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FULL PAPER

The synthesis of *closo*- and *nido*-(aminoalkyl)dicarbaboranes: a re-examination of contradictory literature reports, crystal structure of [7-{$H_3N(CH_2)_3$}-7,8-$C_2B_9H_{11}$]·NH_2NH_2 †

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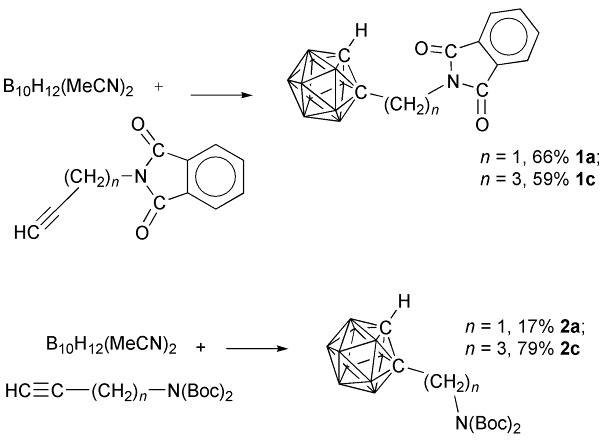
The reaction of Li[1-$^tBuMe_2Si$-1,2-$C_2B_{10}H_{10}$] with *N*-(bromoethyl)phthalimide or *N*-3-(bromopropyl)phthalimide generates unusual carboranyl heterocycles, resulting from nucleophilic substitution followed by insertion of a phthalimide carbonyl into the C–Si bond. The structure of one was determined by single crystal X-ray diffraction. Reaction of the heterocycles with $^nBu_4NF$ affords *closo*-1-{$C_6H_4(CO)_2N(CH_2)_n$}-1,2-$C_2B_{10}H_{11}$ (**1b** $n = 2$ and **1c** $n = 3$) together with the anions *nido*-[7-{$C_6H_4(CO)_2N(CH_2)_n$}-7,8-$C_2B_9H_{11}$]$^-$ as minor side-products on prolonged reaction. The prolonged reaction of **1b** and **1c** with hydrazine results in deboronation to give hydrazine solvates of zwitterionic *nido*-[7-{$H_3N(CH_2)_n$}-7,8-$C_2B_9H_{11}$]. A single crystal X-ray diffraction study for one reveals an elegant dimeric architecture supported by hydrazine-bridged hydrogen bonds. The reaction of the heterocycles with ethanolic KOH results in cluster deboronation and partial deprotection of the amine group to give *nido*-[7-(2-$O_2CC_6H_4CONH$)-$(CH_2)_n$-7,8-$C_2B_9H_{11}$]$^{2-}$ as potassium salts which can be metathesised to less hygroscopic Me_3NH^+ salts. The molecular structure of one of the latter displays hydrogen bonding generating a dimeric unit. Complete deprotection of the amine function in these salts by water–HCl gives zwitterionic aminoalkylcarboranes *nido*-7-{$H_3N(CH_2)_n$}-7,8-$C_2B_9H_{11}$.

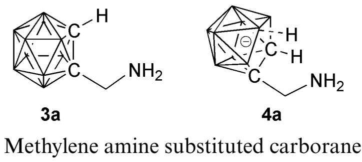
Introduction

The development of new carboranes for potential use in boron neutron capture therapy (BNCT) remains an active area of research.[1] One such class of compounds, 1-(aminoalkyl)-1,2-dicarba-*closo*-dodecaboranes, *closo*-1-{$R_2N(CH_2)_n$}-1,2-$C_2B_{10}H_{11}$,[2] and their structural analogues have also been used as precursors to amino acid-,[3] polyamine-[4] and nucleoside-substituted[5] carboranes, and as metal extractants or sensors,[6] yet remain problematical to prepare. The approach exploited independently by both Soloway[7] and Sjöberg[8] and their co-workers and outlined in Scheme 1 requires preparation of terminal alkynes bearing protected amine functions, pth-$(CH_2)_nC{\equiv}CH$ (pth = $C_6H_4(CO)_2N$) or $(Boc)_2N(CH_2)_nC{\equiv}CH$ (Boc = *tert*-butoxycarbonyl), followed by their reaction with $B_{10}H_{12}(NCMe)_2$ to afford either 1-{pth$(CH_2)_n$}-1,2-$C_2B_{10}H_{11}$ ($n = 1$, 66% **1a**; $n = 3$, 59% **1c**)‡ or 1-{$(Boc)_2N(CH_2)_n$}-1,2-$C_2B_{10}H_{11}$ ($n = 1$, 17% **2a**; $n = 3$, 79% **2c**). Recently Kang and co-workers reported the coupling of Li[1,2-$C_2B_{10}H_{11}$] with *commercially available N*-(bromoalkyl)phthalimides, Br$(CH_2)_n$-pth to afford **1** ($n = 1$, 0% **1a**; $n = 2$, 81% **1b**; $n = 3$, 36% **1c**).[9] Related compounds containing additional functional groups,[10] *e.g.* 1-[(pth)CH_2]-2-[$PhOCH_2CH_2$]-1,2-$C_2B_{10}H_{10}$ from the alkyne (pth)$CH_2C{\equiv}CCH_2CH_2OPh$, and aminoalkyl substituted *para*-carboranes, prepared from 1-[$HO(CH_2)_n$]-1,12-$C_2B_{10}H_{11}$, have been reported.[11]



Scheme 1 The preparation of alkylamine substituted carboranes by the reaction of $B_{10}H_{12}(MeCN)_2$ with alkynes bearing protected amines.

Since neither approach is ideal with respect to yield and procedure we felt alternative strategies were worthy of investigation. However, it is the reaction of **1a** with hydrazine hydrate that is of most interest. Nagakawa *et al.*[12] reported the product to be 1-(aminomethyl)-1,2-dicarba-*closo*-dodecaborane, 1-(H_2NCH_2)-1,2-$C_2B_{10}H_{11}$, **3a** (Scheme 2), whereas Soloway and co-workers[7] suggested reformulation as a hydrazinium salt of the deboronated 7-(aminomethyl)-7,8-



Scheme 2 Methylene amine substituted carboranes **3a** and **4a**.

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† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b102009i/

‡ Throughout this paper compounds designated **a** contain aminomethylene or $(CH_2)_n$ with $n = 1$, **b** contain aminoethylene or $n = 2$, and **c** contain aminotrimethylene or $n = 3$ groups respectively.

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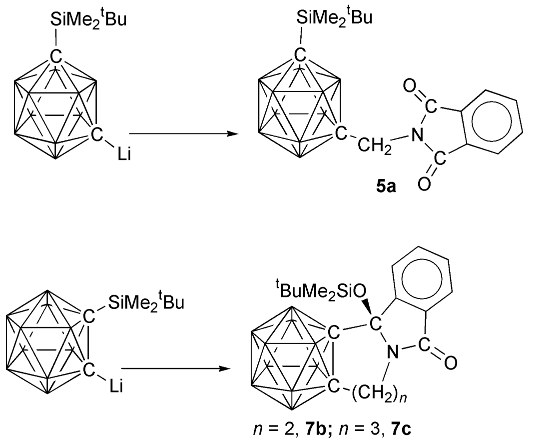
dicarba-*nido*-undecaborate(10) anion, *nido*-[7-(H_2NCH_2)-7,8-$C_2B_9H_{11}$]$^-$, **4a**, which would be akin to aminoalkylcyclopentadienes, prepared *via* phthalimides[13] and other routes,[14] and used to prepare amido- and imido-cyclopentadienylmetal complexes.[15] We were interested in preparing ligands such as **4** containing *nido*-carborane fragments connected to amines by di- and tri-methylene units in order to explore their transition metal coordination chemistry. We considered mono-methylene linkers to be too short to provide stable bidentate ligands, and so have not explored their synthesis. Although alternative procedures are available for the isolation of **3** as hydrochloride salts,[7] to the best of our knowledge no further reports have appeared on the novel *nido* species, **4**.

Here we report a high yield route to **1**, reinvestigation of their reactions with hydrazine hydrate, structural characterisation of the disputed products and a new route to the *nido* derivatives. During this work we discovered an unusual insertion reaction leading to a novel carboranyl heterocycle.

Results and discussion

Hawthorne and co-workers pioneered the use of $^tBuMe_2Si$ as a protecting group in the preparation of mono-substituted derivatives of *ortho*-carborane.[16] Wilbur has shown that treatment of the *meta*-carborane derivative Li[1-(Me_3Si)-1,3-$C_2B_{10}H_{10}$] with $BrCH_2pth$ affords 1-(*tert*-butyldimethylsilyl)-3-(phthalimidomethyl)-1,3-dicarba-*closo*-dodecaborane, **5a** (Scheme 3).[17] By analogy the reaction of the *ortho*-carborane analogue Li[1-($^tBuMe_2Si$)-1,2-$C_2B_{10}H_{10}$] with $Br(CH_2)_n pth$ might be expected to afford 1-(*tert*-butyldimethylsilyl)-2-(phthalimidoalkyl)-1,2-dicarba-*closo*-dodecaboranes, **6**. In practice only carboranyl heterocycles, **7** (Schemes 3 and 4), are isolated in essentially *quantitative yield*. These products are obtained regardless of variation in experimental procedure (rate of addition, temperature, dilution or scale).



Scheme 3 Products of the reactions of isomeric *meta* and *ortho* silyl protected lithio-carboranes with *N*-(bromoalkyl)phthalimides.

Spectroscopic data clearly demonstrate that the products do not have the molecular mirror plane expected for **6**. Thus, the ^1H NMR spectrum of 2-(3′-*tert*-butyldimethylsiloxy-1′-oxo-1′,3′-dihydroisoindol-3′-yl)-1,2′-ethano-1,2-dicarba-*closo*-dodecaborane, **7b**, displays informative doublet of doublet of doublet resonances at δ 4.24 and 3.20 which are attributed to the diastereotopic *N*-methylene unit. The $^{13}C-\{^1H\}$ NMR spectrum exhibits two unique resonances for the carbonyl and silyl ether units, δ 165.6 and 144.6 respectively. The $^{11}B-\{^1H\}$ NMR spectrum confirms the presence of 10 B atoms and retention of the *closo* framework, and the spectroscopic data of **7c** are similar, with an additional diastereotopic CH_2 group. In order to confirm the structure of these novel heterocycles, we carried out a structural determination on **7c**. The asymmetric unit contains three molecules of pentane and two independent molecules of **7c**, however the structural parameters are so similar only one molecule will be discussed. The molecular structure of one molecule of **7c** is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The bonds between polyhedral carbon and *exo*-polyhedral carbon atoms are found to be C(1)–C(22) 1.587(4) Å and C(2)–C(13) 1.526(4) Å whilst the polyhedral carbon separation C(1)–C(2) is 1.684(4) Å. These parameters are normal for compounds of this type and indicate that there is only nominal ring strain within the molecule.

Table 1 Selected bond lengths (Å) and angles (°) for one of the two molecules in the asymmetric unit of **7c**

Si(1)–O(1)	1.685(2)	C(1)–C(22)	1.587(4)
O(1)–C(22)	1.391(3)	C(1)–C(2)	1.684(4)
O(2)–C(23)	1.226(4)	C(2)–C(13)	1.526(4)
N(1)–C(23)	1.385(4)	C(13)–C(14)	1.525(5)
N(1)–C(15)	1.455(4)	C(14)–C(15)	1.513(5)
N(1)–C(22)	1.475(4)		
C(22)–O(1)–Si(1)	131.23(18)	C(14)–C(13)–C(2)	118.2(3)
C(22)–C(1)–C(2)	121.3(2)	C(15)–C(14)–C(13)	112.8(3)
C(13)–C(2)–C(1)	123.0(2)	N(1)–C(15)–C(14)	114.5(3)

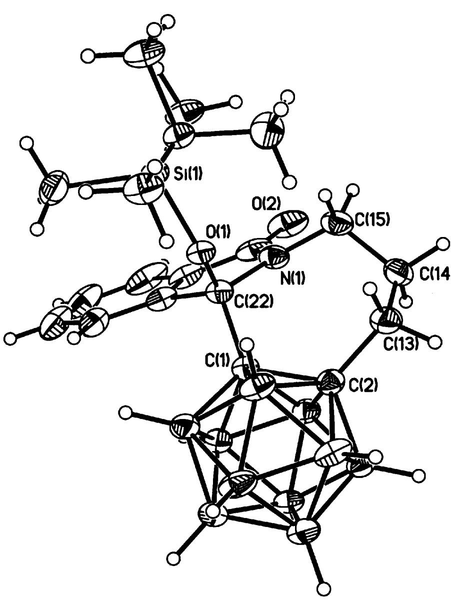
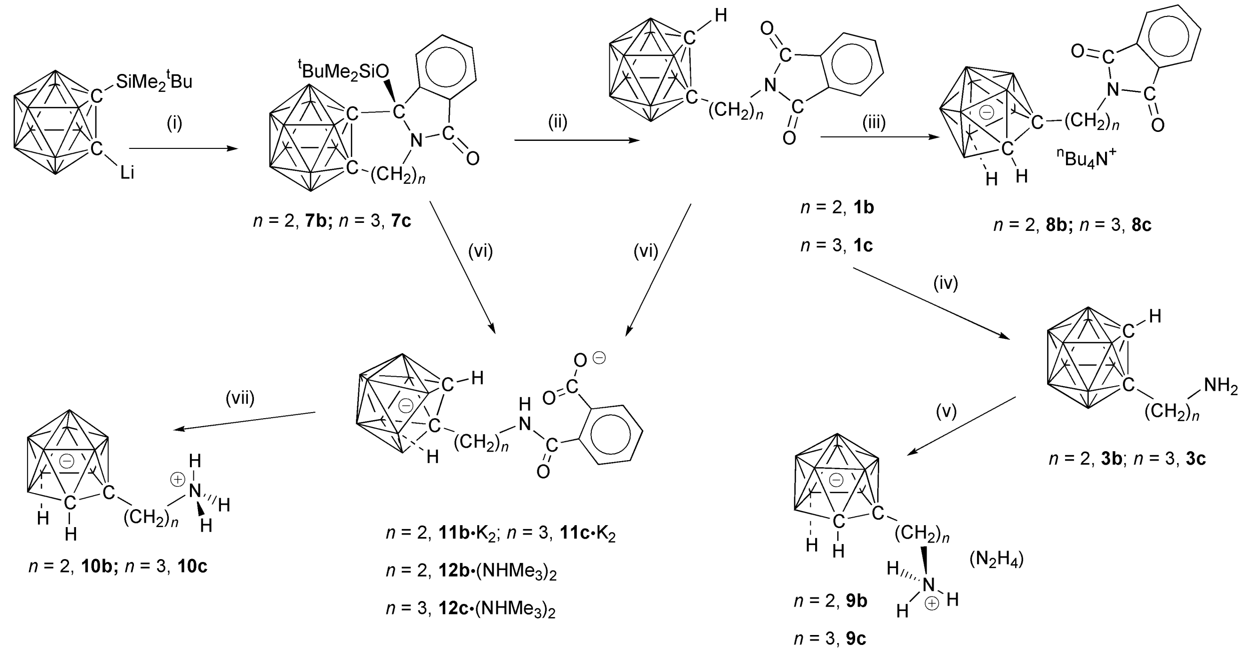


Fig. 1 The molecular structure of **7c** in 40% displacement ellipsoids, with hydrogen atoms as arbitrary sized spheres.

It seems likely that the mechanism by which **7b** and **7c** are formed involves initial nucleophilic attack of Li[1-($^tBuMe_2Si$)-1,2-$C_2B_{10}H_{10}$] on $Br(CH_2)_n pth$, leading to displacement of LiBr, generating **6** as a putative intermediate which undergoes subsequent insertion of one phthalimide carbonyl group into the C–Si bond.[18] There is no evidence that **7a** and **7b** are in equilibrium with acyclic **6** in solution, yet the subsequent reactivity studies indicate that **7a** and **7b** can be converted into acyclic species by ring opening of the carboranyl heterocycle. Photolysis of *N*-(trimethylsilylmethyl)phthalimide generates an azomethine ylid which undergoes cycloaddition reactions to give heterocycles that are structurally similar to **7b** and **7c**.[19] There is no evidence that **7b** and **7c** are photochemically generated, or that the same mechanism holds. The Bu_4NF promoted cyclisation of *ortho*-carborane substituted aldehydes and ketones[20] gives five, six or seven membered hydroxycarboracycles, which are also the products from reaction of trimethylsilyl *ortho*-carborane with α,β-unsaturated carbonyl compounds,[21] where the reaction involves insertion of carbonyl into the carborane–silicon bond but the silyl group is subsequently cleaved by $^nBu_4NF$. Similar insertion reactions without loss of silyl group have also been observed.[22]



Scheme 4 Reactions reported in this work. Reagents: (i) Br(CH$_2$)$_n$N(CO)$_2$C$_6$H$_4$; (ii) ^{n}Bu$_4$NF, 2 h; (iii) ^{n}Bu$_4$NF, 5–7 d; (iv) N$_2$H$_4$·H$_2$O, 20 °C; (v) N$_2$H$_4$·H$_2$O, 80 °C; (vi) KOH–EtOH, then Me$_3$NHCl; (vii) HCl.

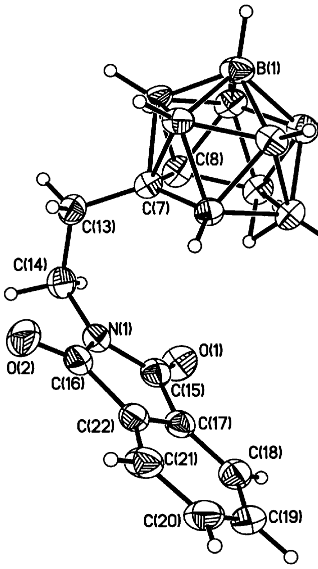


Fig. 2 The molecular structure of the anion in **8b** in 40% displacement ellipsoids; the ^{n}Bu$_4$N$^+$ cation is omitted.

Table 2 Selected bond lengths (Å) and angles (°) for the anion in **8b**

C(8)–C(7)	1.561(3)	C(14)–N(1)	1.458(3)
C(7)–C(13)	1.512(3)	C(15)–O(1)	1.208(2)
C(13)–C(14)	1.521(3)	C(16)–O(2)	1.207(2)
C(8)–C(7)–C(13)	116.99(17)	C(13)–C(14)–N(1)	113.13(18)
C(7)–C(13)–C(14)	114.69(18)		

Upon treatment of **7b** and **7c** with ^{n}Bu$_4$NF at 0 °C as a methanol suspension the heterocycle is readily cleaved and the silyl substituent removed to afford 1-(phthalimidoalkyl)-1,2-dicarba-*closo*-dodecaboranes, *closo*-1-{C$_6$H$_4$(CO)$_2$N(CH$_2$)$_n$}-1,2-C$_2$B$_{10}$H$_{11}$ ($n = 2$, **1b**; $n = 3$, **1c**) directly as microcrystalline solids, in essentially *quantitative yield*. The formulation is confirmed by comparison of spectroscopic properties with those reported by Kang and co-workers[9] and in the case of **1b** by a single crystal X-ray diffraction study. The structure of **1b** is not reported here since it is identical to that recently reported,[23] and comparable to those previously reported for **1a**[24] and **1c**.[9]

In both the reaction of **7b** and **7c** with ^{n}Bu$_4$NF a minor product (<5%) is isolated from the reaction liquor. Treating **7** with an *excess* of ^{n}Bu$_4$NF as a methanol suspension for 7 d affords sufficient quantities of these products to permit identification as the products of fluoride ion promoted deboronation giving the new 7-(phthalimidoalkyl)-7,8-dicarba-*nido*-undecaborate(10) anions, *nido*-[7-{C$_6$H$_4$(CO)$_2$N(CH$_2$)$_n$}-7,8-C$_2$B$_9$H$_{11}$]$^-$ ($n = 2$, **8b**; $n = 3$, **8c**) as ^{n}Bu$_4$N$^+$ salts. The deboronation generates asymmetry that is duly reflected in the NMR data. Accordingly **8b** exhibits distinct complex resonances in the ^{1}H NMR spectrum for each proton of the diastereotopic *N*-CH$_2$ unit; δ 3.69 (ddd, 1H, *J*(HH) = 6, 10, 13) and 3.81 (ddd, 1H, *J*(HH) = 6, 10, 13 Hz). Whilst resonances for the *C*-methylene are obscured by those of the ^{n}Bu$_4$N$^+$ cation, the broad singlet observed at δ 1.68 is characteristic of a cage CH. This formulation is supported by a single crystal X-ray diffraction study for the ethylene derivative **8b** which shows a discrete *nido*-[7-{C$_6$H$_4$(CO)$_2$NCH$_2$CH$_2$}-7,8-C$_2$B$_9$H$_{11}$]$^-$ anion (Fig. 2) and ^{n}Bu$_4$N$^+$ cation with no short inter-ion contacts. The structural parameters (Table 2) fall within the normal range for mono-substituted *nido* derivatives. The deboronation of carboranes by wet fluoride ions is well established and may be invoked to account for the formation of **8**.[25] Since such reactions are normally quite rapid, the largely heterogeneous nature of our deprotection procedure may minimise this undesirable side reaction.

Having established a reliable, high yield and synthetically simple route to **1b** and **1c** we next turned our attention to their reaction with hydrazine hydrate. Even in the presence of a large excess of hydrazine hydrate at ambient temperature 1-(aminoalkyl)-1,2-dicarba-*closo*-decaboranes, **3**, are observable (^{11}B, ^{1}H NMR, see Experimental section), as previously claimed.[12] Furthermore they are intermediates *en route* to the *nido* derivatives they were incorrectly reformulated as.[7] In our hands *nido*-derivatives, **9**, are only obtained at elevated temperature with an excess of hydrazine hydrate. Most importantly the formulation of **9** proposed by Soloway and co-workers[7] is subtly erroneous in a way which cannot be elucidated from NMR or analytical data alone. Thus, a structural study of **9c** establishes the correct formulation as zwitterionic *nido*-7-{H$_3$N(CH$_2$)$_3$}-7,8-C$_2$B$_9$H$_{11}$ which exists in the solid state as a hydrazine-bridged hydrogen-bonded dimer lying across a crystallographically imposed

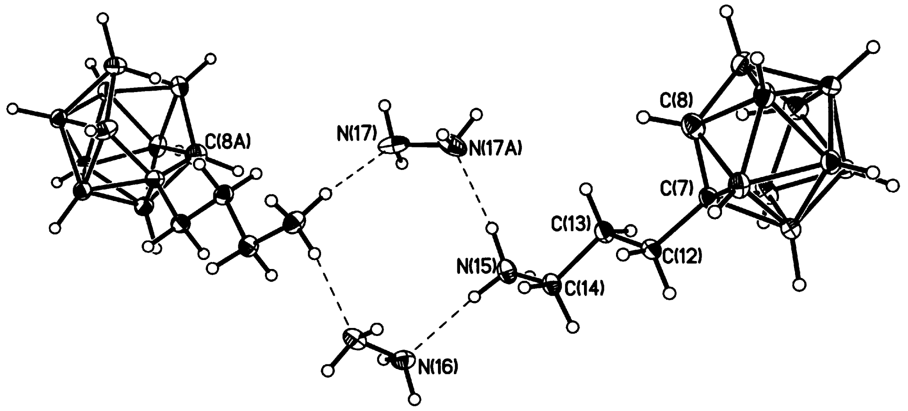


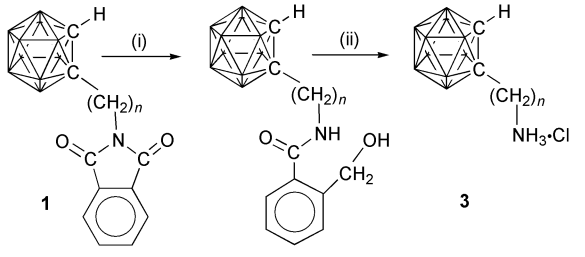
Fig. 3 The hydrogen-bonded dimeric structure of **9c** in 40% displacement ellipsoids showing two molecules linked through the hydrazine.

Table 3 Selected bond lengths (Å) and angles (°) for **9c**

C(7)–C(12)	1.520(2)	N(17)–N(17A)	1.442(3)
C(7)–C(8)	1.569(2)	H(153) · · · N(16)	2.09(2)
C(12)–C(13)	1.526(2)	H(151) · · · N(17)	2.85(2)
C(13)–C(14)	1.516(2)	N(15) · · · N(16)	2.869(2)
C(14)–N(15)	1.490(2)	N(15) · · · N(17)	3.682(2)
N(16)–N(16A)	1.442(3)		
C(12)–C(7)–C(8)	119.53(15)	C(14)–C(13)–C(12)	109.01(14)
C(7)–C(12)–C(13)	114.08(14)	N(15)–C(14)–C(13)	113.08(14)

inversion centre, as shown in Fig. 3. Selected bond lengths and angles appear in Table 3.

We find the purification of **3** and **9** unreliable and the yields after recrystallisation are consistently low. Thus, we chose to explore alternative procedures for the removal of the phthalimide residue from **7** or **1**. The reaction which attracted our interest is the reported sequential treatment of **1** with $NaBH_4$ and HOAc/HCl to afford **3**·HCl (Scheme 5).[7]



Scheme 5 Reaction sequence in the treatment of **1** with (i) $NaBH_4$ followed by (ii) HOAc/HCl to afford **3**.

If deboronation could be effected at the same time as hemi-deprotection of the phthalimide then acidification may afford *nido*-7-$\{H_3N(CH_2)_n\}$-7,8-$C_2B_9H_{11}$, **10** directly. Indeed, treating either **1** or **7** with KOH as an ethanol solution affords the new dianions 7-(*o*-carboxybenzoylaminoalkyl)-7,8-dicarba-*nido*-undecaborate(11), *nido*-[7-(*o*-$O_2CC_6H_4CONH)(CH_2)_n$-7,8-$C_2B_9H_{11}]^{2-}$, $n = 2$ **11b** or 3 **11c**, as their dipotassium salts in essentially *quantitative yield*. Owing to the hygroscopic nature of the K^+ derivatives the bis-$NHMe_3^+$ salts, **12b** and **12c**, were prepared for micro-analytical purposes and ease of handling. In the case of the ethylene derivative **12b** a single crystal X-ray diffraction study (Fig. 4 and Table 4) confirms that reaction with KOH cleaves one arm of the phthalimide residue to generate an amino and carboxylate group. In addition the cage is deboronated and the resulting *nido* framework is comparable to the two previously discussed structures. The hydrogen bonds formed by NH and CO_2 units result in a dimeric molecular architecture which once again lies across a crystallographically imposed inversion centre. All NMR data are consistent with this formulation.

Our preliminary studies seem to confirm that treating either **11** or **12** with dilute HCl affords **10**. Spectroscopic data indicate that **10b** and **10c** contain both phthalic acid and *nido*-7-$\{H_3N(CH_2)_n\}$-7,8-$C_2B_9H_{11}$ which are spectroscopically identical in solution to the same species isolated as the hydrazine co-crystallisates in **9b** and **9c**. Unfortunately we have yet to obtain crystalline samples of **10b** and **10c**. Given the predilection for hydrogen bonding exhibited by both amino and ammonio substituents a crystallographic study will be required to establish the precise relationship between the phthalic acid and the aminoalkylcarborane.

In conclusion we have developed and refined synthetic routes to aminoalkyl *closo*- and *nido*-carboranes; during this work we have encountered an unusual carborane heterocycle, which nevertheless behaves as its acyclic form in reactions with fluoride and base. With aminoalkyl *nido*-carboranes at hand, their transition metal coordination chemistry will be reported on in future papers.

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. Absolute alcohols were degassed prior to use. NMR solvents were vacuum-distilled from suitable drying agents and stored under a dry nitrogen atmosphere. Elemental analysis was performed on an Exeter Analytical CHN analyser by the micro-analytical service within this department. NMR spectra were recorded on the following instruments: Varian Unity-300 (^1H, ^{11}B, ^{13}C), Varian 500 (^1H, ^{13}C, HETCOR); ^1H and ^{11}B NMR on the Unity-300 unless otherwise stated. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^1H NMR spectra were referenced to residual protio impurity in the solvent ($CHCl_3$, δ 7.26; $CDHCl_2$, δ 5.32; $CHD_2(CD_3)CO$, δ 2.16). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$, δ 77.0; CD_2Cl_2, δ 53.8; $(CD_3)_2CO$, δ 206.0). ^{11}B NMR were referenced externally to $Et_2O·BF_3$, δ 0.0. Except where otherwise indicated, all spectra were recorded at ambient temperature.

Syntheses

2-(3′(*tert*-Butyldimethylsiloxy)-1′-oxo-1′,3′-dihydroisoindol-3′-yl)-1,2′-ethano-1,2-dicarba-*closo*-dodecaborane 7b. A cooled 2 : 1 benzene–Et_2O solution (25 ml) (0 °C) of freshly prepared Li[1-($^tBuMe_2Si$)-1,2-$C_2B_{10}H_{10}$][16] (1.00 g, 3.7 mmol) was treated dropwise with $C_6H_4(CO)_2N(CH_2)_2Br$ (1.10 g, 4.0 mmol) as a 2 : 1 benzene–Et_2O solution (25 ml) and allowed to warm to room temperature. The solution was gradually brought to

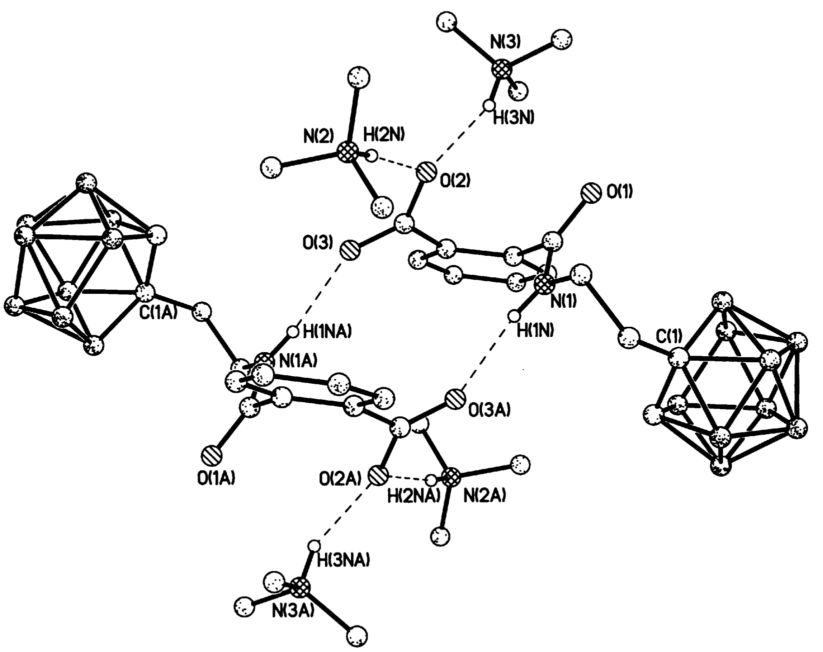


Fig. 4 The molecular structure of **12b** showing the hydrogen bonding between two dianions and their accompanying Me_3NH^+ cations. Hydrogen atoms, other than N–H, are omitted for clarity.

Table 4 Selected bond lengths (Å) and angles (°) for **12b**

O(1)–C(5)	1.240(2)	C(1)–C(2)	1.568(3)
O(2)–C(6)	1.284(2)	C(3)–C(4)	1.535(3)
O(3)–C(6)	1.238(2)	H(2N) ··· O(2)	1.77(2)
N(1)–C(5)	1.335(2)	H(3N) ··· O(2)	1.91(3)
N(1)–C(4)	1.459(2)	H(1N) ··· O(3A)	2.03(2)
C(1)–C(3)	1.524(2)		
C(5)–N(1)–C(4)	121.87(15)	C(1)–C(3)–C(4)	113.66(15)
C(3)–C(1)–C(2)	117.37(15)	N(1)–C(4)–C(3)	113.64(15)

reflux and heating continued for 2 d to afford a pale yellow-orange solution. Solvent was removed on a rotary evaporator and the residue triturated with methanol (*ca.* 30 ml). The mixture was cooled overnight (−10 °C) to afford a colourless micro-crystalline solid which was isolated by filtration, washed with an aliquot of chilled methanol and dried *in vacuo* to afford **7b**, 1.20 g. Further crops were obtained by reduction of solvent volume and cooling (−10 °C), 0.38 g. Yield 1.58 g, 97%. Analytically pure samples were obtained by slow evaporation of a hexane–Et_2O solution (Found C 50.21; H 7.76; N 3.10 $C_{18}H_{33}B_{10}NO_2Si$ requires C 50.09; H 7.71; N 3.24%); δ_H $CDCl_3$ −0.62 (s, 3 H, SiMe), −0.18 (s, 3 H, SiMe), 0.93 (s, 9 H, Bu), 2.54 (m, 2 H, CH_2), 3.20 (ddd, 1 H, NCH, *J*(HH) = 6, 12, 12), 4.24 (ddd, 1 H, NCH, *J*(HH) = 2, 6, 12), 7.59–7.84 (m, 4 H, C_6H_4); δ_C CD_2Cl_2 165.6 (CO), 144.6 (aromatic *C*COSi), 131.8–123.8 (Ar), 87.4, 80.6, 77.2 (C_2B_{10} and COSi), 32.0 (CH_2), 31.7 (CH_2), 25.7 (C*Me*$_3$), 18.6 (*C*Me$_3$), −4.2, −4.5 (SiMe); δ_B $CDCl_3$ −1.9 (1B), −4.7 (1B), −8.3 (2B), −9.9 (3B), −12.2 (3B).

An identical procedure was followed for the synthesis of **7c**. Yield 1.60 g, 95% (Found C 53.89; H 8.71; N 2.76. $C_{19}H_{35}B_{10}NO_2Si\cdot0.5C_5H_{12}$ requires C 53.60; H 8.58; N 2.91%); δ_H $CDCl_3$ −0.39 (s, 3 H, SiMe), −0.18 (s, 3 H, SiMe), 0.98 (s, 9 H, Bu), 1.80–2.20 (m, 2H, CH_2), 2.80 (m, 2 H, CH_2), 3.22 (ddd, 1 H, NCH, *J*(HH) = 4, 10, 14), 4.29 (ddd, 2 H, NCH, *J*(HH) = 4, 4, 15), 7.58–7.85 (m, 4 H, C_6H_4); δ_C $CDCl_3$ 166.7 (CO), 145.1 (aromatic *C*COSi), 131.5–123.6 (Ar), 93.3, 86.8, 82.7 (C_2B_{10} and *C*OSi), 39.1 (CH_2), 39.0 (CH_2), 26.1 (C*Me*$_3$), 25.1 (CH_2), 18.9 (*C*Me$_3$), −2.5, −4.4 (SiMe); δ_B $CDCl_3$ −1.9 (1B), −4.7 (1B), −8.3 (2B), −9.9 (3B), −12.2 (3B).

1-(Phthalimidoalkyl)-1,2-dicarba-*closo*-dodecaboranes 1. A methanol solution (10 ml) of $^nBu_4NF$ (0.65 g, 2.5 mmol) was added dropwise over a period of 2 h to a cooled (0 °C) methanol suspension (10 ml) of **5b** (1.0 g, 2.3 mmol) and then left slowly to stir for 12 h. The resulting colourless micro-crystalline precipitate was isolated by filtration, washed with cold methanol (2 × 2 ml) and dried *in vacuo* to afford **1b**. Yield 0.69 g, 94%. An identical procedure was followed for the synthesis of **1c**. Yield 0.68 g, 91%. Comparison of spectroscopic properties with samples prepared by literature methods[9] confirmed the formulation.

Tetra-n-butylammonium 7-(phthalimidoalkyl)-7,8-dicarba-*nido*-undecaborates(10) 8. A methanol suspension (5 ml) of $^nBu_4NF$ (8.2 g, 30 mmol) was added dropwise to a methanol suspension (25 ml) of **1b** (1.0 g , 3.1 mmol) and then left slowly to stir for 5–7 d or until conversion was complete as determined by ^{11}B NMR. The resulting micro-crystalline pale yellow precipitate was isolated by filtration, washed with cold methanol (2 × 2 ml) and dried *in vacuo* to afford **8b**. Yield 0.88 g, 51% (Found C 60.89; H 10.18; N 4.91. $C_{28}H_{54}B_9N_2O_2$ requires C 61.37; H 9.93; N 5.11%); δ_H $(CD_3)_2CO$ −2.63 (br s, 1 H, BH), 0.99 (t, 12 H, Me), 1.45 (m, 8 H, CH_2), 1.68 (s, 1 H, cage CH), 1.78 (ddd, 1 H, NCH), 1.84 (m, 8 H, CH_2), 1.99 (m, 1 H, CH_2), 3.69 (ddd, 1 H, NCH, *J*(HH) = 6, 10, 13), 3.81 (ddd, 1 H, NCH, *J*(HH) = 6, 10, 13), 7.83 (s, 4 H, C_6H_4); δ_C $(CD_3)_2CO$ 168.5 (CO), 134.7, 133.3, 123.5 (3 × Ar), 59.3 (cation NCH_2), 45.5 (br, cage CH), 39.6, 38.5 (2 × CH_2), 24.4, 20.3, 13.8 (cation); δ_B $(CD_3)_2CO$ −5.7 (1B), −5.9 (1B), −8.8 (1B), −10.8 (1B), −14.1 (2B), −16.7 (1B), −28.1 (1B), −32.2 (1B).

An identical procedure was followed for the synthesis of **8c** from **1c**. Yield 0.61 g, 36% (Found C 60.70; H 10.18; N 4.77. $C_{29}H_{57}B_9N_2O_2\cdot H_2O$ requires C 61.97; H 10.04; N 4.98%); δ_H $(CD_3)_2CO$ 0.88 (t, 12 H, Me), 1.33 (m, 10 H, CH_2), 1.74 (m, 10 H, CH_2), 3.36 (m, 9 H, CH_2 and CH), 3.49 (t, 2 H, CH_2), 7.74 (s, 4 H, C_6H_4); δ_C $(CD_3)_2CO$ 168.1 (CO), 134.2, 132.5, 123.0 (3 × Ar), 58.7 (cation NCH_2), 46.0 (br, cage CH), 38.2 (CH_2), 37.2 (CH_2), 30.4 (CH_2), 23.8, 19.7, 13.2 (cation); δ_B $(CD_3)_2CO$ −11.0 (2B), −13.9 (1B), −16.8 (1B), −18.5 (2B), −22.2 (1B), −33.4 (1B), −37.3 (1B).

7-(Ammonioalkyl)-7,8-dicarba-*nido*-undecaborate(10) derivatives 9. An ethanol solution (25 ml) of hydrazine monohydrate (3 ml, 62 mmol) was added to a stirred ethanol suspension (25 ml) of **1b** (1.0 g, 3.1 mmol) and then gradually brought to reflux

Table 5 Crystal data for compounds **7c**, **8b**, **9c** and **12b**

	7c	**8b**	**9c**	**12b**
Formula	$C_{19}H_{35}B_{10}NO_2Si{\cdot}1.5\ C_5H_{12}$	$C_{28}H_{54}B_9N_2O_2$	$C_5H_{24}B_9N_3$	$C_{18}H_{40}B_9N_3O_3$
M	553.89	548.02	223.56	443.82
System	Triclinic	Monoclinic	Orthorhombic	Monoclinic
T/K	120(2)	150(2)	120(2)	100(2)
Space group	$P\bar{1}$	$P2_1/n$	$C222(1)$	$P2_1/n$
a/Å	14.448(1)	11.267(3)	10.707(2)	9.430(2)
b/Å	14.680(1)	17.101(4)	12.477(2)	23.019(5)
c/Å	16.137(1)	17.462(4)	20.805(4)	12.140(3)
$α$/°	101.58(1)			
$β$/°	90.07(1)	95.638(4)		103.43(1)
$γ$/°	96.13(1)			
U/Å^3	3332.9(4)	3348.2(14)	2779.5(9)	2563(1)
Z	4	4	8	4
μ(Mo-Kα)/mm^{-1}	0.071	0.062	0.055	0.070
Reflections measured	37934	39997	15543	23620
Unique reflections	3881	9520	3359	5890
R(int)	0.0454	0.0462	0.0468	0.0665
Reflections with $I \geq 2\sigma(I)$	3270	5619	2939	4005
$R[F^2 > 2\sigma(F^2)]$	0.0835	0.0653	0.0437	0.0510
$wR(F^2)$, all data	0.2750	0.2012	0.0988	0.1313

and heating continued with rapid stirring for 48 h or until conversion was complete as determined by ^{11}B NMR. The resulting flocculent precipitate of, $C_6H_4(CO)_2NNH_2$ was removed by filtration, the solvent volume was reduced by half under reduced pressure and the solution cooled overnight (−10 °C) to ensure removal of all $C_6H_4(CO)_2NNH_2$ and filtered cold once more. Removal of solvent affords a hygroscopic waxy solid which after recrystallisation from EtOH–Et_2O–light petroleum, 1 : 6 : 2 affords a crystalline solid which was dried *in vacuo* to give **9b**. Yield 0.31 g, 47%. ^{11}B NMR data indicate a quantitative reaction. Addition of hexanes to the remaining solution separates a colourless syrup which after prolonged drying *in vacuo* yields a waxy solid with identical spectroscopic properties. Whilst not analytically pure this material may be used for subsequent manipulations. The product is hygroscopic (Found C 28.73; H 10.27; N 17.47. $C_4H_{22}B_9N_3{\cdot}C_2H_5OH$ requires C 28.20; H 11.04; N 16.44%); δ_H $(CD_3)_2CO$ 3.20 (m, CH_2), 1.95 (m, CH_2); δ_C $(CD_3)_2CO$ 57.0 (br, cage), 44.0 (br, cage), 40.9 (CH_2), 36.4 (CH_2); δ_B $(CD_3)_2CO$ −10.6 (1B), −11.5 (1B), −14.3 (2B), −19.8 (3B), −32.9 (1B), −37.0 (1B).

An identical procedure was followed for the synthesis of hygroscopic **9c** from **1c**. Yield 0.38 g, 56% (Found C 26.80; H 10.62; N 16.30. $C_5H_{24}B_9N_3$ requires C 26.86; H 10.82; N 18.80%); δ_H $(CD_3)_2CO$ 3.51 (cage CH), 2.63 (m, 1H, CH_2), 2.23 (m, 2H, CH_2), 2.11 (m, 3H, CH_2); δ_C $(CD_3)_2CO$ 48.6 (CH_2), 46.0 (br, cage), 36.6 (CH_2), one CH_2 obscured by solvent; δ_B $(CD_3)_2CO$ −11.0 (2B), −14.0 (1B), −15.8 (1B), − 19.1 (2B), −21.6 (1B), −33.1 (1B), −37.0 (1B).

Observation of 1-aminopropyl-1,2-dicarba-*closo*-dodecaborane, 3c. Following the method above for the synthesis of **9c**, an ethanol solution of hydrazine hydrate was added to a stirred ethanol suspension of **1c**, and prior to reflux an aliquot was removed and allowed to stand at room temperature. After several hours a white precipitate formed and was separated by centrifuge. The solid was identified as $C_6H_4(CO)_2NNH_2$, by ^{1}H NMR. The solvent was removed under reduced pressure from the filtrate and the residue dissolved in $CDCl_3$. ^{1}H NMR confirmed the absence of aromatic resonances and ^{11}B NMR identified the retention of a *closo* framework. δ_B $CDCl_3$ −3.7 (1B), −7.3 (1B), −10.7 (2B), −12.9 (2B), −13.5 (2B), −14.5 (2B).

Dipotassium 7-(2-carboxybenzoylaminoalkyl)-7,8-dicarba-*nido*-undecaborates(10) 11. An ethanol solution (25 ml) of KOH (1.0 g, 18 mmol) was added to a stirred ethanol suspension (25 ml) of **1b** (1.0 g, 3.1 mmol) and then brought to reflux for 12 h. The precipitate was isolated by filtration and dried *in vacuo* to afford extremely hygroscopic **11b**. δ_H $(CD_3)_2CO$ 1.71 (s, 1 H, CH), 1.80 (m, 2 H, CH_2), 3.39 (t, 2 H, CH_2), 7.30–7.61 (m × 2, 4 H, C_6H_4). δ_C $(CD_3)_2CO$ 175.1 (CO_2), 171.1 (CO), 142.2–128.0 (Ar), 69.1 (C_2B_9), 41.8, 39.5 (2 × CH_2). δ_B $(CD_3)_2CO$ −11.3 (2B), −14.1 (1B), −16.1 (1B), −18.6 (2B), −21.0 (1B), −32.8 (1B), −37.2 (1B).

A modified procedure was required for the synthesis of **11c** from **1c**. Following deboronation, an excess of solid CO_2 was added to generate insoluble $KHCO_3$ which was removed by filtration. Removal of solvent under reduced pressure affords extremely hygroscopic **11c**. δ_H $(CD_3)_2CO$ 1.61 (m, 5 H, CH and 2 × CH_2), 3.18 (t, 2 H, CH_2), 7.29–7.62 (m, 4 H, C_6H_4). δ_C $(CD_3)_2CO$ 174.9 (CO_2), 171.6 (CO), 141.8–127.4 (Ar), 40.8, 37.8, 31.4 (3 × CH_2), cage resonances not observed. δ_B $(CD_3)_2CO$ −15.4 (2B), −17.9 (1B), −21.0 (2B), −22.0 (2B), −26.1 (1B), −37.2 (1B), −41.2 (1B).

Analytically pure samples of the bis-$NHMe_3$ salts were obtained by recrystallisation from water–EtOH solutions following cation metathesis. **12b** Yield 1.32 g, 96% (Found C 45.68; H 9.10; N 9.24. $C_{18}H_{40}B_9N_3O_3{\cdot}H_2O$ requires C 46.81; H 9.17; N 9.10). **12c** Yield 1.30 g, 93% (Found C 46.20; H 8.99; N 9.36. $C_{19}H_{42}B_9N_3O_3{\cdot}2H_2O$ requires C 46.21; H 9.39; N 8.51%).

7-(Ammonioalkyl)-7,8-dicarba-*nido*-undecaborate(10) derivatives 10. Slow addition of degassed dilute HCl (1 M) to degassed aqueous solutions of either **11** or **12** affords, after 12 h and removal of solvent under reduced pressure, crude compounds with NMR data comparable to those of **9**. **10b**: δ_H $(CD_3)_2CO$ 3.20 (m, 2H, CH_2), 1.95 (m, 2H, CH_2); δ_C $(CD_3)_2CO$ 41.3, 36.6 (2 × CH_2), cage resonances not observed; δ_B $(CD_3)_2CO$ −10.8 (1B), −11.8 (1B), −14.1 (2B), −20.3 (3B), −32.6 (1B), −37.0 (1B). **10c**: δ_B −11.1 (2B), −14.0 (1B), −15.6 (1B), −18.8 (2B), −21.3 (1B), −32.8 (1B), −36.9 (1B).

X-Ray crystallography

Single crystal X-ray diffraction experiments were carried out with a SMART 1K CCD area detector, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The reflection intensities were not corrected for absorption. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL programs.[26] Crystal data and experimental details are listed in Table 5.

CCDC reference numbers 160969–160972.

See http://www.rsc.org/suppdata/dt/b1/b102009i/ for crystallographic data in CIF or other electronic format.

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