.5 Hz, CH_3), 2.2 ÷ 0.2 (br s, 8H, BH), −0.7 (br s, 1H, BHB). ^{1}H NMR (acetone-d_6, ppm): δ 2.71 (q, 2H, J = 7.6 Hz, CH_2), 1.88 (s, 2H, CH_{carb}), 1.28 (t, 3H, J = 7.6 Hz, CH_3), 2.3–0.1 (br s, 8H, BH), −0.5 (br s, 1H, BHB). ^{13}C NMR ($CDCl_3$, ppm): δ 112.9 (N≡C), 45.0 (CH$_{carb}$), 12.0 (CH$_2$), 8.7 (CH$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −11.2 (d, J = 144 Hz, 2B), −14.5 (d, J = 140 Hz, 2B), −18.3 (d, J = 174 Hz, 1B), −20.8 (d, J = 155 Hz, 2B), −28.9 (s, 1B), −38.1 (d, J = 144 Hz, 1B). ^{11}B NMR (acetone-d_6, ppm): δ −10.5 (d, J = 138 Hz, 2B), −16.1 (d, J = 140 Hz, 2B), −20.3 (d, J = 179 Hz, 1B), −22.5 (d, J = 153 Hz, 2B), −25.2 (s, 1B), −39.2 (d, J = 142 Hz, 1B). IR (film, cm^{-1}): 2950 (br, ν_{C-H}), 2922 (br, ν_{C-H}), 2549 (br, ν_{B-H}), 2345 ($\nu_{N\equiv C}$). ESI HRMS: m/z for $C_5H_{16}B_9N$: calcd 206.2498 $[M + NH_4]^+$, obsd 206.2499 $[M + NH_4]^+$.

4.3. Synthesis of 10-EtC(OH)═HN-7,8-$C_2B_9H_{11}$ (3)

To a solution of **2** (0.10 g, 0.53 mmol) in acetonitrile (3 ml) distilled water (2 ml) was added and the solution was heated under reflux for about 3 h. The reaction mixture was cooled to room temperature and evaporated to dryness in a vacuum to obtain 0.10 g (92%) of a white crystalline product. ^{1}H NMR ($CDCl_3$, ppm): δ 10.39 (br s, 1H, OH), 7.25 (s, 1H, NH), 2.65 (q, 2H, J = 7.5 Hz, CH_2), 2.23 (s, 2H, CH_{carb}), 1.32 (t, 3H, J = 7.5 Hz, CH_3), 2.2–0.3 (br s, 8H, BH), −1.2 (br s, 1H, BHB). ^{13}C NMR ($CDCl_3$, ppm): δ 182.5 (NH═C), 45.5 (CH$_{carb}$), 28.0 (CH$_2$), 8.9 (CH$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −14.8 (d, J = 125 Hz, 4B), −19.4 (d, J = 152 Hz, 3B), −24.1 (s, 1B), −38.4 (d, J = 144 Hz, 1B). IR (film, cm^{-1}): 3613 (br, ν_{O-H}), 3336 (br, ν_{N-H}), 3188 (br, ν_{N-H}), 2985 (br, ν_{C-H}), 2945 (br, ν_{C-H}), 2551 (br, ν_{B-H}), 1645 ($\nu_{N=C}$), 1524, 1458, 1387, 1215. ESI HRMS: m/z for $C_5H_{18}B_9NO$: calcd 229.2168 $[M + Na]^+$, obsd 229.2158 $[M + Na]^+$.

4.4. Synthesis of Et_3NH[10-EtC(O)-HN-7,8-$C_2B_9H_{11}$] (4)

To a solution of **3** (0.09 g, 0.44 mmol) in acetonitrile (2 ml) Et_3N (2 ml) was added and the solution was heated under reflux for about 15 min. The reaction mixture was cooled to room temperature and evaporated to dryness in a vacuum to obtain 0.12 g (89%) of a yellow crystalline product. ^{1}H NMR (acetone-d_6, ppm): δ 6.94 (br s, 1H, NH═C), 5.93 (s, 1H, Et_3NH), 3.37 (q, 6H, J = 7.3 Hz, NCH_2CH$_3$), 2.20 (q, 2H, J = 7.5 Hz, CH_2), 1.74 (s, 2H, CH_{carb}), 1.42 (t, 9H, J = 7.3 Hz, NCH$_2$CH_3), 1.06 (t, 3H, J = 7.5 Hz, CH_3), 2.1 ÷ 0.1 (br s, 8H, BH), −0.5 (br s, 1H, BHB). ^{13}C NMR (acetone-d_6, ppm): δ 177.3 (NHC), 46.9 (NCH$_2$CH$_3$), 40.4 (CH$_{carb}$), 30.2 (CH$_2$), 9.8 (CH$_3$), 8.5 (NCH$_2$$CH_3$). ^{11}B NMR (acetone-$d_6$, ppm): δ −10.2 (d, J = 134 Hz, 2B), −15.9 (d, J = 131 Hz, 2B), −21.3 (d, J = 184 Hz, 1B), −22.9 (d, J = 155 Hz, 2B), −23.4 (s, 1B), −39.4 (d, J = 135 Hz, 1B). IR (film, cm^{-1}): 3401 (br, ν_{N-H}), 2984, 2940, 2879, 2701, 2530 (br, ν_{B-H}), 1616 ($\nu_{C=O}$), 1502, 1466, 1453, 1408. ESI HRMS: m/z for $C_5H_{17}B_9NO$: calcd 205.2190 $[M]^-$, obsd 205.2193 $[M]^-$.

4.5. Synthesis of 10-EtC(OMe)═HN-7,8-$C_2B_9H_{11}$ (5a, 5b)

A solution of **2** (0.10 g, 0.53 mmol) in anhydrous methanol (3 ml) was heated under reflux for about 2 h. The reaction mixture was cooled to room temperature and evaporated to dryness in a vacuum. The mixture of E and Z isomers was separated by column chromatography on silica with CH_2Cl_2 as an eluent to give white crystalline products **5a** and **5b**.

5a. Yield 53.5 mg (46%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.18 (s, 1H, NH), 4.22 (s, 3H, OCH_3), 3.20 (q, 2H, J = 7.5 Hz, CH_2), 1.98 (s, 2H, CH_{carb}), 1.35 (t, 3H, J = 7.5 Hz, CH_3), 2.2–0.1 (br s, 8H, BH), −0.7 (br s, 1H, BHB). ^{13}C NMR ($CDCl_3$, ppm): δ 181.7 (NH═C), 57.3 (OCH$_3$), 41.9 (CH$_{carb}$), 24.1 (CH$_2$), 9.2 (CH$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.5 (d, J = 127 Hz, 2B), −15.9 (d, J = 132 Hz, 2B), −20.1 (d, J = 163 Hz, 1B), −23.0 (d, J = 155 Hz, 2B), −23.6 (s, 1B), −39.0 (d, J = 139 Hz, 1B). IR (film, cm^{-1}): 3384 (br, ν_{N-H}), 2955 (br, ν_{C-H}), 2892 (br, ν_{C-H}), 2546 (br, ν_{B-H}), 1635 ($\nu_{N=C}$), 1506, 1424, 1382, 1250. ESI HRMS: m/z for $C_6H_{20}B_9NO$: calcd 243.2327 $[M + Na]^+$, obsd 243.2316 $[M + Na]^+$.

5b. Yield 50.0 mg (43%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.71 (s, 1H, NH), 4.41 (s, 3H, OCH_3), 2.95 (q, 2H, J = 7.6 Hz, CH_2), 1.89 (s, 2H, CH_{carb}), 1.33 (t, 3H, J = 7.6 Hz, CH_3), 2.3–0.2 (br s, 8H, BH), −0.4 (br s, 1H, BHB). ^{13}C NMR ($CDCl_3$, ppm): δ 182.1 (NH═C), 58.7 (OCH$_3$), 42.0 (CH$_{carb}$), 25.2 (CH$_2$), 8.7 (CH$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.5 (d, J = 127 Hz, 2B), −15.8 (d, J = 124 Hz, 2B), −20.1 (d, J = 164 Hz, 1B), −22.1 (d, J = 155 Hz, 2B), −25.3 (s, 1B), −39.0 (d, J = 139 Hz, 1B). IR (film, cm^{-1}): 3352 (br, ν_{N-H}), 2923 (br, ν_{C-H}), 2853 (br, ν_{C-H}), 2546 (br, ν_{B-H}), 1628 ($\nu_{N=C}$), 1507, 1425, 1403, 1319, 1251. ESI HRMS: m/z for $C_6H_{20}B_9NO$: calcd 238.2776 $[M + NH_4]^+$, obsd 238.2762 $[M + NH_4]^+$.

4.6. Synthesis of 10-EtC(OEt)═HN-7,8-$C_2B_9H_{11}$ (6a, 6b)

The procedure was analogous to that described for the synthesis of **5a** and **5b** using **2** (0.10 g, 0.53 mmol) and anhydrous ethanol (3 ml) to give white crystalline products **6a** and **6b**.

6a. Yield 58.2 mg (47%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.57 (s, 1H, NH), 4.21 (q, 2H, J = 6.9 Hz, OCH_2CH$_3$), 3.15 (q, 2H, J = 7.6 Hz, CH_2), 2.09 (s, 2H, CH_{carb}), 1.54 (t, 3H, J = 6.9 Hz, OCH$_2$CH_3), 1.38 (t, 3H, J = 7.6 Hz, CH_3), 2.0–0.1 (br s, 8H, BH), −0.7 (br s, 1H, BHB). ^{13}C NMR ($CDCl_3$, ppm): δ 180.9 (NH═C), 66.1 (OCH$_2$CH$_3$), 43.7 (CH$_{carb}$), 25.7 (CH$_2$), 13.3 (OCH$_2$$CH_3$), 9.4 ($CH_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.4 (d, J = 142 Hz, 2B), −15.1 (d, J = 134 Hz, 2B), −19.7 (d, J = 183 Hz, 1B), −21.5 (d, J = 153 Hz, 2B), −24.3 (s, 1B), −38.6 (d, J = 141 Hz, 1B). IR (film, cm^{-1}): 3381 (br, ν_{N-H}), 3353 (br, ν_{N-H}), 2990 (br, ν_{C-H}), 2941 (br, ν_{C-H}), 2863 (br, ν_{C-H}), 2551 (br, ν_{B-H}), 2526 (br, ν_{B-H}), 2500 (br, ν_{B-H}), 1627 ($\nu_{N=C}$), 1491, 1449, 1396, 1303. ESI HRMS: m/z for $C_7H_{22}B_9NO$: calcd 257.2465 $[M + Na]^+$, obsd 257.2473 $[M + Na]^+$.

6b. Yield 54.5 mg (44%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.83 (s, 1H, NH), 4.53 (q, 2H, J = 7.0 Hz, OCH_2CH$_3$), 2.70 (q, 2H, J = 7.3 Hz, CH_2), 2.05 (s, 2H, CH_{carb}), 1.65 (t, 3H, J = 7.0 Hz, OCH$_2$CH_3), 1.32 (t, 3H, J = 7.3 Hz, CH_3), 2.0–0.1 (br s, 8H, BH), −0.4 (br s, 1H, BHB). ^{13}C NMR ($CDCl_3$, ppm): δ 181.4 (NH═C), 68.7 (OCH$_2$CH$_3$), 41.6 (CH$_{carb}$), 24.4 (CH$_2$), 14.1 (OCH$_2$$CH_3$), 9.7 ($CH_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.2 (d, J = 136 Hz, 2B), −15.7 (d, J = 133 Hz, 2B), −19.6 (d, J = 156 Hz, 1B), −22.0 (d, J = 159 Hz, 2B), −25.5 (s, 1B), −38.9 (d, J = 143 Hz, 1B). IR (film, cm^{-1}): 3353 (br, ν_{N-H}), 3210 (br, ν_{N-H}), 2950 (br, ν_{C-H}),

2922 (br, ν_{C-H}), 2852 (br, ν_{C-H}), 2579 (br, ν_{B-H}), 2550 (br, ν_{B-H}), 2523 (br, ν_{B-H}), 1623 ($\nu_{N=C}$), 1555, 1512, 1465, 1387, 1318, 1268. ESI HRMS: *m*/*z* for $C_7H_{22}B_9NO$: calcd 252.2907 $[M + NH_4]^+$, obsd 252.2919 $[M + NH_4]^+$.

4.7. Synthesis of 10-EtC(OiPr)═HN-7,8-$C_2B_9H_{11}$ (7a, 7b)

The procedure was analogous to that described for the synthesis of **5a** and **5b** using **2** (0.10 g, 0.53 mmol) and isopropanol (3 ml) to give white crystalline products **7a** and **7b**.

7a. Yield 57.7 mg (44%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.51 (s, 1H, N*H*), 4.70 (m, 1H, *J* = 6.0 Hz, OC*H*$(CH_3)_2$), 3.11 (q, 2H, *J* = 7.5 Hz, CH_2), 2.10 (s, 2H, CH_{carb}), 1.46 (s, 3H, OCH(C$H_3)_2$), 1.44 (s, 3H, OCH(C$H_3)_2$), 1.36 (t, 3H, *J* = 7.5 Hz, CH_3), 2.1–0.3 (br s, 8H, B*H*), −0.7 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 179.8 (NH═*C*), 75.1 (O*C*H$(CH_3)_2$), 41.9 (*C*H$_{carb}$), 25.4 (*C*H$_2$), 20.6 (OCH(*C*H$_3)_2$), 9.0 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.4 (d, *J* = 137 Hz, 2B), −15.0 (d, *J* = 131 Hz, 2B), −19.7 (d, *J* = 185 Hz, 1B), −21.4 (d, *J* = 158 Hz, 2B), −24.3 (s, 1B), −38.6 (d, *J* = 146 Hz, 1B). IR (film, cm^{-1}): 3345 (br, ν_{N-H}), 3228 (br, ν_{N-H}), 2985 (br, ν_{C-H}), 2940 (br, ν_{C-H}), 2926 (br, ν_{C-H}), 2545 (br, ν_{B-H}), 1618 ($\nu_{N=C}$), 1484, 1387, 1295. ESI HRMS: *m*/*z* for $C_8H_{24}B_9NO$: calcd 249.2857 $[M + H]^+$, obsd 249.2811 $[M + H]^+$.

7b. Yield 56.4 mg (43%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.79 (s, 1H, N*H*), 5.02 (m, 1H, *J* = 6.1 Hz, OC*H*$(CH_3)_2$), 2.71 (q, 2H, *J* = 7.2 Hz, CH_2), 2.04 (s, 2H, CH_{carb}), 1.59 (s, 3H, OCH(C$H_3)_2$), 1.58 (s, 3H, OCH(C$H_3)_2$), 1.32 (t, 3H, *J* = 7.2 Hz, CH_3), 2.0–0.1 (br s, 8H, B*H*), −0.3 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 180.4 (NH═*C*), 77.5 (O*C*H$(CH_3)_2$), 41.9 (*C*H$_{carb}$), 24.4 (*C*H$_2$), 22.0 (OCH(*C*H$_3)_2$), 10.4 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.3 (d, *J* = 137 Hz, 2B), −15.8 (d, *J* = 134 Hz, 2B), −19.8 (d, *J* = 166 Hz, 1B), −22.1 (d, *J* = 155 Hz, 2B), −25.5 (s, 1B), −39.0 (d, *J* = 150 Hz, 1B). IR (film, cm^{-1}): 3398 (br, ν_{N-H}), 3357 (br, ν_{N-H}), 2990 (br, ν_{C-H}), 2936 (br, ν_{C-H}), 2920 (br, ν_{C-H}), 2540 (br, ν_{B-H}), 1628 ($\nu_{N=C}$), 1490, 1461, 1388, 1255. ESI HRMS: *m*/*z* for $C_8H_{24}B_9NO$: calcd 265.3147 $[M + NH_4]^+$, obsd 265.3107 $[M + NH_4]^+$.

4.8. Synthesis of 10-EtC(OBu)═HN-7,8-$C_2B_9H_{11}$ (8a, 8b)

The procedure was analogous to that described for the synthesis of **5a** and **5b** using **2** (0.10 g, 0.53 mmol) and dry butanol (3 ml) to give white crystalline products **8a** and **8b**.

8a. Yield 62.4 mg (45%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.56 (s, 1H, N*H*), 4.10 (t, 2H, *J* = 6.2 Hz, OCH_2CH$_2$CH$_2$CH$_3$), 3.15 (q, 2H, *J* = 7.5 Hz, CH_2), 2.08 (s, 2H, CH_{carb}), 1.86 (m, 2H, *J* = 6.4 Hz, OCH$_2$CH_2CH$_2$CH$_3$), 1.48 (m, 2H, *J* = 7.5 Hz, OCH$_2$CH$_2$CH_2CH$_3$), 1.39 (t, 3H, *J* = 7.5 Hz, CH_3), 1.01 (t, 3H, *J* = 7.3 Hz, OCH$_2$CH$_2$CH$_2$CH_3), 2.1–0.2 (br s, 8H, B*H*), −0.7 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 179.9 (NH═*C*), 69.7 (O*C*H$_2$CH$_2$CH$_2$CH$_3$), 43.7 (*C*H$_{carb}$), 25.6 (OCH$_2$*C*H$_2$CH$_2$CH$_3$), 25.8 (*C*H$_2$), 18.8 (OCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.5 (OCH$_2$CH$_2$CH$_2$*C*H$_3$), 9.2 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.4 (d, *J* = 143 Hz, 2B), −15.1 (d, *J* = 134 Hz, 2B), −19.8 (d, *J* = 185 Hz, 1B), −21.5 (d, *J* = 157 Hz, 2B), −24.3 (s, 1B), −38.6 (d, *J* = 144 Hz, 1B). IR (film, cm^{-1}): 3350 (br, ν_{N-H}), 2967 (br, ν_{C-H}), 2941 (br, ν_{C-H}), 2876 (br, ν_{C-H}), 2559 (br, ν_{B-H}), 2534 (br, ν_{B-H}), 2499 (br, ν_{B-H}), 1626 ($\nu_{N=C}$), 1488, 1464, 1397, 1300. ESI HRMS: *m*/*z* for $C_9H_{26}B_9NO$: calcd 262.2988 $[M + H]^+$, obsd 262.2998 $[M + H]^+$.

8b. Yield 62.4 mg (45%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.81 (s, 1H, N*H*), 4.46 (t, 2H, *J* = 6.4 Hz, OCH_2CH$_2$CH$_2$CH$_3$), 2.72 (q, 2H, *J* = 7.2 Hz, CH_2), 2.04 (s, 2H, CH_{carb}), 1.96 (m, 2H, *J* = 7.0 Hz, OCH$_2$CH_2CH$_2$CH$_3$), 1.62 (m, 2H, *J* = 7.4 Hz, OCH$_2$CH$_2$CH_2CH$_3$), 1.31 (t, 3H, *J* = 7.2 Hz, CH_3), 1.05 (t, 3H, *J* = 7.4 Hz, OCH$_2$CH$_2$CH$_2$CH_3), 2.4–0.2 (br s, 8H, B*H*), −0.3 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 180.9 (NH═*C*), 72.5 (O*C*H$_2$CH$_2$CH$_2$CH$_3$), 43.0 (*C*H$_{carb}$), 30.8 (OCH$_2$*C*H$_2$CH$_2$CH$_3$), 25.0 (*C*H$_2$), 18.8 (OCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.6 (OCH$_2$CH$_2$CH$_2$*C*H$_3$), 8.9 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.3 (d, *J* = 125 Hz, 2B), −15.9 (d, *J* = 132 Hz, 2B), −19.7 (d, *J* = 152 Hz, 1B), −22.1 (d, *J* = 157 Hz, 2B), −25.5 (s, 1B), −39.1 (d, *J* = 143 Hz, 1B). IR (film, cm^{-1}): 3405 (br, ν_{N-H}), 3351 (br, ν_{N-H}), 2961 (br, ν_{C-H}), 2935 (br, ν_{C-H}), 2875 (br, ν_{C-H}), 2541 (br, ν_{B-H}), 1636 ($\nu_{N=C}$), 1499, 1457, 1382, 1242. ESI HRMS: *m*/*z* for $C_9H_{26}B_9NO$: calcd 285.2797 $[M + Na]^+$, obsd 285.2787 $[M + Na]^+$.

4.9. Synthesis of 10-EtC(SEt)═HN-7,8-$C_2B_9H_{11}$ (9a, 9b)

A solution of **2** (0.12 g, 0.64 mmol) in ethanethiol (4 ml) was stirred for 20 min at room temperature and the reaction mixture was evaporated to dryness in a vacuum. The *E*- and *Z*- isomers was separated by column chromatography on silica with CH_2Cl_2 as an eluent to give white crystalline products **9a** and **9b**.

9a. Yield 70.3 mg (44%). ^{1}H NMR (acetone-d_6, ppm): δ 9.08 (s, 1H, N*H*), 3.20 (q, 2H, *J* = 7.5 Hz, CH_2), 2.86 (q, 2H, *J* = 7.4 Hz, SCH_2CH$_3$), 1.99 (s, 2H, CH_{carb}), 1.47 (t, 3H, *J* = 7.5 Hz, CH_3), 1.26 (t, 3H, *J* = 7.4 Hz, SCH$_2$CH_3), 2.3–0.2 (br s, 8H, B*H*), −0.7 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 197.6 (NH═*C*), 42.9 (*C*H$_{carb}$), 31.2 (*C*H$_2$), 27.0 (S*C*H$_2$CH$_3$), 13.6 (SCH$_2$*C*H$_3$), 11.9 (*C*H$_3$). ^{11}B NMR (acetone-d_6, ppm): δ −10.1 (d, *J* = 140 Hz, 2B), −15.4 (d, *J* = 135 Hz, 2B), −19.4 (d, *J* = 181 Hz, 1B), −21.7 (d, *J* = 152 Hz, 2B), −24.2 (s, 1B), −38.7 (d, *J* = 142 Hz, 1B). IR (film, cm^{-1}): 3366 (br, ν_{N-H}), 2976 (br, ν_{C-H}), 2930 (br, ν_{C-H}), 2864 (br, ν_{C-H}), 2551 (br, ν_{B-H}), 1559 ($\nu_{N=C}$), 1448, 1419, 1387, 1264. ESI HRMS: *m*/*z* for $C_7H_{22}B_9NS$: calcd 268.2696 $[M + NH_4]^+$, obsd 268.2691 $[M + NH_4]^+$.

9b. Yield 68.7 mg (43%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.73 (s, 1H, N*H*), 3.24 (q, 2H, *J* = 7.4 Hz, CH_2), 2.88 (q, 2H, *J* = 6.2 Hz, SCH_2CH$_3$), 2.14 (s, 2H, CH_{carb}), 1.56 (t, 3H, *J* = 7.4 Hz, CH_3), 1.33 (t, 3H, *J* = 6.2 Hz, SCH$_2$CH_3), 1.9–0.1 (br s, 8H, B*H*), −0.5 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 196.2 (NH═*C*), 44.0 (*C*H$_{carb}$), 31.6 (*C*H$_2$), 27.2 (S*C*H$_2$CH$_3$), 13.6 (SCH$_2$*C*H$_3$), 10.1 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −10.0 (d, *J* = 132 Hz, 2B), −15.0 (d, *J* = 133 Hz, 2B), −19.0 (d, *J* = 174 Hz, 1B), −21.4 (d, *J* = 174 Hz, 2B), −24.5 (s, 1B), −38.5 (d, *J* = 150 Hz, 1B). IR (film, cm^{-1}): 3367 (br, ν_{N-H}), 2977 (br, ν_{C-H}), 2934 (br, ν_{C-H}), 2874 (br, ν_{C-H}), 2547 (br, ν_{B-H}), 1569 ($\nu_{N=C}$), 1457, 1422, 1399, 1373, 1263. ESI HRMS: *m*/*z* for $C_7H_{22}B_9NS$: calcd 251.2427 $[M + H]^+$, obsd 251.2426 $[M + H]^+$.

4.10. Synthesis of 10-EtC(SBu)═HN-7,8-$C_2B_9H_{11}$ (10a, 10b)

The procedure was analogous to that described for the synthesis of **9a** and **9b** using **2** (0.12 g, 0.64 mmol) and 1-butanethiol (4 ml) to give white crystalline products **10a** and **10b**.

10a. Yield 78.2 mg (44%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.40 (s, 1H, N*H*), 3.20 (q, 2H, J = 7.5 Hz, CH_2), 2.86 (t, 2H, J = 7.3 Hz, SCH_2CH$_2$CH$_2$CH$_3$), 2.09 (s, 2H, CH_{carb}), 1.72 (m, 2H, J = 7.3 Hz, SCH$_2$CH_2CH$_2$CH$_3$), 1.49 (m, 2H, J = 7.0 Hz, SCH$_2$CH$_2$CH_2CH$_3$), 1.47 (t, 3H, J = 7.5 Hz, CH_3), 0.98 (t, 3H, J = 7.3 Hz, SCH$_2$CH$_2$CH$_2$CH_3), 2.4–0.3 (br s, 8H, B*H*), −0.6 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 195.2 (NH=*C*), 43.9 (*C*H$_{carb}$), 30.3 (*C*H$_2$), 30.2 (S*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.5 (SCH$_2$*C*H$_2$CH$_2$CH$_3$), 21.9 (SCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.4 (SCH$_2$CH$_2$CH$_2$*C*H$_3$), 11.8 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −9.8 (d, J = 135 Hz, 2B), −15.0 (d, J = 134 Hz, 2B), −19.4 (d, J = 174 Hz, 1B), −21.4 (d, J = 154 Hz, 2B), −24.0 (s, 1B), −38.5 (d, J = 142 Hz, 1B). IR (film, cm^{-1}): 3352 (br, $\nu_{N–H}$), 2960 (br, $\nu_{C–H}$), 2933 (br, $\nu_{C–H}$), 2874 (br, $\nu_{C–H}$), 2547 (br, $\nu_{B–H}$), 1580 ($\nu_{N=C}$), 1464, 1417, 1382, 1258, 1229. ESI HRMS: m/z for $C_9H_{26}B_9NS$: calcd 296.3005 [M + NH$_4$]$^+$, obsd 296.3005 [M + NH$_4$]$^+$.

10b. Yield 78.2 mg (44%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.74 (s, 1H, N*H*), 3.18 (q, 2H, J = 7.4 Hz, CH_2), 2.87 (t, 2H, J = 6.6 Hz, SCH_2CH$_2$CH$_2$CH$_3$), 2.14 (s, 2H, CH_{carb}), 1.82 (m, 2H, J = 7.3 Hz, SCH$_2$CH_2CH$_2$CH$_3$), 1.58 (m, 2H, J = 7.2 Hz, SCH$_2$CH$_2$CH_2CH$_3$), 1.32 (t, 3H, J = 7.4 Hz, CH_3), 1.04 (t, 3H, J = 7.3 Hz, SCH$_2$CH$_2$CH$_2$CH_3), 2.2–0.3 (br s, 8H, B*H*), −0.5 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 196.2 (NH=*C*), 43.8 (*C*H$_{carb}$), 32.5 (S*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.6 (*C*H$_2$), 30.3 (SCH$_2$*C*H$_2$CH$_2$CH$_3$), 21.9 (SCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.5 (SCH$_2$CH$_2$CH$_2$*C*H$_3$), 10.0 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −9.8 (d, J = 135 Hz, 2B), −15.0 (d, J = 134 Hz, 2B), −19.4 (d, J = 174 Hz, 1B), −21.4 (d, J = 154 Hz, 2B), −24.5 (s, 1B), −38.5 (d, J = 142 Hz, 1B). IR (film, cm^{-1}): 3293 (br, $\nu_{N–H}$), 2958 (br, $\nu_{C–H}$), 2928 (br, $\nu_{C–H}$), 2856 (br, $\nu_{C–H}$), 2543 (br, $\nu_{B–H}$), 1567 ($\nu_{N=C}$), 1457, 1423, 1375. ESI HRMS: m/z for $C_9H_{26}B_9NS$: calcd 301.2560 [M + Na]$^+$, obsd 301.2559 [M + Na]$^+$.

4.11. Synthesis of 10-EtC(SHx)=HN-7,8-$C_2B_9H_{11}$ (11a, 11b)

The procedure was analogous to that described for the synthesis of **9a** and **9b** using **2** (0.12 g, 0.64 mmol) and 1-hexanethiol (4 ml) to give white crystalline products **11a** and **11b**.

11a. Yield 90.0 mg (46%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.42 (s, 1H, N*H*), 3.21 (q, 2H, J = 7.5 Hz, CH_2), 2.86 (t, 2H, J = 7.3 Hz, SCH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 2.11 (s, 2H, CH_{carb}), 1.73 (m, 2H, J = 7.5 Hz, SCH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 1.46 (t, 3H, J = 7.5 Hz, CH_3), 1.44 (m, 2H, J = 7.9 Hz, SCH$_2$CH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.33 (m, 4H, SCH$_2$CH$_2$CH$_2$CH_2CH_2CH$_3$), 0.92 (t, 3H, J = 6.8 Hz, SCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3), 2.1–0.3 (br s, 8H, B*H*), −0.5 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 195.1 (NH=*C*), 44.0 (*C*H$_{carb}$), 31.0 (S*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 30.5 (SCH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 30.3 (*C*H$_2$), 28.4 (SCH$_2$CH$_2$-*C*H$_2$CH$_2$CH$_2$CH$_3$), 26.6 (SCH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.3 (SCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.8 (SCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$), 11.8 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −9.8 (d, J = 135 Hz, 2B), −15.0 (d, J = 136 Hz, 2B), −19.4 (d, J = 175 Hz, 1B), −21.3 (d, J = 154 Hz, 2B), −24.0 (s, 1B), −38.5 (d, J = 145 Hz, 1B). IR (film, cm^{-1}): 3352 (br, $\nu_{N–H}$), 2956 (br, $\nu_{C–H}$), 2930 (br, $\nu_{C–H}$), 2858 (br, $\nu_{C–H}$), 2549 (br, $\nu_{B–H}$), 1577 ($\nu_{N=C}$), 1464, 1458, 1417, 1405, 1378. ESI HRMS: m/z for $C_{11}H_{30}B_9NS$: calcd 324.3321 [M + NH$_4$]$^+$, obsd 324.3320 [M + NH$_4$]$^+$.

11b. Yield 86.1 mg (44%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.73 (s, 1H, N*H*), 3.17 (q, 2H, J = 7.5 Hz, CH_2), 2.87 (t, 2H, J = 7.3 Hz, SCH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 2.14 (s, 2H, CH_{carb}), 1.86 (m, 2H, J = 7.5 Hz, SCH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.54 (m, 2H, J = 7.3 Hz, SCH$_2$CH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 1.38 (m, 4H, SCH$_2$CH$_2$CH$_2$CH_2-CH_2CH$_3$), 1.32 (t, 3H, J = 7.5 Hz, CH_3), 0.95 (t, 3H, J = 6.8 Hz, SCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3), 2.1–0.3 (br s, 8H, B*H*), −0.5 (br s, 1H, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): δ 196.1 (NH=*C*), 44.0 (*C*H$_{carb}$), 32.8 (S*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 31.6 (*C*H$_2$), 31.1 (SCH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 28.4 (SCH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 22.4 (SCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 13.9 (SCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$), 10.0 (*C*H$_3$). ^{11}B NMR ($CDCl_3$, ppm): δ −9.8 (d, J = 152 Hz, 2B), −15.0 (d, J = 139 Hz, 2B), −18.9 (d, J = 164 Hz, 1B), −21.4 (d, J = 145 Hz, 2B), −24.5 (s, 1B), −38.5 (d, J = 138 Hz, 1B). IR (film, cm^{-1}): 3297 (br, $\nu_{N–H}$), 2956 (br, $\nu_{C–H}$), 2926 (br, $\nu_{C–H}$), 2855 (br, $\nu_{C–H}$), 2543 (br, $\nu_{B–H}$), 1569 ($\nu_{N=C}$), 1457, 1423, 1378. ESI HRMS: m/z for $C_{11}H_{30}B_9NS$: calcd 329.2872 [M + Na]$^+$, obsd 329.2874 [M + Na]$^+$.

4.12. X-ray diffraction study

Single crystal X-ray studies was carried out with a SMART APEX II CCD diffractometer ($\lambda_{(Mo\text{-}K\alpha)}$ = 0.71073 Å, graphite monochromator, ω-scans) at 120 K. The structures were solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms.

Crystallographic data for 6a. $C_7H_{22}B_9NO$ is monoclinic, space group $P2_1/n$: a = 10.1766(13) Å, b = 10.2752(13) Å, c = 14.3502(18) Å, β = 107.658(3)°, V = 1429.9(3) Å^3, Z = 4, M = 233.54, d_{cryst} = 1.085 g cm^{-3}. wR_2 = 0.1630 calculated on F_{hkl}^2 for all 3071 independent reflections with $2\theta < 27.0°$, (GOF = 1.067, R = 0.0691 calculated on F_{hkl} for 2209 reflections with $I > 2\sigma(I)$). Crystallographic data (including structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 1855272.†

Crystallographic data for 7a. $C_8H_{24}B_9NO$ is monoclinic, space group $P2_1/c$: a = 11.7390(5) Å, b = 11.0686(5) Å, c = 11.8796(5) Å, β = 105.8520(10)°, V = 1484.87(11) Å^3, Z = 4, M = 247.57, d_{cryst} = 1.107 g cm^{-3}. wR_2 = 0.1248 calculated on F_{hkl}^2 for all 4246 independent reflections with $2\theta < 29.8°$, (GOF = 1.043, R = 0.0431 calculated on F_{hkl} for 3391 reflections with $I > 2\sigma(I)$). Crystallographic data (including structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 1855271.†

Crystallographic data for 8a. $C_9H_{26}B_9NO$ is monoclinic, space group $P2_1/c$: a = 12.9892(14) Å, b = 10.2156(11) Å, c = 12.6418(14) Å, β = 110.540(2)°, V = 1570.8(3) Å^3, Z = 4, M = 261.60, d_{cryst} = 1.106 g cm^{-3}. wR_2 = 0.1511 calculated on F_{hkl}^2 for all 4408 independent reflections with $2\theta < 29.6°$, (GOF = 1.018, R = 0.0527 calculated on F_{hkl} for 2934 reflections with $I > 2\sigma(I)$). Crystallographic data (including structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 1855270.†

Crystallographic data for 9b. $C_7H_{22}B_9NS$ is monoclinic, space group $P2_1/n$: a = 13.8859(8) Å, b = 7.9068(5) Å,

c = 14.3032(8) Å, β = 114.974(3)°, V = 1423.56(15)Å^3, Z = 4, M = 249.60, d_{cryst} = 1.165 g cm^{-3}. wR_2 = 0.1793 calculated on $F_{hkl}{}^2$ for all 3984 independent reflections with $2\theta < 29.7°$, (GOF = 1.047, R = 0.0691 calculated on F_{hkl} for 2946 reflections with $I > 2\sigma(I)$). Crystallographic data (including structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 1855273.†

Conflicts of interest

There are no conflicts to declare.

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