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A convenient cyanide-free "one-pot" synthesis of *nido*-Me_3N-7-$CB_{10}H_{12}$ and *nido*-7-$CB_{10}H_{13}^-$ †

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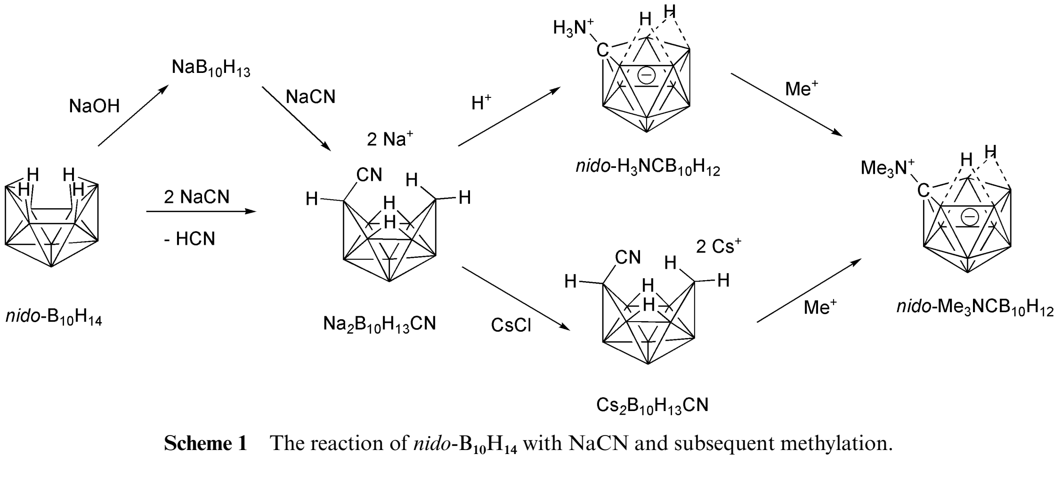
Reaction of *nido*-$^tBuH_2N$-7-$CB_{10}H_{12}$ with Na_2CO_3 and $(MeO)_2SO_2$ in THF results in mono-methylation to give *nido*-^tBuMeHN-7-$CB_{10}H_{12}$, whilst prolonged reaction at elevated temperatures results in a quantitative yield of the trimethyl derivative *nido*-Me_3N-7-$CB_{10}H_{12}$, as a result of metathesis of the *tert*-butyl group. The ^{11}B NMR spectrum of *nido*-^tBuMeHN-7-$CB_{10}H_{12}$ is explored as a function of pH, demonstrating exchange with *nido*-^tBuMeN-7-$CB_{10}H_{12}^-$. Reaction of $B_{10}H_{14}$ with CyNC gives *nido*-CyH_2N-7-$CB_{10}H_{12}$, which is methylated by Na_2CO_3 and $(MeO)_2SO_2$ in THF to give *nido*-$CyMe_2N$-7-$CB_{10}H_{12}$. Deprotonation of *nido*-Me_3N-7-$CB_{10}H_{12}$ and *nido*-$CyMe_2N$-7-$CB_{10}H_{12}$ yields Na[*nido*-Me_3N-7-$CB_{10}H_{11}$] and Na[*nido*-$CyMe_2N$-7-$CB_{10}H_{11}$] respectively. Both trialkyl(amino)carboranes can be converted to Na[*nido*-$CB_{10}H_{13}$], itself a precursor to the poorly coordinating anion *closo*-$CB_{11}H_{12}^-$. The molecular structures of *nido*-^tBuMeHN-7-$CB_{10}H_{12}$ and *nido*-$CyMe_2N$-7-$CB_{10}H_{12}$, determined by single crystal X-ray diffraction, are reported.

Introduction

By contrast with di-carbon carboranes, the chemistry of mono-carbon carboranes is much less widely explored. Monocarborane anions,[1] especially *closo*-$CB_{11}H_{12}^-$, and alkylated[2] or halogenated[3] derivatives, have received attention recently since they are among the best super-weakly coordinating anions available. These *closo*-clusters possess chemical, electrochemical and thermal stability; the anionic charge is highly delocalised, and the clusters have found application in cationic metallocene catalysis,[4] stabilisation of both coordinatively unsaturated cations[5] and of strong Brønsted acids[6] and the preparation of ionic liquids.[7]

We have been exploring the synthesis, reactivity and structural studies of high oxidation-state early transition metal complexes containing the *closo*-$MC_2B_9H_{11}$ unit.[8] By comparison with the wealth of chemistry of metalladicarboranes, the chemistry of metallamonocarboranes has been far less explored.[9,10] We were interested in the possibility of preparing high oxidation state early transition metal examples of *closo*-$MCB_{10}H_{11}$, containing the trianionic *nido*-7-$CB_{10}H_{11}^{3-}$ cluster as a ligand. First we needed to address the synthesis of a suitable *nido*-7-$CB_{10}H_{11+n}^{n-}$ precursor.

The literature synthetic routes to *closo*-$CB_{11}H_{12}^-$ and *nido*-7-$CB_{10}H_{13}^-$ are intimately intertwined. Knoth originally prepared *closo*-$CB_{11}H_{12}^-$ from *nido*-7-$CB_{10}H_{13}^-$ by thermolysis with or without $BH_3{\cdot}NR_3$.[11–13] The anion *nido*-7-$CB_{10}H_{13}^-$ is made by deamination of the zwitterion *nido*-7-Me_3N-7-$CB_{10}H_{13}$.[11,14,15] An alternative preparative route to $CB_{11}H_{12}^-$ was reported later by thermolysis of *nido*-7-Me_3N-7-$CB_{10}H_{13}$ with $BH_3{\cdot}NR_3$ to yield $Me_2NHCB_{11}H_{11}$ which is easily methylated then deaminated to form *closo*-$CB_{11}H_{12}^-$.[16,17] The zwitterion *nido*-7-Me_3N-7-$CB_{10}H_{13}$ has generally been synthesized from either acidification and methylation of $Na_2B_{10}H_{13}CN$ or methylation of $Cs_2B_{10}H_{13}CN$ (Scheme 1).[15–18] The salt $Na_2B_{10}H_{13}CN$ is formed from the reaction of $B_{10}H_{14}$ with NaCN followed by acid,[19] or by the reaction of $B_{10}H_{13}^-$ with NaCN, avoiding the need to use an excess of cyanide.[16] In these reactions the by-



Scheme 1 The reaction of *nido*-$B_{10}H_{14}$ with NaCN and subsequent methylation.

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† Electronic supplementary information (ESI) available: rotatable 3-D molecular structure diagrams of experimental structures of **3a** and **6b**, and of MP2-optimized geometries **I** to **IX** in CHIME format. See http://www.rsc.org/suppdata/dt/b2/b200930g/

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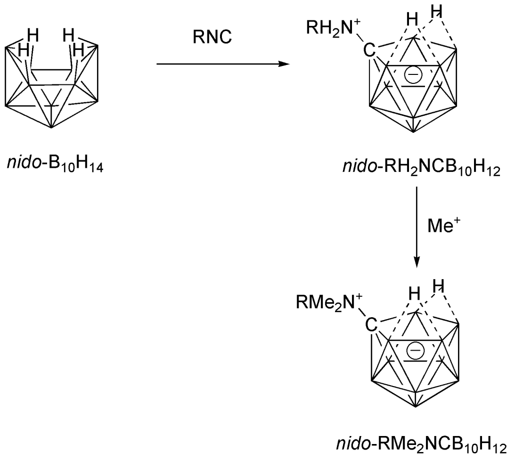
product HCN and the handling of NaCN pose hazards which are unacceptable in view of our departmental safety policy.

Gaines and Bridges demonstrated that the reaction of $Na_2B_{10}H_{12}\cdot 2THF$ with CH_2X_2 (X = Br, I) in THF affords $NaCB_{10}H_{13}$, however the low yield (25%) makes this route uneconomical,[20] and we have been unable to optimise the reaction. Michl and co-workers have recently reported that the cost-effective reaction of $Na_2B_{11}H_{13}$ (generated *in situ* from NaH and *nido*-$B_{11}H_{14}^-$, itself available[21] from $NaBH_4$ and $BF_3\cdot Et_2O$) with $CHCl_3$ produces $CB_{11}H_{12}^-$ in 42% yields.[22] Mixing sodium hydride with halocarbons is however not recommended.[23] The C-phenyl analogue, *closo*-$PhCB_{11}H_{11}^-$ has recently been synthesised[24] using a modification of Brellochs' reaction of PhCHO with $B_{10}H_{14}$.[25]

Therefore we were interested to explore alternative, and more importantly safer, methods for the synthesis of the zwitterion *nido*-$RMe_2NCB_{10}H_{12}$ (R = alkyl) as precursor to *closo*-$CB_{11}H_{12}^-$, *nido*-7-$CB_{10}H_{13}^-$,[11,14,15] metallamonocarboranes and 2-substituted derivatives[26] of $CB_{11}H_{12}^-$.

Monocarbon-carboranes *nido*-7-$RH_2NCB_{10}H_{12}$ (R = Me,[27] Et,[27] ${}^nPr$,[15,27] ${}^tBu$,[27,28] Bz,[12] Ph[29]) may be obtained from $B_{10}H_{14}$ and the respective isocyanide (Scheme 2), a reaction first reported by Todd and co-workers in 1966.[27] The exhaustive N-alkylation of *nido*-7-$RH_2NCB_{10}H_{12}$ to generate *nido*-7-$RMe_2NCB_{10}H_{12}$ has been achieved variously by: (i) reaction with NaH in THF then with $(MeO)_2SO_2$ (50% yield for R = Me);[27] (ii) reaction with NaOH as an aqueous solution, treatment with $(MeO)_2SO_2$ (high yield for R = ${}^nPr$);[15] (iii) reaction using $NaHCO_3$ with MeI in THF–H_2O (high yield for R = ${}^nPr$).[15] The parent carborane anion *nido*-7-$CB_{10}H_{13}^-$ is obtained by the deamination of *nido*-7-$RMe_2NCB_{10}H_{12}$ (R = Me, ${}^nPr$) with sodium metal or sodium hydride in refluxing THF.[14,15]



Scheme 2 The reaction of *nido*-$B_{10}H_{14}$ with isocyanides and subsequent methylation.

Thirty years ago, the cost of alkyl isocyanide RNC relative to NaCN or hazards involved in their preparation[30] were undoubtedly impediments to the widespread adoption of the isocyanide procedure. At present several isocyanides are commercially available, including *tert*-butylisocyanide and cyclohexylisocyanide (CyNC). Here we take advantage of these compounds and report a synthetically expedient, high yield (>95%) "one-pot" synthesis of *nido*-7-$RMe_2NCB_{10}H_{12}$ (R = Me, Cy) directly from $B_{10}H_{14}$ without the use of NaCN. We also describe the molecular structures of *nido*-7-$CyMe_2NCB_{10}H_{12}$ and the monomethyl derivative *nido*-7-${}^tBuMeHNCB_{10}H_{12}$.

Results and discussion

The reactions of decaborane, $B_{10}H_{14}$, with *tert*-butyl- and cyclohexyl-isocyanide (RNC, R = ${}^tBu$, Cy) were performed according to the modified procedure reported by Stone and co-workers,[28] giving *nido*-7-$RH_2NCB_{10}H_{12}$ (R = ${}^tBu$ **1a**, Cy **1b**). The ammonium moiety in these zwitterions is readily deprotonated yielding the anions *nido*-7-$RHNCB_{10}H_{12}^-$ (R = ${}^tBu$ **2a**, Cy **2b**). Since the cyclohexyl derivatives **1b** and **2b** were not known prior to this study, their NMR data are reported here.

As previously mentioned, a variety of procedures are available for the conversion of RH_2N– to a RMe_2H– group. We find that **1a** and **1b** do not react cleanly with either MeI or $(MeO)_2SO_2$ in aqueous basic conditions, these conditions consistently result in the formation of significant quantities of boric acid (${}^{11}B$ NMR) resulting from degradation of the carborane framework. Following these observations we felt it necessary to readdress the synthesis of $RMe_2NCB_{10}H_{12}$ by methylation of **1a** and **1b**.

Here we find that whilst Na_2CO_3 is not sufficiently basic to effect complete deprotonation of the amine it *does* act as an effective buffer during alkylation, allowing a "one-pot" synthesis of dialkyl- (${}^tBuMeHNCB_{10}H_{12}$) (**3a**) and trialkylammonio- ($Me_3NCB_{10}H_{12}$ **5a** and $CyMe_2NCB_{10}H_{12}$ **6b**) charge-compensated mono-carboranes depending on conditions.

At ambient or moderate (< 50 °C) temperature, treatment of tetrahydrofuran solutions of **1a** with $(MeO)_2SO_2$ and Na_2CO_3 affords *only* the zwitterionic mono-methylated derivative, ${}^tBuMeHNCB_{10}H_{12}$, **3a** (Scheme 3).

Our initial attempts to characterise **3a** were complicated by the non-reproducible nature of the ${}^{11}B$ NMR spectrum, similar to spectra (a)–(c) in Fig. 1. Since the related butyl derivative **1a** is a precursor to metallacarboranes,[10,31] we explored the reaction of **3a** with $Ta(NMe_2)_5$ and obtained a ${}^{11}B$ NMR spectrum, (e), confusingly similar to that of *nido*-$CB_{10}H_{13}^-$.[32]

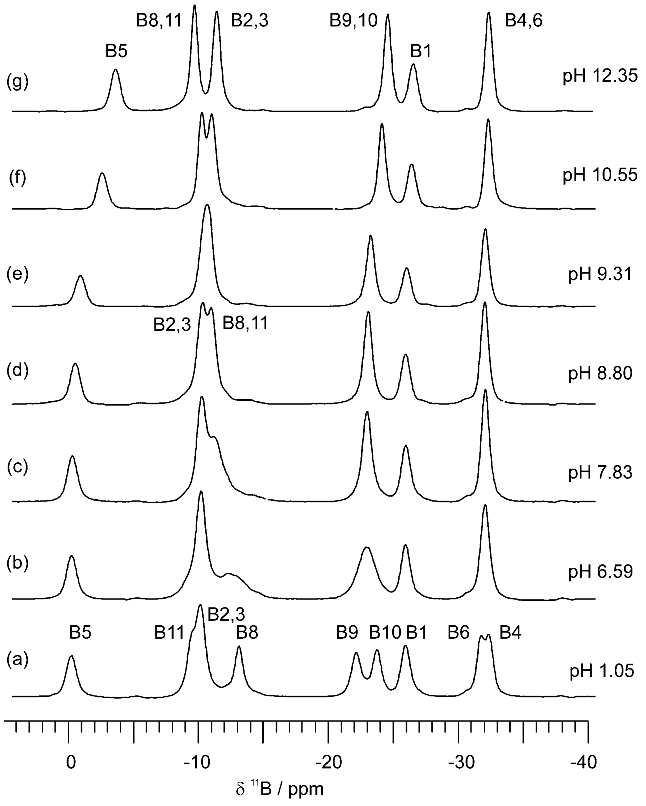
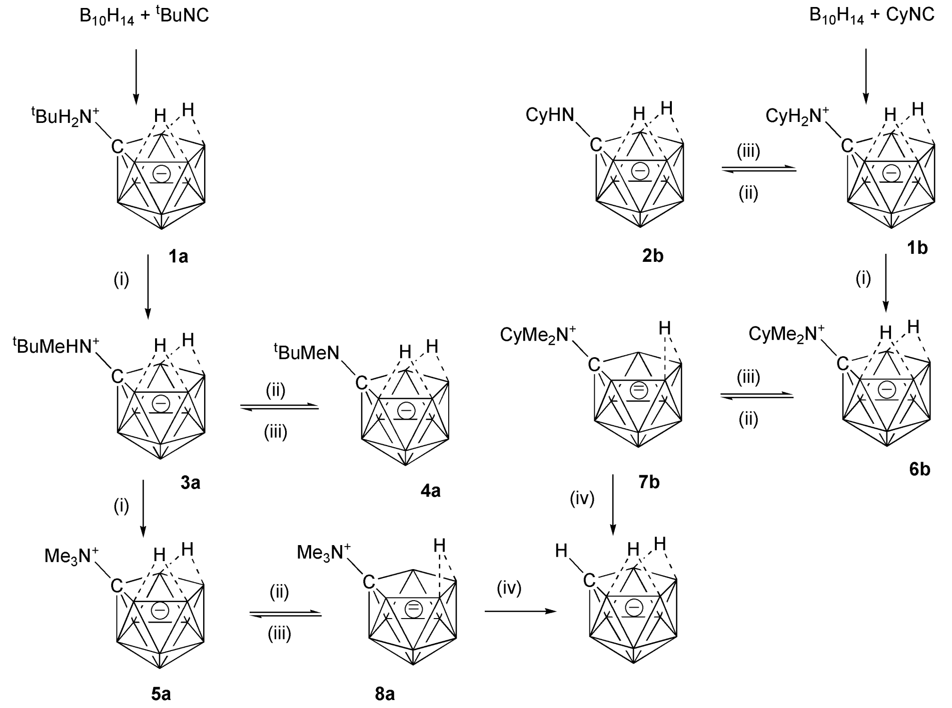


Fig. 1 Selected 96.2 MHz ${}^{11}B$ NMR spectra of ${}^tBuMeHNCB_{10}H_{12}$ **3a**, in equilibrium with ${}^tBuMeNCB_{10}H_{12}^-$ **4a** recorded as a function of pH.

In order to understand this behaviour, we explored the ${}^{11}B$ NMR spectra as a function of pH (Fig. 1). In acidic solution, the only species present is neutral **3a**, which contains a chiral ${}^tBuMeHN$ group and hence has C_1 symmetry. The CB_{10} cage thus contains ten inequivalent boron atoms, and the ${}^{11}B$ NMR spectrum at pH 1.05 shows nine lines, with two lines accidentally equivalent, and close to a third. Under these



Scheme 3 The reactions described in this work. Reagents: (i) $(MeO)_2SO_2$–Na_2CO_3 in THF, (ii) NaOH in CH_3CN, (iii) HCl, (iv) Na.

conditions, the ^{1}H NMR spectrum shows two B–H–B bridge resonances, and the N–Me protons appear as a doublet due to coupling to the N–H.

Deprotonation of the ammonium nitrogen of **3a** gives the stable mono-anion, $[^t\text{BuMeNCB}_{10}\text{H}_{12}]^-$ **4a**, and the completely different ^{11}B NMR spectrum of **3a** at pH 6.59 can be accounted for by rapid reversible deprotonation of the ammonium nitrogen, exchanging **3a** with the small amount (0.03% at pH 6.59) of **4a** present. Since the re-protonation can produce the enantiomer of **3a**, an apparent molecular mirror plane is introduced, exchanging the two enantiomers of **3a**. The mirror plane contains cage atoms C7, B5 and B1 and relates B8,11, B9,10, B2,3, and B4,6. The chemical shifts at pH 6.59 are appropriate averages of those at pH 1.05. Whilst the two enantiomers of **3a** are indistinguishable by NMR, rapid inter-conversion of the enantiomers is observable by the introduction of a pseudo-mirror plane. At pH 6.59, the ^{1}H NMR spectrum shows only one B–H–B resonance of relative integral 2, and the N–Me signal appears as a singlet. In solutions more basic than pH 6.59, the zwitterion **3a** is progressively deprotonated to **4a**, and the spectra between pH 6.59 and 12.35 reflect the weighted average chemical shifts of **3a** and **4a**.

One feature of **3a**/**4a** is that the resonances assigned to B2,3 and B8,11 move in opposite directions on deprotonation, such that at pH 9.31 the two resonances are co-incident (spectrum e). Such a pH is readily achieved by the reaction of **3a** with $Ta(NMe_2)_5$. At pH 13.69 (not shown) the spectrum obtained is that of pure anion **4a**. The greatest change in chemical shift on deprotonation is seen in the ^{11}B NMR resonance assigned to B5, the atom antipodal to the carbon atom and site of substitution. Fitting the pH dependence of this chemical shift gives the pK_a of **3a** as 10.12.

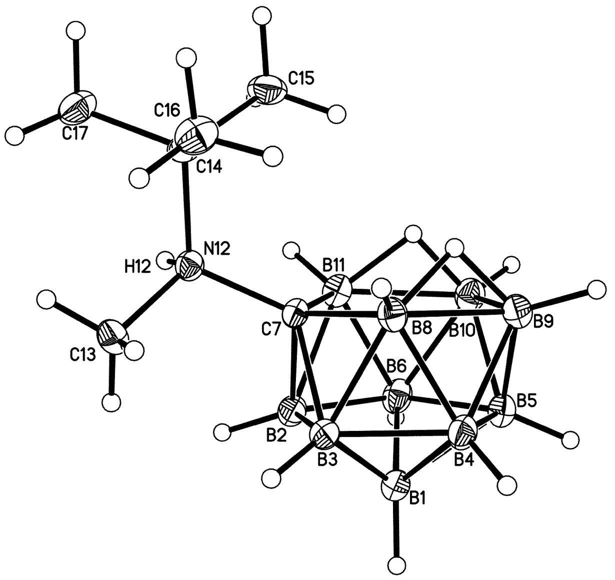


Fig. 2 The molecular structure of $^t\text{BuMeHNCB}_{10}\text{H}_{12}$ **3a**, showing the adopted cage numbering scheme in 50% probability ellipsoids, with hydrogen atoms as arbitrary sized spheres.

The molecular structure of **3a** has been confirmed by single crystal X-ray diffraction and appears in Fig. 2, with selected bond lengths and angles in Table 1. A *nido*-CB_{10} cage with two B–H–B bridges on the open face is substituted by a NHMe^{t}Bu group on the carbon atom, in a fashion which is grossly similar to the structure of **1a**.[28] Given the zwitterionic nature of **3a**, one might expect some interaction between the two charged parts of the molecule, and there is a intermolecular N–H ··· H–B dihydrogen bond[33] between the ammonium hydrogen and the hydrogen atom on B5 with a H ··· H contact distance of 2.412 Å. When the B5–H5 and N12–H12 distances are normalised to compensate for the systematic shortening of hydrogen distances in X-ray structures, the geometry presented in Fig. 3 is obtained, and is characteristic of such B–H ···

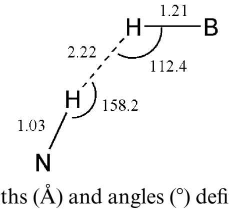


Fig. 3 The bond lengths (Å) and angles (°) defining the N–H ··· H–B dihydrogen bond between two molecules of **3a**, calculated using normalised hydrogen atom positions.

Table 1 Selected bond lengths (Å) and angles (°) for experimentally determined geometries of ^{t}BuH$_2$NCB$_{10}$H$_{12}$ **1a**,[28] ^{t}BuMeHNCB$_{10}$H$_{12}$ **3a** and CyMe$_2$NCB$_{10}$H$_{12}$ **6b** and the MP2-optimized geometry (**III**) of Me$_3$NCB$_{10}$H$_{12}$ **5a**

	1a	**3a**	**6b**	**5a/III**
N(12)–C(14)	1.562(2)	1.577(2)	1.562(2)	1.501
N(12)–C(13)		1.503(2)	1.509(3)	1.502
N(12)–C(20)			1.513(3)	1.502
N(12)–H(12)	0.93(2)	0.88(2)		
N(12)–C(7)	1.508(2)	1.531(2)	1.550(2)	1.527
C(7)–B(8)	1.653(3)	1.658(2)	1.662(3)	1.658
C(7)–B(11)	1.655(3)	1.659(2)	1.667(3)	1.658
B(8)–B(9)	1.854(3)	1.871(2)	1.875(4)	1.837
B(9)–B(10)	1.881(3)	1.901(2)	1.892(4)	1.896
B(10)–B(11)	1.856(3)	1.849(2)	1.865(4)	1.837
N(12)–C(7)–B(8)	118.2(1)	123.20(11)	118.7(2)	116.6
N(12)–C(7)–B(11)	120.1(1)	113.51(10)	117.8(2)	116.6
B(8)–C(7)–B(11)	112.3(1)	111.47(10)	110.9(2)	110.6
C(7)–B(8)–B(9)	109.6(1)	110.12(11)	110.7(2)	111.1
B(8)–B(9)–B(10)	103.8(1)	103.33(10)	103.4(2)	103.1
B(11)–B(10)–B(9)	103.2(1)	102.78(10)	102.9(2)	103.1
C(7)–B(11)–B(10)	110.1(1)	111.39(10)	111.3(2)	111.1
C(13)–N(12)–C(7)	122.1(1)	113.25(10)	110.1(2)	112.8
C(13)–N(12)–C(14)		112.36(10)	107.96(14)	108.4
C(7)–N(12)–C(14)		117.43(10)	110.30(14)	107.1
C(13)–N(12)–C(20)			106.6(2)	107.1
C(20)–N(12)–C(14)			109.8(2)	108.4
C(20)–N(12)–C(7)			112.0(2)	112.8

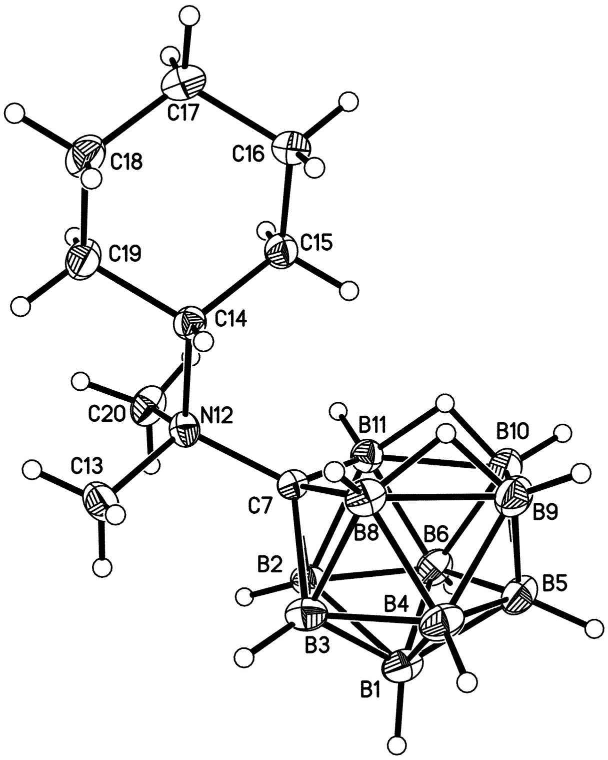


Fig. 4 The molecular structure of CyMe$_2$NCB$_{10}$H$_{12}$ **6b**, showing 50% probability ellipsoids, with hydrogen atoms as arbitrary sized spheres.

H–N structures, albeit with a long H ··· H distance. A similar, though considerably shorter (2.117 Å), dihydrogen bond appears in the structure of **1a**, using a B–H on the open face.

The reaction of ^{t}BuH$_2$NCB$_{10}$H$_{12}$ **1a** with NaH/MeI at ambient temperature is reported to give ^{t}BuMe$_2$NCB$_{10}$H$_{12}$.[10,27] Using Na$_2$CO$_3$ and (MeO)$_2$SO$_2$ at ambient temperatures, even in the presence of a large excess of dimethylsulfate we find no conclusive spectroscopic evidence for the formation of ^{t}BuMe$_2$NCB$_{10}$H$_{12}$. In contrast, at elevated temperatures **1a** appears to be converted quantitatively to Me$_3$NCB$_{10}$H$_{12}$ **5a** whereas under the same conditions **1b** is readily converted to CyMe$_2$NCB$_{10}$H$_{12}$ **6b**. We find evidence for a carborane intermediate along with trimethyl compound **5a** in the ^{11}B NMR spectrum of the reaction mixture at early stages of the reaction at elevated temperatures. The intermediate has ^{11}B NMR resonances at δ 1.6, −8.8, −12.2, −22.4, −26.1 and −30.3 ppm and is tentatively identified as ^{t}BuMe$_2$NCB$_{10}$H$_{12}$ based on calculated ^{11}B NMR data generated from its MP2-optimized geometry (**VII**). These observations may be rationalised by considering Me$_3$C$^+$ as a viable leaving group, whilst Cy$^+$ is not. A similar reaction is observed in the methylation of the isoelectronic tricarborane, 7-^{t}BuH$_2$N-7,8,9-C$_3$B$_8$H$_{10}$, with NaH and excess methyl iodide in glyme to yield 7-Me$_3$N-7,8,9-C$_3$B$_8$H$_{10}$.[34] All spectroscopic data for **5a** were identical to those previously reported.[32,35] Considering spectroscopic data for **6b**, the ^{1}H NMR spectrum confirms retention of the cyclohexyl group and addition of two methyl substituents, whilst the ^{11}B NMR spectrum is in accord with a *nido*-CB$_{10}$ framework and a mirror plane, consistent with conversion to a R′R$_2$N– substituent. The formulation of **6b** was confirmed by a single crystal X-ray diffraction study, and the molecular structure appears in Fig. 4 with selected bond lengths and angles in Table 1.

Now that the C-mono-, di- and tri-alkylamino zwitterions of 7-CB$_{10}$H$_{12}^-$ have been structurally characterised (as **1a**, **3a**, and **6b** respectively) it is clear that the effect of different amino groups on the cage framework is very small (Table 1). The anion of **1a** in the form of the NEt$_3$Bz$^+$ salt was also crystallographically characterised[28] and again shows only slight geometrical changes in the cage framework. The cage framework in the optimised geometry (**III**) of the trimethyl(amino) carborane **5a** at the MP2/6-31G* level of theory is in excellent agreement with the cage frameworks in the crystallographically determined geometries. The misfit values between the optimised geometry **III** and the experimental geometries of **1a**, **3a** and **6b** are only 0.0132, 0.0128 and 0.0167 Å respectively for the heavy cage atoms.

Calculated ^{11}B NMR chemical shifts (at the GIAO-B3LYP/6-311G* level) generated from the optimised geometries of **III** and of the parent *nido*-7-CB$_{10}$H$_{13}^-$ (**I**) are in good agreement with their respective experimental NMR shifts. The slightly worse correlation for **5a** with **III** can be attributed to the rotation of the trimethyl(ammonium) group in solution, since the calculated values represent the *static* geometry.

Deprotonation of the trialkyl derivatives **5a** and **6b** by NaOH in acetonitrile gave the air-sensitive anions Me$_3$NCB$_{10}$H$_{11}^-$ **8a** and CyMe$_2$NCB$_{10}$H$_{11}^-$ **7b**. Given that **5a** is well-known, it is surprising that no characterisation data have been reported previously for the mono-anion **8a**. There are two reports of Na[Me$_3$NCB$_{10}$H$_{11}$] being present as an intermediate in the reaction of **5a** and sodium hydride.[11,35] One is in the formation of *closo*-Me$_3$NCB$_{10}$H$_{10}$ and the other in the formation of *closo*-CB$_{10}$H$_{11}^-$ and the *nido*-8-HO-7-CB$_{10}$H$_{12}^-$ anions. Furthermore, it is logical that the mono-anion would be an intermediate in the deamination of *nido*-7-Me$_3$N-7-CB$_{10}$H$_{12}$ by sodium metal[11,14,15] and in the double deprotonation of *nido*-7-Me$_3$N-7-CB$_{10}$H$_{12}$ by NaH,[14] butyllithium,[26] and (Me$_2$N)$_2$C=NH.[36] Reported ^{11}B NMR chemical shifts for the salt [(Me$_2$N)$_2$C=NH$_2^+$]$_2$[*nido*-7-Me$_3$N-7-CB$_{10}$H$_{10}$]$^{2-}$ are identical to our data for Me$_3$NCB$_{10}$H$_{11}^-$ **8a**. Addition of iodine to a wet acetonitrile solution of **8a** gave *closo*-Me$_3$NCB$_{10}$H$_{10}$, whose ^{11}B NMR data are in agreement with reported values.[36] This implies that the formation of the di-anion [*nido*-7-Me$_3$N-7-CB$_{10}$H$_{10}$]$^{2-}$ is not required prior to the conversion of **5a** to *closo*-Me$_3$NCB$_{10}$H$_{10}$ as proposed previously.[14,36]

As we have yet to isolate salts of the air-sensitive anions **7b** and **8a** suitable for X-ray crystallography, geometry optimisations of the trimethyl anion **8a** were carried out at the MP2/6-31G* level. Two minima were located for **8a**, with a hydrogen bridging B8–B9 (**IV**) and B9–B10 (**V**) respectively. The latter minimum is 5.4 kcal mol^{-1} lower than the former and is shown in Fig. 5 along with selected bond lengths and angles. Since very

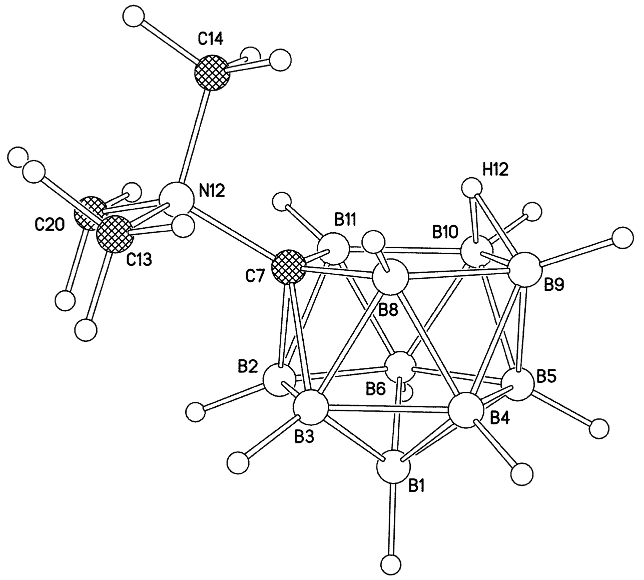


Fig. 5 Optimised geometry (MP2/6-31G*) **V** of the anion Me$_3$-NCB$_{10}$H$_{11}$$^-$ **8a** with near C_s symmetry, corresponding to the lower of two energy minima. Selected bond lengths (Å) and angles (°); C7–B8/B11 1.641, B8–B9/B10–B11 1.767, B9–B10 1.870, C7–N12 1.538, N12–C13/C20 1.495, N12–C14 1.496, B9/B10–H12 1.324; N12–C7–B8/B11 115.4, B8–C7–B11 117.3, C7–B8–B9/C7–B11–B10 106.0, B8–B9–B10/B11–B10–B9 105.3, C7–N12–C13/C20 113.2, C7–N12–C14 105.4.

good fits were found between the experimental and optimised geometries of the alkylated zwitterions here, the MP2-optimized geometry (**V**) shown in the figure is very likely to be found experimentally for **8a**. Confirmation of this geometry is shown by the excellent correlation between the calculated ^{11}B chemical shifts generated from the optimised geometry **V** and those observed experimentally for **8a**.

Double deprotonation of **1a** has been reported to give a di-anion *nido*-7-^{t}BuHN-7-CB$_{10}$H$_{11}$$^{2-}$ whose ^{11}B NMR chemical shifts (−12.7, −17.4, −21.5 and −39.2 ppm)[28] are similar to **8a**, supporting the suggested formulation. Calculations on *nido*-7-^{t}BuHN-7-CB$_{10}$H$_{11}$$^{2-}$ with the hydrogen bridging B9–B10 (**VIII**) and B8–B9 (**IX**) suggest that the bridging hydrogen in the di-anion is likely to be at B9–B10 rather than at B8–B9, the symmetrical geometry (**VIII**) is the more stable of the two by *ca.* 3 kcal mol^{-1} at the MP2/6-31G* level. The carborane di-anion 7-Me$_3$N-7-CB$_{10}$H$_{10}$$^{2-}$ in the salt [(Me$_2$N)$_2$-C=NH$_2$]$_2$$^+$[*nido*-7-Me$_3$N-7-CB$_{10}H_{10}$]$^{2-}$ is in fact the mono-anion 7-Me$_3$N-7-CB$_{10}$H$_{11}$$^-$ **8a** based on identical ^{11}B NMR chemical shifts and the salt is likely to have the formula [(Me$_2$N)$_2$-C=NH]$_2$H$^+$[*nido*-7-Me$_3$N-7-CB$_{10}$H$_{11}$]$^-$. Calculated ^{11}B NMR chemical shifts generated from the MP2-optimized geometry (**VI**) of the di-anion 7-Me$_3$N-7-CB$_{10}$H$_{10}$$^{2-}$ are not in agreement with reported values for the salt.

The trialkyl derivatives Me$_3$NCB$_{10}$H$_{12}$ **5a** and CyMe$_2$NCB$_{10}$-H$_{12}$ **6b** are readily converted to NaCB$_{10}$H$_{13}$ (presumably *via* their anions **8a** and **7b** respectively) by treatment with Na in THF in accordance with the protocol described in the literature.[11] We propose that for the synthesis of NaCB$_{10}$H$_{13}$, the route using cyclohexylisocyanide is preferable due to its lower cost.

In conclusion, the preparation of Me$_3$NCB$_{10}$H$_{12}$ and Cy-Me$_2$NCB$_{10}$H$_{12}$, precursors in the syntheses of *nido*-CB$_{10}$H$_{13}$$^-$ and *closo*-CB$_{11}$H$_{12}$$^-$, may be achieved *without* the use of NaCN, in high yield and at comparable cost. These results are of particular relevance to the continued development of both carborane and metallacarborane chemistry.

Experimental

All manipulations of air- and moisture-sensitive compounds were performed on a conventional vacuum/nitrogen line using standard Schlenk and cannula techniques or in a nitrogen filled glove box. When required, solvents were dried by prolonged reflux over the appropriate drying agent, prior to distillation and deoxygenation by freeze–pump–thaw processes where appropriate. NMR solvents were vacuum-distilled from suitable drying agents and stored under a dry nitrogen atmosphere. ^{t}BuH$_2$NCB$_{10}$H$_{12}$ **1a** was prepared according to Stone.[28] Elemental analyses were performed by the micro-analytical service within this department. NMR spectra were recorded at ambient temperature in d_3-acetonitrile on the following instruments: Varian Unity-300 and Varian Inova 500. 2D ^{11}B–^{11}B COSY, ^{1}H{^{11}B} and ^{1}H{^{11}B selective} spectra were recorded on the Unity. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^{1}H NMR spectra were referenced to residual protio impurity in the solvent (D$_2$HCCN, 1.95 ppm). ^{13}C NMR spectra were referenced to the solvent resonance (d_3-D$_3$CCN, 118.0 ppm). ^{11}B NMR were referenced externally to Et$_2$O·BF$_3$, δ = 0.0 ppm. Both ^{t}BuNC and CyNC were purchased commercially (Aldrich) and used as received.

Syntheses

CyH$_2$NCB$_{10}$H$_{12}$ 1b. This was prepared using B$_{10}$H$_{14}$ (0.50 g, 4.1 mmol) and CyNC (0.50 g, 4.5 mmol) according to the procedure reported by Stone for **1a**.[28] Yield 0.87 g, 92%. (Found C 37.34; H 10.84; N 5.59. C$_7$H$_{25}$B$_{10}$N requires C 36.34; H 10.89; N 6.05%); δ_H ^{1}H{^{11}B}, −3.84 (m, 2H, μ-BH), 0.25 (s, 2H, BH 4,6), 0.95 (m, 1H, CH$_2$), 1.09 (m, 7H, CH$_2$, BH 1,9,10), 1.44 (m, 1H, CH$_2$), 1.61 (m, 2H, CH$_2$), 1.75 (m, 2H, CH$_2$), 1.93 (s, 2H, BH 2,3), 2.00 (s, 2H, BH 8,11), 2.15 (s, 1H, BH 5), 3.11 (m, 1H, ipso), 6.19 (br s, 2H, NH); δ_C 72.3 (cage C), 59.5 (C$_1$), 34.1 (C$_{2,6}$), 26.4 (C$_4$) 25.3 (C$_{3,5}$); δ_B −1.0 (B5), −9.6 (B2,3), −12.2 (B8,11), −22.5 (B9,10), −26.1 (B1), −32.3 (B4,6).

^{t}BuMeHNCB$_{10}$H$_{12}$ 3a. A tetrahydrofuran suspension (50 ml) containing Na$_2$CO$_3$ (1.00 g), **1a** (0.50 g, 2.4 mmol) and (MeO)$_2$SO$_2$ (0.30 g, 0.23 ml, 2.4 mmol) was brought to 50 °C and stirred until the reaction was complete as determined by ^{11}B NMR (like spectrum (c) in Fig. 1, about 12 h). The suspension was filtered and the residue washed with acetonitrile (2 × 25 ml). The solvent was removed from the combined filtrates under reduced pressure to afford a white solid. The solid was triturated in diethyl ether (15 ml) and cooled (−30 °C) to give a bright white precipitate that was isolated by filtration and dried *in vacuo* to afford spectroscopically pure **3a**. Yield 0.38 g, 72%. (Found C 32.70; H 11.69; N 6.56. C$_6$H$_{25}$B$_{10}$N requires C 32.85; H 11.49; N 6.38%). Spectroscopic data (acid solution, pH < 6): δ_H ^{1}H{^{11}B}, −3.82 (m, 1H, μ-BH), −3.65 (m, 1H, μ-BH), 0.50 (s, 2H, BH 4,6), 1.26 (s, 2H, BH 1,10), 1.31 (s, 1H, BH 9), 1.46 (s, 9H, CH$_3$), 2.17 (s, 1H, BH 11), 2.33 (s, 2H, BH 2,3), 2.41 (s, 2H, BH 5,8), 2.73 (d, 3H, CH$_3$, ^3J(HH) = 7 Hz); δ_C 73.9 (br, cage C), 71.4 (*C*Me$_3$), 39.6 (CH$_3$), 26.6 (C*C*H$_3$); δ_B 0.1 (B5), −9.4 (B11), −10.0 (B2,3), −12.9 (B8), −21.8 (B9), −23.5 (B10), −25.7 (B1), −31.6 (B6), −32.1 (B4); (neutral solution, pH *ca.* 7.0): δ_H ^{1}H-{^{11}B}, −3.75 (m, 2H, μ-BH), 0.47 (s, 2H, BH 4,6), 1.23 (s, 3H, BH 1,9,10), 1.43 (s, 9H, CH$_3$), 2.22 (s, 2H, BH 2,3), 2.32 (s, 2H, BH 8,11), 2.40 (s, 1H, BH 5), 2.69 (s, 3H, CH$_3$); δ_B 0.0 (B5), −10.1 (B2,3), −11.4 (B8,11), −22.9 (B9,10), −25.9 (B1), −32.1 (B4,6); (buffered, pH *ca* 9.3): δ_H (^{1}H-{^{11}B}), −3.81 (m, 2H, μ-BH), 0.44 (s, 2H, BH 4,6), 1.18 (s, 3H, BH 1,9,10), 1.38 (s, 9H, CH$_3$), 2.17 (s, 2H, BH 2,3), 2.31 (s, 3H, BH 5,8,11), 2.57 (s, 3H, CH$_3$); δ_B −0.8 (B5), −10.8 (B2,3,8,11), −23.7 (B9,10), −26.1 (B1), −32.2 (B4,6).

"One-pot" synthesis of Me$_3$NCB$_{10}$H$_{12}$ 5a. A cooled (water bath) solution of B$_{10}$H$_{14}$ (5.00 g, 41 mmol) in benzene (100 ml) was treated dropwise with ^{t}BuNC (3.70 g, 4.62 ml, 45 mmol) and left to stir for 1–2 h and then brought to reflux until all the decaborane was consumed as determined by ^{11}B NMR. All volatiles were removed under reduced pressure. The crude solids were dissolved in THF (50 ml) and treated with Na$_2$CO$_3$ (5.0 g) and (MeO)$_2$SO$_2$ (15.51 g, 11.64 ml, 123 mmol). The mixture was brought to reflux and heating continued for 7–8 d. After this time, the solution was filtered whilst warm and the residue washed with warm acetonitrile (2 × 25 ml). The filtrates were combined and volatiles removed under reduced pressure. The resulting solid was washed with cold (0 °C) diethyl ether (2 × 25 ml) to afford Me$_3$NCB$_{10}$H$_{12}$ **5a** as a spectroscopically pure white powder. Yield 7.24 g, 92 %. Spectroscopic properties are in agreement with the literature; δ_{H} ^{1}H-{^{11}B} −3.50 (s, 2H, μ-BH), 0.47 (m, 2H, BH 4,6), 1.20 (s, 1H, BH 1), 1.30 (s, 2H, BH 9,10), 2.26 (s, 2H, BH 8,11), 2.37 (s, 2H, BH 2,3), 2.51 (s, 1H, BH 5), 3.12 (s, 9H, NCH$_3$); δ_{B} 1.0 (B5), −9.7 (B2,3), −13.8 (B8,11), −22.4 (B9,10), −26.1 (B1), −32.9 (B4,6).

CAUTION! On a large scale (> 10 g) we noted this reaction can become violently exothermic following a short induction period of 30–45 s. For large scale preparations we recommend larger solvent volumes and slower addition (> 2 h) of isocyanide for more efficient cooling.

“One-pot” synthesis of CyMe$_2$NCB$_{10}$H$_{12}$ 6b. Using the method described above for **5a**, with CyNC (5.00 g, 45 mmol) affords **6b**. Yield 10.27 g, 96%. (Found C 42.02; H 11.14; N 4.81. C$_9$H$_{29}$B$_{10}$N requires C 41.67; H 11.27; N 5.40%); δ_{H} ^{1}H-{^{11}B}, −3.72 (m, 2H, μ-BH), 0.52 (s, 2H, BH 4,6), 1.04–2.07 (m, 9H, CH$_2$, BH 1,9,10), 2.33 (s, 2H, BH 8,11), 2.39 (s, 2H, BH 2,3), 2.54 (s, 1H, BH 5), 2.96 (s, 6H, CH$_3$), 3.59 (m, 1H, CH$_2$); δ_{C} 85.0 (cage C), 77.5 (CH$_3$), 51.9 (C$_1$), 28.6 (C$_{2,6}$) 25.5 (C$_4$) 24.9 (C$_{3,5}$); δ_{B} 1.3 (B5), −9.3 (B2,3), −13.0 (B8,11), −22.5 (B9,10), −25.4 (B1), −32.0 (B4,6).

Mono-anions. The following mono-anions were prepared by agitation of wet d_3-acetonitrile solutions of neutral precursor in the presence of NaOH.

Na[BuMeNCB$_{10}$H$_{12}$] 4a. δ_{H} (^{1}H-{^{11}B}), −3.90 (s, 2H, μ-BH), 0.36 (m, 2H, BH 4,6), 1.07 (s, 3H, BH 1,9,10), 1.23 (s, 9H, CCH$_3$), 2.04 (s, 2H, BH 2,3), 2.16 (s, 1H, BH 5), 2.25 (s, 2H, BH 8,11), 2.42 (s, 3H, NCH$_3$); δ_{C} 78.2 (cage C), 63.9(*C*Me$_3$), 37.8 (CH$_3$), 27.6 (C*C*H$_3$); δ_{B} −3.1 (B5), −9.8 (B8,11), −11.2 (B2,3), −24.2 (B9,10), −26.4 (B1), −32.2 (B4,6).

Na[Me$_3$NCB$_{10}$H$_{11}$] 8a. δ_{H} (^{1}H-{^{11}B}), −2.76 (s, 1H, μ-BH), 0.11 (s, 1H, BH 1), 0.18 (s, 2H, BH 9,10), 0.45 (s, 1H, BH 5), 0.92 (s, 2H, BH 4,6), 1.31 (s, 2H, BH 2,3), 1.36 (s, 2H, BH 8,11), 2.97 (s, 9H, NCH$_3$); δ_{C} 93.1 (cage C), 56.3 (CH$_3$); δ_{B} −18.3 (B8,11), −19.7 (B4,6), −21.5 (B2,3), −27.1 (B5,9,10), −40.8 (B1). Addition of iodine to the NMR solution gave *closo*-Me$_3$NCB$_{10}$H$_{10}$: δ_{H} (^{1}H-{^{11}B}), 1.65 (1H, BH), 2.00 (4H, BH), 2.09 (5H, BH), 3.13 (9H, NMe$_3$); δ_{B} −4.4 (1B), −11.0 (5B), −14.1 (4B).

Na[CyHNCB$_{10}$H$_{12}$] 2b. δ_{H} (^{1}H-{^{11}B}), −3.77 (s, 1H, μ-BH), 0.35 (s, 2H, BH 4,6), 1.04–1.28 (m, 7H, CH$_2$, BH 1,9,10), 1.60 (d, 1H, CH$_2$), 1.70–1.83 (m, 2H, CH$_2$), 1.83 (s, 2H, BH 2,3), 2.13 (s, 3H, BH 5,8,11), 2.94 (m, 1H, CH$_2$); δ_{C} 72.3 (cage C), 59.5 (C$_1$), 34.1 (C$_{2,6}$), 26.4 (C$_4$), 25.3 (C$_{3,5}$); δ_{B} −3.5 (B5), −9.2 (B2,3), −11.6 (B8,11), −23.7 (B9,10), −27.0 (B1), −32.3 (B4,6).

Na[CyMe$_2$NCB$_{10}$H$_{11}$] 7b. δ_{H} (^{1}H-{^{11}B}), −3.62 (s, 1H, μ-BH), 0.00 (s, 1H, BH 1), 0.20 (s, 2H, BH 9,10), 0.48 (s, 1H, BH 1), 0.98 (s, 2H, BH 4,6), 1.36 (m, 4H, BH 2,3,8,11), 1.33 (m, 8H, CH$_2$, BH 2,3,8,11), 1.96 (m, 6H, CH$_2$,), 2.65 (s, 6H, NCH$_3$); δ_{C} 93.8 (cage C), 76.3 (CH$_3$), 49.3 (C$_1$), 27.8 (C$_{2,6}$), 25.8 (C$_4$), 25.1 (C$_{3,5}$); δ_{B} −17.8 (B8,11), −18.7 (B4,6), −21.5 (B2,3), −27.1 (B5,9,10), −39.9 (B1).

NMR data for 3a as a function of pH and determination of pK_a for 3a

A solution of **3a** (100 mg) in wet CH$_3$CN (5 ml) was made basic by stirring with KOH pellets and the pH determined with a calibrated Jenway 3310 pH meter before the ^{11}B NMR spectrum of an aliquot was recorded. Addition of small portions of aqueous HCl (approx. 1 M) was used to make the solution less basic before recording the ^{11}B NMR spectrum of an aliquot. The ^{11}B NMR chemical shifts of B5 were fitted to the Henderson–Hasselbalch equation,[37] in the following form:

Table 2 Crystal data for compounds **3a** and **6b** at 120 K

	3a	**6b**
Empirical formula	C$_6$H$_{25}$B$_{10}$N	C$_9$H$_{29}$B$_{10}$N
Formula weight	219.37	259.43
Crystal system	Monoclinic	Orthorhombic
Space group	$P2(1)/c$	$P2_12_12_1$
a/Å	11.3418(14)	9.200(4)
b/Å	8.8099(11)	11.114(4)
β/°	95.852(4)	
c/Å	13.7750(15)	15.636(6)
U/Å^3	1369.2(3)	1599(1)
Z	4	4
μ(Mo-Kα)/mm^{-1}	0.050	0.052
Reflections measured	15282	16479
Unique reflections	3403	2105
R(int)	0.0451	0.0949
Reflections with $I \geq 2\sigma(I)$	2662	1818
$R\ [I \geq 2\sigma(I)]$	0.0496	0.0428
$wR(F^2)$, all data	0.1348	0.1153

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} - \log_{10}\left(\frac{[\mathrm{acid}]}{[\mathrm{base}]}\right)$$

$$\text{with } [\mathrm{acid}] + [\mathrm{base}] = 1$$

$$\text{giving } [\mathrm{acid}] = \frac{1}{10^{(\mathrm{pH}-\mathrm{p}K_{\mathrm{a}})}+1}$$

and calculating the chemical shift at each pH value using δ_{calc} = [acid]δ_{acid} + [base]δ_{base} with δ_{acid} = 0 and δ_{base} = 3.37 ppm. The sum of the squares of the difference between observed and calculated chemical shift at each pH value was minimised by varying pK_{a} to give pK_{a} = 10.12 as the best fit. A similar fit to the chemical shift of B9/B10 above pH 7 gives the same value for pK_{a}.

X-Ray crystallography

Single crystal X-ray diffraction experiments were carried out at 120(2) K with a SMART 1K CCD area detector, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL programs.[38] Crystal data and experimental details are listed in Table 2. For **3a**, the XP command HIMP was used to move H12 and H5 to give B–H and N–H distances of 1.21 and 1.03 Å respectively, prior to the calculation of distances and angles in Fig. 3.

CCDC reference numbers 178300 and 178301.

See http://www.rsc.org/suppdata/dt/b2/b200930g/ for crystallographic data in CIF or other electronic format.

Computational section

All *ab initio* computations were carried out with the Gaussian 98 package.[39] The geometries discussed here were optimised at the HF/6-31G* level with no symmetry constraints. No imaginary frequencies were found for these optimised geometries at the HF/6-31G* level. Optimisation of these geometries were then carried out at the computationally intensive MP2/6-31G* level and calculated NMR shifts at the GIAO-B3LYP/6-311G* level. The geometries of the parent anion CB$_{10}$H$_{13}^-$ (**I**) then H$_3$NCB$_{10}$H$_{12}$ (**II**) and finally Me$_3$NCB$_{10}$H$_{12}$ (**III**) and related geometries were optimised. Theoretical ^{11}B chemical shifts at the GIAO-B3LYP/6-311G*//MP2/6-31G* level,[40] were referenced to B$_2$H$_6$ (16.6 ppm)[41] and

Table 3 Zero point (HF/6-31G*) and total (MP2/6-31G*) energies and calculated ^{11}B NMR chemical shifts of calculated structures

Code	Formula	ZPE/kcal mol^{-1}	Total *E*/au	Calculated ^{11}B NMR chemical shifts/ppm
I	$CB_{10}H_{13}^{-\,a}$	116.98	−293.43946	0.2 (5), −12.6 (2,3), −15.2 (8,11), −24.8 (9,10), −27.2 (1), −32.8 (4,6)
II	$H_3NCB_{10}H_{12}$	138.55	−349.11596	1.0 (5), −8.2 (2,3), −17.0 (8,11), −21.6 (9,10), −25.8 (1), −33.1 (4,6)
III	$Me_3NCB_{10}H_{12}$	196.14	−466.60675	4.0 (5), −10.8 (2,3), −17.4 (8,11), −22.0 (9,10), −25.5 (1), −33.9 (4,6)
IV	$Me_3NCB_{10}H_{11}^{-}$ μ-H at 8,9	186.81	−466.05454	−7.4 (10), −9.6 (5), −14.6 (11), −19.6 (3), −21.1 (2), −25.5 (6), −27.6 (8), −35.2 (9), −35.5 (4), −38.0 (1)^{b}
V	$Me_3NCB_{10}H_{11}^{-}$ μ-H at 9,10	186.80	−466.06309	−17.8 (4,6), −21.5 (8,11), −23.8 (2,3), −28.2 (5), −28.2 (9,10), −41.5 (1)
VI	$Me_3NCB_{10}H_{10}^{2-}$	176.80	−465.32250	−22.7 (9,10), −23.9 (5), −27.3 (4,6), −27.6 (2,3), −29.8 (8,11), −51.3 (1)
VII	$^{t}BuMe_2NCB_{10}H_{12}$	254.01	−584.09319	4.4 (5), −9.2 (2,3), −15.4 (8,11), −22.2 (9,10), −25.2 (1), −30.5 (4,6)
VIII	$^{t}BuHNCB_{10}H_{11}^{2-}$ μ-H at 9,10	194.28	−504.60258	−16.3 (8,11), −19.5 (4,6), −19.6 (2,3), −31.7 (5), −31.8 (9,10), −42.1 (1)
IX	$^{t}BuHNCB_{10}H_{11}^{2-}$ μ-H at 8,9	194.28	−504.59800	−6.3 (11), −14.2 (10), −14.3 (3), −14.5 (5), −18.5 (2), −24.6 (6), −27.1 (8), −33.9 (4), −36.3 (9), −39.2 (1)^{c}

[a] Literature:[32] 0.3 (5), −11.2 (2,3), −11.2 (8,11), −22.4 (9,10), −24.8 (1), −30.4 (4,6). [b] Pairwise averaging: −9.6(5), −20.4 (2,3), −21.1 (8,11), −21.3 (9,10), −30.5 (4,6), −38.0 (1). [c] Pairwise averaging: −14.5 (5), −16.4 (2,3), −16.7 (8,11), −25.3 (9,10), −29.2 (4,6), −39.2 (1).

converted to the usual $BF_3{\cdot}OEt_2$ scale: $\delta(^{11}B) = 102.83 - \sigma(^{11}B)$. The relative energy was computed at the MP2/6-31G* level with ZPE (calculated at HF/6-31G*) corrections scaled by 0.89. The root mean squared fitting method used for comparison of experimental and theoretical geometries was carried out using the *ofit* command in the *xp* program as part of the SHELXTL package.[38] The misfit value for heavy atoms between the MP2/6-31G* optimised geometry (**I**) of $CB_{10}H_{13}^{-}$ and the crystallographically determined structure[42] of $CsCB_{10}H_{13}$ is 0.0155 Å. Zero point (HF/6-31G*) energies in kcal mol^{-1} and total energies in au (MP2/6-31G*), and calculated ^{11}B NMR chemical shifts (GIAO-NMR/6-311G*//MP2–6-31G*) are given in Table 3.

See http://www.rsc.org/suppdata/dt/b2/b200930g/ for CHIME files containing Cartesian coordinates of MP2-optimized geometries of **I** to **IX**.

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