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FULL PAPER

Halogen derivatives of monocarbon carboranes, *nido*-7-Me_3N-7-$CB_{10}H_{12}$, *closo*-2-Me_3N-2-$CB_{10}H_{10}$ and *closo*-1-Me_3N-1-$CB_{11}H_{11}$ ‡

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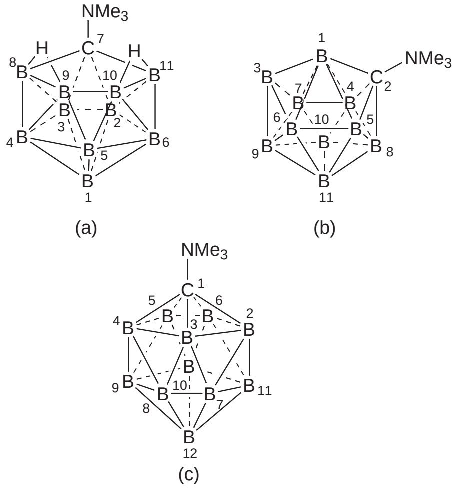
Electrophilic iodination and bromination (X_2–$AlCl_3$) of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ gave *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ and *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ and the bromine-substituted analogues *nido*-4-Br-7-Me_3N-7-$CB_{10}H_{11}$ and *nido*-4,6-Br_2-7-Me_3N-7-$CB_{10}H_{10}$. Electrophilically induced nucleophilic substitution (HI–$AlCl_3$) gave *nido*-9-I-7-Me_3N-7-$CB_{10}H_{10}$. These compounds readily deprotonated to the dianions [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$, [*nido*-4-I-7-Me_3N-7-$CB_{10}H_9$]$^{2-}$ and [*nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_8$]$^{2-}$, and oxidation (chemical or electrochemical) gave derivatives of *closo*-2-Me_3N-2-$CB_{10}H_{10}$ and *closo*-3-I-2-Me_3N-2-$CB_{10}H_9$. Low temperature insertion reactions of the anions with $PhBCl_2$ gave *closo*-8-I-2-Ph-1-Me_3N-1-$CB_{11}H_9$ and *closo*-8-Br-2-Ph-1-Me_3N-1-$CB_{11}H_9$, while electrophilic iodination occurred at B(12) to give *closo*-12-I-1-Me_3N-1-$CB_{11}H_{10}$. Palladium catalysed substitution of iodine resulted in the *nido* and *closo* derivatives *closo*-8-CH_2=$CHCH_2$-2-Ph-1-Me_3N-1-$CB_{11}H_9$ and *nido*-4-CH_2=$CHCH_2$-7-Me_3N-7-$CB_{10}H_{11}$. AM1 Calculations were used to help rationalise a mechanism for the boron insertion reactions.

In the search for monocarbon carboranes with biologically active functional substituents for application in ^{10}B neutron capture therapy we required as synthons halogenated derivatives with a replaceable halogen such as iodine, amenable to further substitution by palladium-catalysed reactions with Grignard reagents or other organometallic derivatives. We also require to be able to achieve iodine substitution for ^{131}I radiolabelled derivatives. Such iodine derivatives of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ have not been reported to date, although 7,12 disubstitution of [$CB_{11}H_{12}$]$^-$ has been reported.[1] Monoiodination of *closo*-1,2- and 1,7-$C_2B_{10}H_{12}$ was accomplished by electrophilic halogenation to yield mainly the 9-I-substituted products.[2] The halogenation reactions of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ using Cl_2, *N*-chlorosuccinimide, and Br_2 were reported under vigorous conditions to occur at the 4(6) position for monosubstitution, or at the 4,6 positions for disubstitution,[3] but the reactions failed to yield iodine-substituted compounds. Other substitution reactions of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ have given isomeric products, depending on the reaction conditions. The compound *nido*-4-Cl-7-Me_3N-7-$CB_{10}H_{11}$ was obtained by electrochemical oxidation using a chloride electrolyte, whereas *nido*-9-Cl-7-Me_3N-7-$CB_{10}H_{11}$ and 6,9-Cl_2-7-Me_3N-7-$CB_{10}H_{10}$ resulted from electrophilic-induced nucleophilic substitution using HCl and $AlCl_3$.[4]

In this work we have investigated the electrophilic and electrophilically induced nucleophilic substitution of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ and *closo*-1-Me_3N-1-$CB_{11}H_{11}$ using I_2, Br_2 or HI in the presence of $AlCl_3$, and reactions of the dianion [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$ with halogens generated chemically and electrochemically. We report studies of the electrochemical oxidation of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ and *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$, and the dianions [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$ and [*nido*-4-I-7-Me_3N-7-$CB_{10}H_9$]$^{2-}$ to give the *closo* compounds *closo*-2-Me_3N-2-$CB_{10}H_{10}$ and *closo*-3-I-2-Me_3N-2-$CB_{10}H_9$.

We have also achieved low-temperature insertion reactions into iodine-substituted *nido* derivatives to yield the substituted derivatives *closo*-8-I-2-Ph-1-Me_3N-1-$CB_{11}H_{10}$ and *closo*-8-Br-2-Ph-1-Me_3N-1-$CB_{11}H_{10}$, and have investigated the mechanism of the boron insertion reaction using semiempirical (AM1) calculations. Palladium-catalysed substitution of *nido* and *closo* iodinated derivatives was also performed to give the organic derivatives 4-CH_2=$CHCH_2$-7-Me_3N-7-$CB_{10}H_{11}$ and 8-CH_2=$CHCH_2$-2-Ph-1-Me_3N-1-$CB_{11}H_{10}$ for the first time. The structures and numbering schemes for the clusters in this work are illustrated in Scheme 1.



Scheme 1 Structures and numbering schemes[5] for (a) *nido*-7-Me_3N-7-$CB_{10}H_{12}$, (b) *closo*-2-Me_3N-2-$CB_{10}H_{10}$ and (c) *closo*-1-Me_3N-1-$CB_{11}H_{11}$

Results and Discussion

Preparative chemical reactions

The preparation of the previously unknown 4-iodine-substituted derivatives of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ was achieved through the electrophilic substitution reaction of iodine in the presence of aluminium chloride and CH_2Cl_2. The products *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ **1** and *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ **2** were obtained by selecting the reactant ratios of 1 : 1 or 1 : 2 respectively, and their structures determined from their ^{11}B NMR spectra. A similar electrophilic substitution of *closo*-1-Me_3N-1-$CB_{11}H_{11}$ gave *closo*-12-I-1-Me_3N-1-$CB_{11}H_{10}$ **3**. The

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‡ *Non-SI units employed*: cal = 4.184 J, hartree ≈ 4.36×10^{-18} J.

corresponding electrophilic monobromination was less straightforward, and with catalytic quantities of either $AlCl_3$ or $FeCl_3$ a mixture of the mono- and di-bromo derivatives **4** and **5** and starting compound was usually obtained. Careful control of reactant ratios and temperature was required to achieve the pure monosubstituted product *nido*-4-Br-7-Me_3N-7-$CB_{10}H_{11}$ **4**. Using $AlCl_3$, with a reactant ratio of 1 : 2, the major substituted product was *nido*-4,6-Br_2-7-Me_3N-7-$CB_{10}H_{10}$ **5**.

In order to achieve substitution at a different boron site several different approaches were attempted. In earlier work[4] electrophilically induced nucleophilic chlorination was attained with HCl in the presence of $AlCl_3$; a similar electrophilically induced nucleophilic iodination using HI in the presence of $AlCl_3$ resulting in substitution at B(9) was achieved in this work after carefully controlling reactant ratios, quantity of catalyst, and temperature and reaction time. The reaction of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ with HI was much faster than that with HCl, yielding *nido*-9-I-7-Me_3N-7-$CB_{10}H_{11}$ **6**, and extensive further substitution or I–Cl exchange with the catalyst resulting in chlorinations occurred when stoichiometric quantities of $AlCl_3$ were used.

The electrophilic substitution of [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$ **7** was also examined as a route to substitution at a different boron site. The anion, prepared by deprotonation of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ using $(Me_3N)_2C{=}NH$, equation (1), underwent oxidation with I_2 in CH_2Cl_2 to yield *closo*-2-Me_3N-2-$CB_{10}H_{10}$ **8** rather than give the 9-substituted *nido* product expected on the basis of charge distribution in the dianion; this is similar to the reaction observed from deprotonation with sodium hydride.[3]

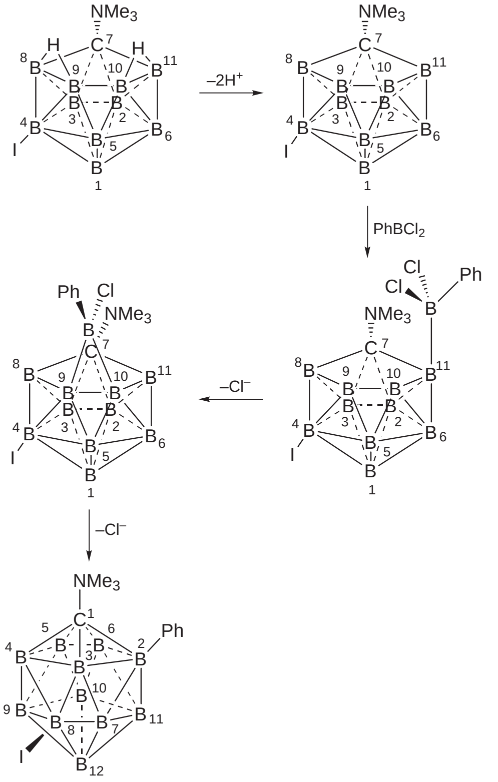
$$\textit{nido}\text{-7-Me}_3\text{N-7-CB}_{10}\text{H}_{12} + 2(\text{Me}_2\text{N})_2\text{C=NH} \xrightarrow{\text{MeCN or CH}_2\text{Cl}_2} [(\text{Me}_2\text{N})_2\text{C=NH}_2]^+{}_2\,[\textit{nido}\text{-7-Me}_3\text{N-7-CB}_{10}\text{H}_{10}]^{2-}\ (\mathbf{7}) \xrightarrow{\text{I}_2\text{–CH}_2\text{Cl}_2} \textit{closo}\text{-2-Me}_3\text{N-2-CB}_{10}\text{H}_{10}\ (\mathbf{8}) \quad (1)$$

An alternative strategy for the preparation of other isomers may have resulted from rearrangement of the deprotonated dianions [*nido*-4-I-7-Me_3N-7-$CB_{10}H_9$]$^{2-}$ **9** and [*nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_8$]$^{2-}$ **10** obtained from reaction of $(Me_2N)_2C{=}NH$ with *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ **1** and *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ **2**. Such rearrangements occur readily in dicarbaundecaborates. The oxidation of the *nido* anions **9** and **10** with I_2 gave iodinated *closo* anions, a single isomer of *closo*-3-I-2-Me_3N-2-$CB_{10}H_9$ **11**, and a mixture of isomers of *closo*-I_2-2-Me_3N-2-$CB_{10}H_8$.

Although the direct electrophilic iodination of *closo*-1-Me_3N-1-$CB_{11}H_{11}$ resulted in substitution at B(12), the introduction of an iodine or bromine substituent at B(8) has been achieved by a low-temperature boron insertion reaction[6] on a B(4)-substituted *nido* precursor, whereas previous attempts to prepare chlorine-substituted analogues using the high temperature insertion with $Et_3N{\cdot}BH_3$ resulted in removal of the substituent and isolation of the unsubstituted *closo*-1-Me_3N-1-$CB_{11}H_{11}$.[4]

The reaction (2) to produce **12** proceeded without removal of the iodine substituent, and without rearrangement of the dianion prior to boron insertion. Attempts to carry out similar insertion reactions on the disubstituted derivative **10** have so far been unsuccessful. However the insertion reaction was successful using $PhBCl_2$ and the anions derived from the 4-Br derivative **4**. The iodine of the substituted *closo*-derivative **12** reacted with allylmagnesium bromide in the presence of $[Pd(PPh_3)_4]$ in thf to give the corresponding allyl-substituted carborane *closo*-8-$CH_2{=}CHCH_2$-2-Ph-1-Me_3N-1-$CB_{11}H_9$ **13**, as had been obtained earlier in *closo*-$C_2B_{10}H_{12}$.[7] A similar reaction on *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ **1** gave *nido*-4-$CH_2{=}CHCH_2$-7-Me_3N-7-$CB_{10}H_{11}$ **14**.

$$\text{PhBCl}_2 + [\textit{nido}\text{-4-I-7-Me}_3\text{N-7-CB}_{10}\text{H}_9]^{2-} \xrightarrow{-2\text{Cl}^-} \textit{closo}\text{-8-I-2-Ph-1-Me}_3\text{N-1-CB}_{11}\text{H}_9\ (\mathbf{12}) \quad (2)$$



Scheme 2 Proposed mechanism for boron insertion reactions, illustrated by *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ and $PhBCl_2$

Semiempirical methods for rationalising the mechanism of boron insertions

The experimental observations on the low-temperature boron insertion reactions involving compounds **7**, **9** and **10** with $PhBCl_2$ indicate that the mechanism is probably complex. By analogy with known reactions of boron–boron bonds in B_6H_{10} and $[B_5H_8]^-$, the first step in this reaction is assumed to involve the formation of a Lewis base–Lewis acid complex between the dianion and the incoming boron reagent, as indicated in Scheme 2. The effect of iodine on the charge distribution in the anions may have influenced the electron density on the boron atoms of the open face of the dianions **9** and **10**, *i.e.* B(8), B(9), B(10) and B(11), and thus their ability to co-ordinate to the vacant orbital of the boron in $PhBCl_2$ at the initial stage of the reaction. Alternatively, the approach of the incoming boron may be affected by the steric constraints induced on substitution. AM1 Calculations were made on the model reaction systems between the anions **7**, **9** and **10** and $MeBCl_2$. This led to the total energies of selected molecules (Table 1), enthalpies of Lewis base–Lewis acid reactions, the optimised geometries of the base–acid complexes (which are the presumed first intermediates in the boron insertion reactions), and the natural charge distributions in the anions and complexes (Table 2). The calculations showed (a) that the geometry optimised so as to place the inserting reagent on a specific atom, rather than at an edge, and (b) that the inserting reagent attached at B(8) or B(11) in preference to B(9), B(10) or C(7); the effect of iodine substitution was to reduce the enthalpy of the reaction to form the complex in which the reagent attached at the site closest to the iodine substituent thus differentiating B(8) and B(11) in monosubstituted **9**. These enthalpy changes are indicated in Scheme 3.

These calculations do not take into account any kinetic factors in the reactions. Although the natural charges on B(8,11) were marginally less negative than those on B(9,10) in the anions suggesting that these sites may be less favoured by the incoming reagent, the relative enthalpies of the Lewis base–Lewis acid complexes indicated more stable complexes at these sites.

$[nido\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}]^{2-} + MeBCl_2 \longrightarrow$
$[nido\text{-}8\text{-}MeBCl_2\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}]^{2-}$; ΔH −46.68 kcal mol^{-1}

$[nido\text{-}4(6)\text{-}I\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_9]^{2-} + MeBCl_2 \longrightarrow$
$[nido\text{-}8\text{-}MeBCl_2\text{-}4\text{-}I\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_9]^{2-}$; ΔH −37.90 kcal mol^{-1}

$[nido\text{-}4(6)\text{-}I\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_9]^{2-} + MeBCl_2 \longrightarrow$
$[nido\text{-}8\text{-}MeBCl_2\text{-}6\text{-}I\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_9]^{2-}$; ΔH −41.42 kcal mol^{-1}

$[nido\text{-}4,6\text{-}I_2\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_9]^{2-} + MeBCl_2 \longrightarrow$
$[nido\text{-}8\text{-}MeBCl_2\text{-}4,6\text{-}I_2\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_9]^{2-}$; ΔH −33.39 kcal mol^{-1}

Scheme 3

Table 1 The AM1 calculated heats of formation

Compound	Heat of formation/kcal mol^{-1}
7	+126.06
9	+105.59
10	+86.88
$MeBCl_2$	−75.82
7·8-$MeBCl_2$	+3.56
7·9-$MeBCl_2$	+8.79
9·8-$MeBCl_2$	−8.13 (4-I)
9·8-$MeBCl_2$	−11.65 (6-I)
9·9-$MeBCl_2$	−2.01 (4-I)
9·9-$MeBCl_2$	−8.13 (6-I)
10·8-$MeBCl_2$	−22.33
10·9-$MeBCl_2$	−11.48
7·8-$PhBCl_2$	+35.51 (Ph over cage)
7·8-$PhBCl_2$	+33.53 (Ph *exo* to cage)
7·9-$PhBCl_2$	+39.12 (Ph over cage)
7·9-$PhBCl_2$	+36.75 (Ph *exo* to cage)
6*·8-$MeBCl_2$	+1.56
6*·11-$MeBCl_2$	−13.18
7·9,10-MeBCl	−8.04
closo-2-Me-1-Me_3N-1-$CB_{11}H_{10}$	+53.08
Cl^-	−37.66

* Deprotonated compound **6** ($[nido\text{-}9\text{-}I\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_9]^{2-}$).

The substantial reduction in reaction enthalpy and the steric restrictions indicated in the space-filling model of compound **10** (Fig. 1) together suggest that the failure to achieve boron insertion with **10** primarily resulted from the steric effects of iodine substitution. Kinetic factors may play an important part here.

The validity of the AM1 data was supported by single point *ab initio* calculations at the HF/6-31G* level on adducts **7**·8-$MeBCl_2$ and **7**·9-$MeBCl_2$ giving total energies of −1446.954 603 6 and −1446.933 545 5 hartrees respectively; this indicated that the addition product at position 8 was more stable than that at position 9 by 13.12 kcal mol^{-1}. The second step in the insertion process is assumed to involve dissociation of Cl^- from the Lewis base–Lewis acid complex, and the product calculated to have the lowest heat of formation was the intermediate in which the inserting boron occupied a bridging site between B(9) and B(10). The third step involved elimination of a second Cl^- to give the final *closo* product. The enthalpy changes in these two steps are given in equations (3) and (4).

$$\mathbf{7}\cdot 8\text{-}MeBCl_2 \longrightarrow \mathbf{7}\cdot 9,10\text{-}MeBCl + Cl^-; \quad \Delta H = -42.14 \text{ kcal mol}^{-1} \qquad (3)$$

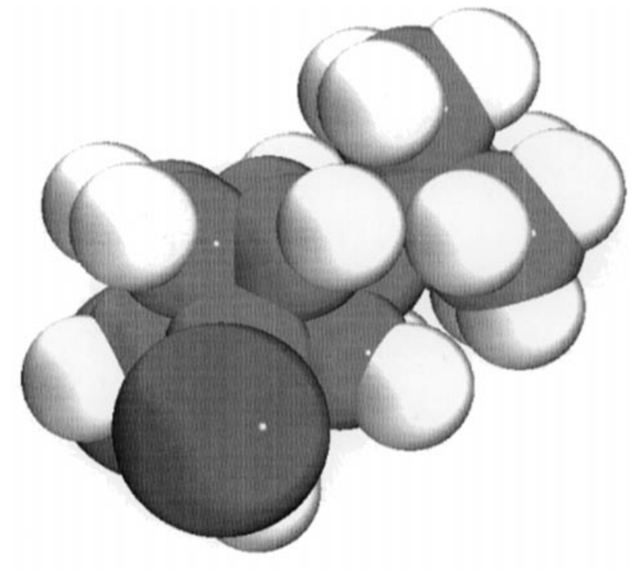


Fig. 1 Space-filling model of $[nido\text{-}4,6\text{-}I_2\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_8]^{2-}$

Table 2 Semiempirical (AM1) natural charge distributions

Compound	B(1)	B(2)	B(3)	B(4)	B(6)	B(5)	B(8)	B(11)	B(9)	B(10)	C(7)
$Me_3NCB_{10}H_{12}$	−0.07	0.01	0.01	−0.21	−0.21	0.07	−0.05	−0.05	−0.09	−0.09	−0.43
7	−0.17	−0.16	−0.16	−0.13	−0.13	−0.09	−0.07	−0.07	−0.08	−0.08	−0.32
9 (6-I)	−0.16	−0.15	−0.14	−0.12	−0.25	−0.06	−0.06	−0.04	−0.10	−0.06	−0.33
10 (4,6-I_2)	−0.15	−0.13	−0.13	−0.25	−0.25	−0.03	−0.03	−0.03	−0.08	−0.08	−0.34
7·8-$MeBCl_2$	−0.11	−0.17	−0.01	−0.19	−0.06	−0.09	−0.07	0.01	0.04	−0.16	−0.34
7·9-$MeBCl_2$	−0.03	−0.09	−0.25	−0.11	−0.13	−0.09	0.05	−0.11	−0.16	−0.01	−0.25
9·8-$MeBCl_2$ (6-I)	−0.10	−0.16	0.00	−0.18	−0.19	−0.06	−0.08	0.03	0.03	−0.14	−0.35
9·8-$MeBCl_2$ (4-I)	−0.10	−0.16	−0.02	−0.32	−0.01	−0.06	−0.05	0.01	0.05	−0.17	−0.36
9·9-$MeBCl_2$ (6-I)	−0.04	−0.06	−0.24	−0.13	−0.28	−0.06	0.11	−0.06	−0.24	0.00	−0.26
9·9-$MeBCl_2$ (4-I)	−0.02	−0.07	−0.23	−0.26	−0.13	−0.15	0.07	−0.11	−0.17	−0.01	−0.25
10·8-$MeBCl_2$ (4,6-I_2)	−0.09	−0.15	−0.01	−0.32	−0.20	−0.03	−0.05	0.04	0.04	−0.15	−0.34
10·9-$MeBCl_2$ (4,6-I_2)	−0.09	−0.07	−0.20	−0.20	−0.29	0.02	0.04	−0.04	−0.23	−0.02	−0.31
7 *	−0.20	−0.10	−0.01	−0.16	−0.16	−0.15	−0.08	−0.08	−0.34	−0.34	−0.56

* *Ab initio* at the HF/6-31G* level.

Table 3 Voltammetric data (mV) for oxidations and reductions

	Me_3NCB_{10}-H_{12}[a]	**1**[a]	**2**[a]	**7**[b]
A First oxidation[c]	>2200	2200	>2200	1800[d]
B First reduction[e]	<−1000[f,g]	−600 to −700[h]	−600[f]	Obscd.
Oxidation after B[i]	50	270	600–700	
Other oxidations[i]	400	450	900–950	
		750–800		
	900–990	1050	1900–1960	

[a] In NBu_4PF_6. [b] In $[(Me_2N)_2CNH_2]BF_4$. [c] SW potential scans from 300 to 2200 mV. [d] Scans from 500 to 2400 mV; broad peak commencing near 1100 mV. [e] SW. [f] SW scans from 900 to −1000 mV. [g] CV at −1100 mV in NBu_4BF_4. [h] SW scans from 0 to −1900 mV. [i] The current was determined by the extent to which the scan was carried into the first reduction B.

$$\mathbf{7}\cdot 9,10\text{-MeBCl} \longrightarrow closo\text{-2-Me-1-Me}_3\text{N-1-CB}_{11}\text{H}_{10}; \quad \Delta H = 23.46\ \text{kcal mol}^{-1} \quad (4)$$

These reaction enthalpies neglect the lattice energy of the formation of the LiCl by-product (−203.6 kcal mol^{-1}) which will drive the reactions forward. Indeed, attempts to perform boron insertion reactions using tetramethylguanidinium salts of the dianons were unsuccessful.

Voltammetry and electrochemical oxidation/substitution

Voltammetry. In order to understand better the nature of the halogenation reactions, cyclic (CV) and square wave (SWV) voltammetry of *nido*-7-Me_3N-7-$CB_{10}H_{12}$, *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ **2**, *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ **1** and [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$ **7** were examined in MeCN using platinum working and counter electrodes, a silver wire reference, and NBu_4BF_4, $[(Me_2N)_2CNH_2]BF_4$, or NBu_4PF_6 as supporting electrolytes. The results are presented in Table 3.

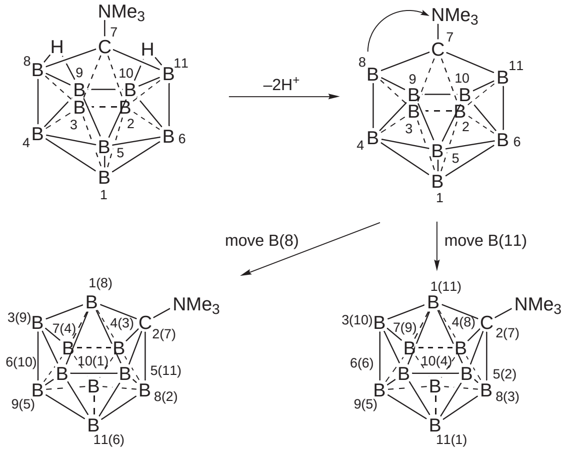
All the electrochemical processes observed were irreversible, and the oxidation and reduction peaks in the CV and SWV often depended on the potential limits employed and the direction of the potential scan. No significant oxidation of the neutral compounds was observed below *ca.* +2.0 V (silver wire), provided the voltammetric scan did not commence at a (negative) potential sufficient to achieve reduction. Since the voltammetric currents have not been related to the number of electrons involved, their interpretation must be somewhat speculative. The primary oxidation of the *nido* compounds must have involved the formation of radical cations (or dications) which then rapidly eliminated hydrogen ions ultimately to lead to *closo*-2-Me_3N-2-$CB_{10}H_{10}$ **8** or its iodinated analogues, equation (5). The primary reduction also may have produced

$$nido\text{-7-Me}_3\text{N-7-CB}_{10}\text{H}_{12} \xrightarrow{+e^-} [\text{Me}_3\text{NCB}_{10}\text{H}_{12}]^{\bullet +} \xrightarrow{+e^-\ -2H^+} closo\text{-2-Me}_3\text{N-2-CB}_{10}\text{H}_{10} \quad (5)$$

radical anions which underwent loss of $H^{\bullet}$ to give the monoanions, and disproportionation or further reduction and H_2 loss to give the dianions, equation (6). It is possible that the secondary oxidation peaks are due to oxidation of the mono- and dianions, the potentials of which were a function of their degree of substitution.

$$nido\text{-7-Me}_3\text{N-7-CB}_{10}\text{H}_{12} \xrightarrow{+e^-} [\text{Me}_3\text{NCB}_{10}\text{H}_{12}]^{\bullet +} \xrightarrow{+e^-\ -H_2} [nido\text{-7-Me}_3\text{N-7-CB}_{10}\text{H}_{10}]^{2-} \quad (6)$$

Bulk electrochemical reactions. The bulk electrochemical oxidation of [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$ **7** in acetonitrile with $[(Me_2N)_2C{=}NH_2]BF_4$ supporting electrolyte led to *closo*-2-Me_3N-2-$CB_{10}H_{10}$ **8** whereas a similar electrochemical reaction on *nido*-7-Me_3N-7-$CB_{10}H_{12}$ resulted only in the isolation of unchanged starting compound, although this may have been in part due to the instability of **8** on SiO_2 during chromatographic work-up. The corresponding electrochemical oxidation of [*nido*-4-I-7-Me_3N-7-$CB_{10}H_9$]$^{2-}$ **9** yielded the monoiodine-substituted derivative *closo*-3(7 or 10)-I-2-Me_3N-2-$CB_{10}H_9$ **11** whose identity was inferred from its ^{11}B NMR data. This compound is almost certainly fluxional in the same way as other 11-vertex *closo*-polyhedra, including *closo*-2-Me_3N-2-$CB_{10}H_{10}$ **8**.



Scheme 4 Vertex swing mechanism for generation of *closo*-2-Me_3N-2-$CB_{10}H_{10}$ from *nido*-7-Me_3N-7-$CB_{10}H_{12}$, with numbering schemes (The numbers in parentheses are those of the boron atoms in the *nido* precursor.)

Structures from ^{11}B and ^{1}H NMR and mass spectra

NMR data. The ^{11}B NMR data for the compounds are presented in Table 4. Unambiguous assignments have been made on the basis of the observed couplings (singlets for substituted borons, and bridge hydrogen coupled broadening in neutral *nido* derivatives) and ^{11}B–^{11}B COSY correlations. The assignments of the spectra of **7** and **9** were ambiguous, even with COSY data, but clearly differed from those of the neutral compounds.

The structures of the *nido* compounds, determined from their NMR spectra, established that iodine and bromine substitution occurred at B(4) and B(4,6) in **1**, **2**, **4** and **5**, and B(9) in **6**, and these substituted positions were retained on deprotonation to the dianions. Furthermore, the boron with the substituent does not undergo rearrangement during the oxidation from *nido*- to *closo*-CB_{10} either chemically or electrochemically. A substituent in position B(4) of the *nido*-carboranes is expected to appear at position B(7) or B(10) of the *closo*-carboranes in conjunction with a vertex swing of B(8) or B(11) in the parent to B(1) of the product. If the substituted *closo*-carborane is fluxional, positions B(7) and B(10) in the product are indistinguishable and equivalent to B(3), B(6) and B(11), but should appear in the NMR spectrum at three chemical shift positions with relative intensities of 1:2:2, due to B(3) (substituted), B(6,7) and B(10,11); furthermore, B(1), B(4), B(8) and B(5) form a separate equivalent set of boron sites of relative intensity 4. In the unsubstituted *closo* compound which is known to be fluxional, B(3), B(7), B(10), B(11) and B(6) are also equivalent and give one chemical shift of relative intensity 5. See Scheme 4 for the generation of *closo*- from *nido*-CB_{10} carborane.

The structure of the *closo*-CB_{11} compound **3** is unambiguously determined to be B(12) substituted in view of the resonances with relative intensities 1:5:5 (singlet at δ −16.5,

Table 4 Boron-11 NMR data in CD_3CN

Compound	δ	J_{BH}/Hz	Intensity	Assignment	^{11}B–^{11}B COSY correlations
1	2.88	143.8	1B	B(5)	B(1; 4; 6; 9; 10)
	−8.57	155.3	1B	B(3)	B(1; 4)
	−9.14	?	1B	B(2)	B(1; 6)
	−11.76	138.6	1B	B(8)	B(4)
	−14.46	130	1B	B(11)	B(6)
	−19.20	110	1B	B(9)	B(4; 5; 10)
	−21.67	120.7	1B	B(10)	B(5; 6; 9)
	−23.68	150.2	1B	B(1)	B(2; 3; 4; 5; 6)
	−31.96	150.2	1B	B(6)	B(1; 2; 5; 10; 11)
	−40.61 (s)	—	1B	B(4)	B(1; 3; 5; 8; 9)
2	4.53	156.6	1B	B(5)	B(9,10)
	−8.00	161.8	2B	B(2,3)	B(1; 4,6)
	−12.23	132.2	2B	B(8,11)	B(4,6)
	−18.53	127.1	2B	B(9,10)	B(4,6; 5)
	−21.35	150.2	1B	B(1)	B(2,3; 4,6)
	−40.34 (s)	—	2B	B(4,6)	B(1; 5; 2,3; 8,11; 9,10)
4	2.82	138.6	1B	B(5)	
	−8.85	148.9	1B	B(3)	
	−9.95	147.6	1B	B(2)	
	−12.60	139.9	1B	B(8)	
	−15.99	137.4	1B	B(11)	
	−20.12	152.8	1B	B(9)	
	−22.26	141.2	1B	B(10)	
	−23.90 (s)	—	1B	B(4)	
	−24.44	150	1B	B(1)	
	−32.65	146.3	1B	B(6)	
6	2.44	154	1B	B(5)	
	−9.62	?	?	impurity	
	−10.89	150.2	1B	B(3)	
	−12.53	?	1B	B(8)	
	−13.97	155	1B	B(2)	
	−14.95	~100	1B	B(11)	
	−16.91 (s)	—	1B	B(10)	
	−20.43	152	1B	B(9)	
	−27.94	143.8	1B	B(1)	
	−30.17	147.7	1B	B(4)	
	−33.07	154.0	1B	B(6)	
5	4.20	155.3	1B	B(5)	
	−9.30	157.9	2B	B(2,3)	
	−14.87	137.4	2B	B(8,11)	
	−20.16	147.6	2B	B(9,10)	
	−23.81 (s + d)	—	3B	B(1,4,6)	
7	−18.05	154.0	2B	B(9,10)	B(5; 4,6; 8,11)
	−19.52	161.7	2B	B(4,6)	B(1; 5; 2,3; 8,11; 9,10)
	−21.35	145.8	2B	B(2,3)	B(4,6)
	−26.78	123.2	3B	B(8,11;5)	B(4,6; 9,10)
	−40.59	129.7	1B	B(1)	B(2,3; 4,6)
9	−16.38	116.8	1B	B(8)	B(9)
	−19.48	119.4	1B	B(11)	B(6; 10)
	−19.81	114.3	1B	B(3)	B(1; 4)
	−21.22	133.5	2B	B(2,6)	B(1; 5; 10; 11)
	−22.58	133.5	1B	B(9)	B(8)
	−23.98	142.5	1B	B(5)	B(1; 4; 6; 10)
	−27.22 (s)	—	1B	B(4)	B(1; 3; 5)
	−28.05	?	1B	B(10)	B(5; 6; 11)
	−38.96	137.4	1B	B(1)	B(2; 3; 4; 5; 6)
10	−17.47	130.9	2B	B(8,11)	B(5; 4,6; 9,10)
	−20.08	150.2	2B	B(2,3)	B(1; 4,6; 8,11)
	−21.99	156	1B	B(5)	B(1; 4,6; 9,10)
	−23.55	≈160	2B	B(9,10)	B(5; 4,6; 8,11)
	−28.11 (s)	—	2B	B(4,6)	B(1; 5; 2,3; 8,11; 9,10)
	−37.04	143.8	1B	B(1)	B(5; 2,3; 4,6)
8	−4.28	138.6	1B	B(9)	
	−10.88	146.3	5B	B(3,6,7,10,11)	
	−14.03	155.3	4B	B(1,4,5,8)	

Table 4 (*Contd.*)

Compound	δ	J_{BH}/Hz	Intensity	Assignment	^{11}B–^{11}B COSY correlations
11	8.08 (s)	—	1B	B(3)	
	−11.01	141.2	4B	B(1,4,5,8)	
	−13.82	156.6	2B		
	−18.46	150.2	2B		
	−22.15	159.2	1B	B(9)	
3	−11.76	147.6	5B	B(7,8,9,10,11)	
	−14.39	160.5	5B	B(2,3,4,5,6)	
	−16.50	—	1B	B(12)	
12	−4.00 (s)	—	1B	B(2)	B(3; 7; 11)
	−4.29	?	1B	B(12)	B(7; 8; 10)
	−9.14	159.2	1B	B(7)	B(2; 3; 8; 11)
	−10.66	161.7	1B	B(11)	B(2,12; 6,7,10)
	−12.95	152.7?	2B	B(3,4)	B(2,12; 7; 8)
	−14.76	148.9	3B	B(5,9,10)	B(11)
	−15.81	?	1B	B(6)	B(11)
	−26.19 (s)	—	1B	B(8)	B(3,4,7,12)
13	−5.17	unresolved	3B	B(2,8,12)	
	−10.20	≈170	1B	B(7)	
	−11.46	150	1B	B(11)	
	−13.96	?	2B	B(3,4)	
	−14.2 (sh)	?	1B	B(5)	
	−15.57	≈150	2B	B(9,10)	
	−17.47	≈160	1B	B(6)	
14	2.43	134.8	1B	B(5)	
	−8.94	140	1B	B(3)	
	−10.03	145.1	1B	B(2)	
	−13.35	127.1	1B	B(8)	
	−15.74	161	1B	B(11)	
	−21.14	130	1B	B(9)	
	−22.58	≈200	1B	B(10)	
	−23.66 (s)	—	1B	B(4)	
	−25.02	135	1B	B(1)	
	−32.67	144	1B	B(6)	
15	−4.40	Unresolved	1B	B(12)	
	−5.05 (s)	—	1B	B(2)	
	−9.98		1B	B(7)	
	−10.90		2B	B(3,4)	
	−11.60		1B	B(11)	
	−14.06		3B	B(5,9,10)	
	−14.86 (s)	—	1B	B(8)	
	−17.94		1B	B(6)	

doublets at δ −14.39 and −11.76). The structure of **12** was established by the complexity, indicating the lack of a plane of symmetry, and COSY correlations which are best interpreted by the substituents at B(8)–I and B(2)–Ph. The structures of **13** and **15** were then assigned by analogy with **12**.

The ^{1}H NMR spectra of compounds **12**, **13** and **15** showed two groups of resonances near δ 7.36 and 7.76 (relative intensity 2:3) due to phenyl hydrogens, and singlets (relative intensity 9) near δ 3.05 due to the NMe_3 group. Additionally **13** and **14** showed multiplets of relative intensities 1:2:2 near δ 5.9 (=CH), 4.74 (=CH_2) and 1.65 (broad) (BCH_2) from the allyl group, consistent with observations on *B*-allyl-1,2-dicarba-*closo*-dodecaborane.[7] The effects of halogen substitution on the ^{11}B chemical shifts are best illustrated by schematic correlation diagrams, Fig. 2.

Mass spectra. The mass spectra of the *nido* derivatives further supported the structures, with the observation in **2** of molecular ions M^+ and fragment ions near *m*/*z* 431 due to $[M - BH]^+$, with more extensive cluster degradation/rearrangement giving ions near *m*/*z* 327 (due to species containing $CB_{11}I$), 200 (CB_{11}), 190 (CB_{10}) and 178 (CB_9). The mass spectrum of **11** gave no molecular ion, but instead a mixture of the molecular ions of species containing $CB_{11}I$ (*m*/*z* 328–326), CB_9I (304–302), and fragment ions due to iodine loss from all the molecular ions, *e.g.* *m*/*z* 200 (CB_{11}), 190 (CB_{10}) and 178 (CB_9). The mass spectrum of **3** showed the expected ions due to M^+ (*m*/*z* 327) and $[M - I]^+$ (*m*/*z* 200).

Experimental

Electrophilic iodination (1:1 and 1:2) of *nido*-7-Me_3N-7-$CB_{10}H_{12}$

Preparation of *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ 1. A mixture of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (1.91 g, 10 mmol), I_2 (2.54 g, 10 mmol) and $AlCl_3$ (1.33 g, 10 mmol) in dry CH_2Cl_2 (20 cm^3) was refluxed for 15–20 min. After the reaction was complete (when the condensate became colourless) the mixture was poured into water (30 cm^3), the organic layer separated, and the aqueous layer extracted with CH_2Cl_2 (15 cm^3). The extracts were combined, washed with water, and dried over $MgSO_4$. The solvent was removed *in vacuo* and crystallisation of the residue from MeCN–EtOH yielded *compound* **1** (2.92 g, 92%), m.p. 275 °C (with decomposition) (Found: C, 16.13; H, 6.72; N, 4.66. $C_4H_{20}B_{10}IN$ requires C, 15.14; H, 6.31; N, 4.42%).

Preparation of *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ 2. A mixture of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (1.91 g, 10 mmol), I_2 (5.0 g, 20 mmol) and $AlCl_3$ (1.33 g, 10 mmol) in dry CH_2Cl_2 (30 cm^3) was refluxed for 30 min. After the reaction was complete the mixture

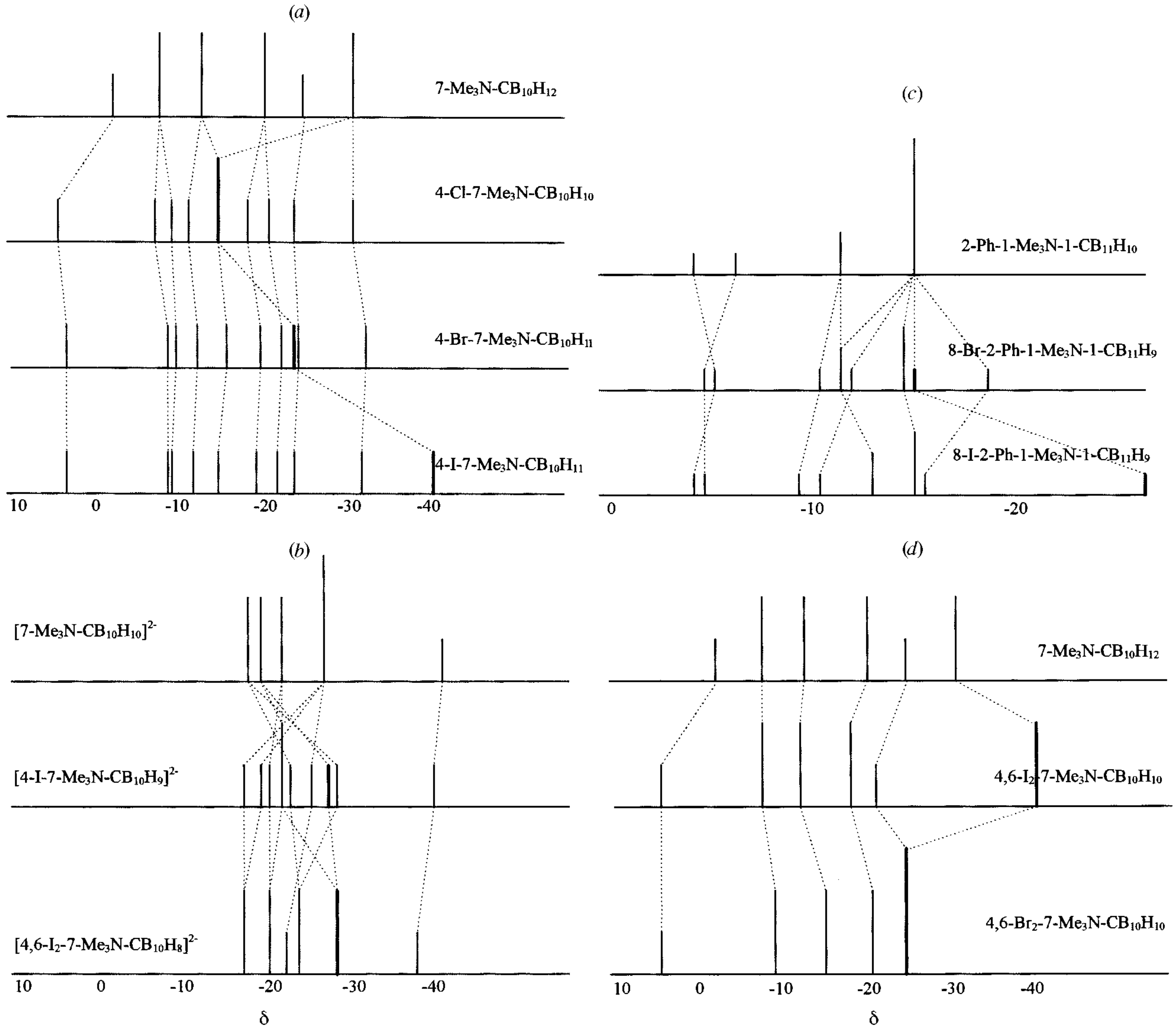


Fig. 2 Schematic ^{11}B NMR correlation diagrams: (*a*) monosubstituted derivatives of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ **1** and **4** (including data from ref. 4); (*b*) *nido* dianions **7**, **9** and **10**; (*c*) *closo* compounds **12** and 8-Br-2-Ph-1-Me_3N-1-$CB_{11}H_9$ **15**; (*d*) *nido*-disubstituted compounds **2** and **5**

was worked up as for compound **1**. Crystallisation of the residue from MeCN–EtOH yielded *compound* **2** (3.99 g, 90%), m.p. 258–260 °C (with decomposition) (Found: C, 11.10; H, 4.29; N, 3.09. $C_4H_{19}B_{10}I_2N$ requires C, 10.84; H, 4.29; N, 3.16%).

Electrophilic iodination of *closo*-1-Me_3N-1-$CB_{11}H_{11}$

Preparation of *closo*-12-I-1-Me_3N-1-$CB_{11}H_{10}$ 3. *Compound* **3** was synthesized in a manner similar to that for **1** from 1-Me_3N-1-$CB_{11}H_{11}$ (0.4 g, 2 mmol), I_2 (0.51 g, 2 mmol) and $AlCl_3$ (0.27 g, 2 mmol), except that the reaction mixture was boiled for 1 h. After column chromatography on SiO_2 (eluent CH_2Cl_2–MeCN 1 : 1) compound **3** was obtained (0.53 g, 81%), m.p. 330 °C (decomp.) (Found: C, 15.18; H, 5.66; N, 4.36. $C_4H_{19}B_{11}IN$ requires C, 14.69; H, 5.81; N, 4.28%). *m*/*z* 328 (60), 327 (72), 326 (57), 325 (26, M^+), 202 (42), 201 (94), 200 (100), 199 (73) and 198 (46%, M − I).

Electrophilic bromination (1 : 1 and 1 : 2) of *nido*-7-Me_3N-7-$CB_{10}H_{12}$

Preparation of *nido*-4-Br-7-Me_3N-7-$CB_{10}H_{11}$ 4. A mixture of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (1 g, 5.5 mmol), Br_2 (0.93 g, 5.8 mmol) and $AlCl_3$ (0.025 g, 0.19 mmol) in dry CH_2Cl_2 (20 cm^3) was stirred for 1 h until the solution became colourless. The mixture was poured into water, the organic layer separated, washed with water, and dried over $MgSO_4$. The solvent was removed *in vacuo* and crystallisation of the residue from MeCN–EtOH yielded compound **4** (1.38 g, 93%), m.p. 300–302 °C. In other reactions using $AlCl_3$ or $FeCl_3$ at reflux for 10–15 min, a three-component mixture was obtained as indicated by TLC analysis on Silufol plates (eluent CH_2Cl_2): R_f 0.5, 0.4 and 0.3 corresponding to starting compound, mono- and di-bromo-derivatives. These were separated by suspending the product in EtOH (15 cm^3), refluxing for 30 min, and filtering the hot suspension to remove undissolved *nido*-7-Me_3N-7-$CB_{10}H_{12}$. Ethanol was distilled off *in vacuo* to give a mixture of 4-bromo- and 4,6-dibromo-substituted monocarboranes which were separated by column chromatography on SiO_2 (eluent CH_2Cl_2–Et_2O, 1 : 1) to yield compound **4** (Found: C, 18.07; H, 7.31; Br, 28.97; N, 5.04. Calc. for $C_4H_{20}B_{10}BrN$: C, 17.78; H, 7.41; Br, 29.65; N, 5.18%).

Preparation of *nido*-4,6-Br_2-7-Me_3N-7-$CB_{10}H_{10}$ 5. A mixture of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (0.45 g, 2.4 nmol), Br_2 (0.77 g, 4.8 mmol) and $AlCl_3$ (0.08 g, 0.6 mmol) in dry CH_2Cl_2 (20 cm^3) was refluxed for 15 min. The mixture was poured into water, the organic layer separated and dried over $MgSO_4$. Thin-layer chromatographic analysis on a Silufol plate indicated only one major product with only traces of monobromo-substituted compound. The solvent was distilled off *in vacuo*, and crystallisation of the residue yielded *compound* **5** (0.66 g, 79%), m.p. °C (Found: C, 14.44; H, 5.81; Br, 32.74; N, 4.09. $C_4H_{19}B_{10}Br_2N$ requires C, 13.75; H, 5.45; Br, 45.84; N, 4.01%).

Electrophilically induced nucleophilic iodination

Preparation of *nido*-9-I-7-Me_3N-7-$CB_{10}H_{11}$ 6. A mixture of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (0.955 g, 5 mmol) and $AlCl_3$ (0.07 g, 0.5 mmol) in dry CH_2Cl_2 (20 cm^3) was cooled to −40 °C. Gaseous HI (0.852 g, 6.5 mmol) was condensed in, the mixture warmed to 20 °C, and stirred for 4 h until the starting *nido*-7-Me_3N-7-$CB_{10}H_{12}$ had reacted (TLC analysis). The mixture was poured into water, the organic layer separated, washed with water, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue purified by column chromatography on SiO_2 (eluted with CH_2Cl_2) to yield the *product* **6** (1.41 g, 89%) as a white powder, m.p. 305–307 °C, identified by its ^{11}B NMR spectrum.

Similar reactions with stoichiometric quantities of $AlCl_3$ gave products whose NMR spectra indicated polysubstitution with iodine and/or chlorine.

Deprotonation and anion oxidation

Deprotonation of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ by $(Me_2N)_2C{=}NH$. A suspension of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (0.573 g, 3 mmol) in CH_2Cl_2 or MeCN (20 cm^3) was treated under nitrogen with $(Me_2N)_2C{=}NH$ (0.69 g, 6 mmol). The reaction mixture was stirred for 20 min to give a clear solution of the tetramethylguanidinium salt of the dianion [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$ **7**, identified by its NMR spectrum.

Reaction of [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$ with I_2. The compound *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (0.573 g, 3 mmol) in CH_2Cl_2 (20 cm^3) was deprotonated with $(Me_2N)_2C{=}NH$ (0.69 g, 6 mmol) as before, and then treated with I_2 (0.762 g, 3 mmol) at 20 °C. The solution was stirred for 1 h (until the iodine colour disappeared), then poured into water. The aqueous layer was separated and extracted with CH_2Cl_2–MeCN (1 : 1). The extract, combined with the organic layer, was washed with 5% aqueous Na_2SO_3 solution, then water, and dried over $MgSO_4$. Solvent was removed *in vacuo*, the residue chromatographed on SiO_2 (eluent CH_2Cl_2), to give *closo*-2-Me_3N-2-$CB_{10}H_{10}$ **8** (0.45 g, 79%) identified by its ^{11}B NMR spectrum.

Deprotonation of *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ 1 and *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ 2 by $(Me_2N)_2C{=}NH$, and subsequent reactions with I_2. A suspension of *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ **1** (0.317 g, 1 mmol) in CH_2Cl_2 or MeCN (20 cm^3) was treated under nitrogen with $(Me_2N)_2C{=}NH$ (0.23 g, 2 mmol). The reaction mixture was stirred for 20 min at 20 °C to give a clear solution of the *salt* $[(Me_2N)_2C{=}NH_2]^+{}_2$[*nido*-4-I-7-$Me_3N$-7-$CB_{10}H_9$]$^{2-}$ **9**. Iodine (0.254 g, 1 mmol) was added under nitrogen and the solution stirred for 2 h then poured into water. The organic layer was separated, dried over $MgSO_4$, and solvent distilled off *in vacuo*. Crystallisation of the residue yielded *closo*-3-I-2-Me_3N-2-$CB_{10}H_9$ **11** (0.26 g, 81%), identified from its ^{11}B NMR spectrum.

A similar reaction using *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ **2** gave the anion [*nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_8$]$^{2-}$ **10** which on further reaction with I_2 gave a poor yield of an isomer mixture of *closo*-I_2-2-Me_3N-2-$CB_{10}H_8$.

Low temperature boron insertions

Preparation of 8-I-2-Ph-1-Me_3N-1-$CB_{11}H_9$ 12. To a solution of 4-I-7-Me_3N-7-$CB_{10}H_{11}$ **1** (1.08 g, 3.4 mmol) in dry thf (25 cm^3) was added $LiBu^n$ (2.5 cm^3, 7.1 mmol) in hexane at 15–20 °C with stirring under a nitrogen atmosphere, and Li_2[4-I-7-Me_3N-7-$CB_{10}H_9$] separated as an oil on stirring for 30 min at 20 °C. It was then treated with $PhBCl_2$ (0.6 g, 3.7 mmol) at 15 °C, and boiled for 30 min to give a clear solution. Volatiles were removed *in vacuo* and the residue purified by column chromatography on SiO_2 (eluted with CH_2Cl_2) to yield the *product* **12** (0.8 g, 57%) as a white powder, m.p. 250–252 °C (ethanol) (Found: C, 23.16; H, 6.18; N, 3.75. $C_{10}H_{23}B_{11}IN$ requires C, 23.79; H, 5.71; N, 3.48%). Similar reactions on *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ **2** yielded only the deprotonated anion **10** and on 4-Br-7-Me_3N-7-$CB_{10}H_{11}$ **4** gave a mixture of **15** and unchanged starting compound, characterised by their ^{11}B and ^1H NMR spectra.

Palladium-catalysed allyl substitution

Preparation of *closo*-8-$CH_2{=}CHCH_2$-2-Ph-1-Me_3N-1-$CB_{11}H_9$ 13. A mixture of 8-I-2-Ph-1-Me_3N-1-$CB_{11}H_9$ **12** (0.39 g, 0.96 mmol), allylmagnesium bromide (2.9 mmol) and $[Pd(PPh_3)_4]$ (0.06 g, 0.052 mmol) in thf (15 cm^3) was refluxed for 12 h in a N_2 atmosphere until all the starting compound had dissolved. The mixture was treated with water, washed with 5% hydrochloric acid, dried over $MgSO_4$, and solvent distilled off *in vacuo*. The residue was purified by column chromatography on SiO_2 (eluent CH_2Cl_2–Et_2O 1 : 1) to yield the *product* **13** (0.25 g, 82%) as a white powder, m.p. 182–184 °C (EtOH) (Found: C, 47.87; H, 9.23; N, 3.78. $C_{13}H_{28}B_{11}N$ requires C, 49.24; H, 8.84; N, 4.42%).

Preparation of *nido*-4-$CH_2{=}CHCH_2$-7-Me_3N-7-$CB_{10}H_{11}$ 14. In a reaction similar to that of compound **13**, 4-I-7-Me_3N-7-$CB_{10}H_{11}$ **1** (1.08 g, 3.4 mmol) was treated with allylmagnesium bromide (2.9 mmol) and $[Pd(PPh_3)_4]$ (0.06 g, 0.052 mmol) in thf (15 cm^3). The *product* **14** was purified similarly, and characterised by its ^{11}B and ^1H NMR spectra.

NMR spectroscopy

The ^{11}B (128.38 MHz) and ^1H (400.14 MHz) NMR spectra were obtained on a Bruker AMX400 spectrometer. Lock was maintained with deuteriated solvents (mainly CD_3CN) and shifts were referenced to external standards ($SiMe_4$ for ^1H and $BF_3{\cdot}OEt_2$ for ^{11}B).

Cyclic and square wave voltammetry of *nido*-7-Me_3N-7-$CB_{10}H_{12}$, *nido*-4-I-7-Me_2N-7-$CB_{10}H_{11}$ 1, *nido*-4,6-I_2-7-Me_3N-7-$CB_{10}H_{10}$ 2 and [*nido*-7-Me_3N-7-$CB_{10}H_{10}$]$^{2-}$ 7

Voltammetry was performed on an E.G. & G. Ltd. model 273 potentiostat, under the control of an Apple IIe computer with demonstration software supplied by E.G. & G. Ltd. using platinum working and secondary electrodes and a silver wire reference electrode. The solvent was MeCN dried and distilled from CaH. Supporting electrolytes (0.1 M) were NBu_4BF_4, NBu_4PF_6 (Fluka) and $[(Me_2N)_2C{=}NH_2]BF_4$ (prepared from NH_4BF_4 and tetramethylguanidine in MeCN). The CV scan rate was normally 200 mV s^{-1}; SW voltammetry was at 100 Hz and scan increment 5 mV.

Two-phase electrochemical oxidation/substitution in CH_2Cl_2–water

***nido*-7-Me_3N-7-$CB_{10}H_{12}$.** NBu_4I *electrolyte*. A simple one-compartment cell was charged with a solution of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (0.8 g, 3.98 mmol), and NBu_4I (3 g, 8.17 mmol) in CH_2Cl_2 (50 cm^3) above which was placed a solution of NaI (1 g, 6.7 mmol) in water (30 cm^3). The electrodes were platinum foil and were inserted in the two phase solution such that the anode was exposed only to the CH_2Cl_2 phase, and the cathode only to the aqueous phase. A current of 0.2 A was applied from a constant current/constant voltage power supply until a total of 384 C (4 mmol) of charge had passed. The CH_2Cl_2 layer was separated, and evaporated *in vacuo*, and the residue extracted three times with hot water (15 cm^3) to remove NBu_4I. The solid was redissolved in CH_2Cl_2, dried over $MgSO_4$, evaporated to dryness, and recrystallised from EtOH to yield *closo*-2-Me_3N-2-$CB_{10}H_{10}$ **8** (0.78 g, 95%) identified by its ^{11}B NMR spectrum.

NBu_4BF_4 *electrolyte.* In a similar reaction, solutions of *nido*-7-Me_3N-7-$CB_{10}H_{12}$ (0.2 g, 1 mmol) and NBu_4BF_4 (0.329 g, 1 mmol) in CH_2Cl_2 (10 cm^3) and $NaBF_4$ (1 g) in water (10 cm^3)

were electrolysed at 0.063 A until 193 C (2 mmol) of charge had passed. Gas evolution was observed at both anode and cathode. The organic layer, worked up as before, yielded only starting compound.

***nido*-4-I-7-Me$_3$N-7-CB$_{10}$H$_{11}$.** NBu$_4$BF$_4$ *electrolyte.* A similar reaction to the above using *nido*-4-I-7-Me$_3$N-7-CB$_{10}$H$_{11}$ (0.2 g, 0.63 mmol), and passing 122 C at 0.062 A, also gave gas evolution at both electrodes, and some iodine was liberated in the anode compartment. The product, worked up similarly, showed the main component to be starting compound with a smaller proportion of *nido*-7-Me$_3$N-7-CB$_{10}$H$_{12}$ from deiodination.

Divided cell electrochemical oxidation/substitution

Controlled potential electrochemical reactions were carried out in a cell which comprised two compartments each of *ca.* 25 cm^3 capacity connected by flanged joints. A Nafion 390 membrane, sealed by lightly coating around its edge for about 1 mm on each side with Dow silicone rubber sealant, was inserted between the flanges. The anode was a platinum foil *ca.* 2 cm^2 area, the cathode was 2 cm platinum wire, and the reference was silver wire. Acetonitrile was distilled from CaH$_2$ before use. The electrolytes were those employed for CV and SWV.

***nido*-7-Me$_3$N-7-CB$_{10}$H$_{12}$.** [(Me$_2$N)$_2$CNH$_2$]BF$_4$ *electrolyte.* The anode compartment of the divided cell was charged with [(Me$_2$N)$_2$CNH$_2$]BF$_4$ (0.203 g, 1 mmol) and *nido*-7-Me$_3$N-7-CB$_{10}$H$_{12}$ (0.19 g, 1 mmol) dissolved in MeCN (10 cm^3). The cathode compartment was charged with a solution (10 cm^3) of NH$_4$BF$_4$ (0.208 g, 2 mmol) in MeCN. The potential of the platinum anode was adjusted to 2.2 V, and electrolysis continued until the current fell to 1 mA resulting in the passage of 160 C of charge (83% of that required for 2 mmol electrons). The ^{11}B NMR spectrum of the resulting solution showed only starting compound and [BF$_4$]$^-$ with no other detectable boron-containing product.

NBu$_4$PF$_6$ *electrolyte.* In a similar reaction the anode compartment contained NBu$_4$PF$_6$ (0.387 g, 1 mmol) and *nido*-7-Me$_3$N-7-CB$_{10}$H$_{12}$ (0.19 g, 1 mmol) dissolved in MeCN (10 cm^3), and cathode compartment contained NH$_4$PF$_6$ (1 g) dissolved in MeCN (10 cm^3). The applied potential was initially 2.30 V to enable 38 mA current to flow. The anode contents became yellow after 177 C had passed. After 193 C, at which the current had fallen to 17 mA, the potential was reduced to 2.1 V and the current to 2.5 mA. The only isolable boron-containing product was starting compound.

***nido*-4-I-7-Me$_3$N-7-CB$_{10}$H$_{11}$.** NBu$_4$PF$_6$ *electrolyte.* The anode compartment contained NBu$_4$PF$_6$ (0.387 g, 1 mmol) and *nido*-4-I-7-Me$_3$N-7-CB$_{10}$H$_{11}$ (0.2 g, 0.63 mmol) dissolved in MeCN (10 cm^3), and cathode compartment contained NH$_4$PF$_6$ (1 g) dissolved in MeCN (10 cm^3). A potential of 2.21 V was applied and gave an initial current of ≈30 mA. An initial yellow colour in the anode compartment rapidly dissipated. After about 2/3 of the expected charge (≈80 C) significant iodine colour was apparent in the anode compartment, but rapidly dispersed as through a solution reaction. The electrolysis was stopped after 126 C had passed. Work-up of the product gave starting compound as the only identifiable species.

[*nido*-7-Me$_3$N-7-CB$_{10}$H$_{10}$]$^{2-}$. [(Me$_2$N)$_2$CNH$_2$]BF$_4$ *electrolyte.* In the anode compartment of the two-compartment cell was placed [(Me$_2$N)$_2$CNH$_2$]BF$_4$ (0.203 g, 1 mmol), (Me$_2$N)$_2$CNH (0.23 g, 2 mmol) and *nido*-7-Me$_3$N-7-CB$_{10}$H$_{12}$ (0.19 g, 1 mmol) in MeCN (10 cm^3). The cathode compartment was charged with NH$_4$BF$_4$ (1.0 g, 10 mmol) in MeCN (10 cm^3) and a solution (5 cm^3) of [(Me$_2$N)$_2$CNH$_2$]BF$_4$ (0.1 M) in MeCN. The two compartments were separated by a Nafion cation exchange membrane. The potential of the platinum foil anode was adjusted between 1.0 and 1.3 V (with respect to a silver wire reference) as the electrolysis proceeded. The current decayed to less than 3 mA and a total of 173 C of charge was passed. The ^{11}B NMR spectra of the anode solution, before and after solvent evaporation, indicated the product to be *closo*-2-Me$_3$N-2-CB$_{10}$H$_{10}$ with only a trace of starting compound or other degradation products. Attempts to purify the product by column chromatography resulted in compound degradation and isolation only of starting material and degraded CB$_9$ species.

[*nido*-4-I-7-Me$_3$N-7-CB$_{10}$H$_9$]$^{2-}$. [(Me$_2$N)$_2$CNH$_2$]BF$_4$ *electrolyte.* The anode compartment of the cell was charged with a solution (10 cm^3) of *nido*-4-I-7-Me$_3$N-7-CB$_{10}$H$_{11}$ (0.317 g, 1 mmol), [(Me$_2$N)$_2$CNH$_2$]BF$_4$ (0.203 g, 1 mmol) and (Me$_2$N)$_2$CNH (0.23 g, 2 mmol) in MeCN. The cathode compartment was loaded with NH$_4$BF$_4$ (0.208 g, 2 mmol) in MeCN (10 cm^3). A potential of 1.1 V was applied initially, and this was reduced after 57 C had passed to 0.9 V. After 165 C had passed and the current had fallen to 52 mA the solution began to turn yellow (I$_2$). The electrolysis was discontinued after 179 C (93% of that required for two-electron oxidation). The ^{11}B NMR spectrum of the anode solution showed only a small quantity of starting compound together with a complex mixture of degraded products which appeared to include substituted CB$_9$ derivatives.

Computational studies

The AM1 calculations were performed using the SPARTAN molecular modelling package on a Silicon Graphics Indigo 2 computer; GAUSSIAN 94 ready files[8] were prepared on the optimised geometries within the SPARTAN program and single point *ab initio* calculations were run at the HF/6-31G* level on a Silicon Graphics Origin 200 computer. Optimised structures were obtained after starting from several different starting geometries.

Acknowledgements

We thank The Royal Society for an ex-quota fellowship (to V. A. O.) and International Association for the promotion of cooperation with scientists from the New Independent States of the Former Soviet Union (INTAS) for financial support.

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Received 19*th January*, 1998; *Paper* 8/00489G