2-Substituted Icosahedral Monocarbon Carboranes. Part 1. Synthesis *via* Boron Insertion†

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New 2-substituted icosahedral monocarbon carboranes have been synthesised by functionalised boron insertion. The compounds [NBu$^n{}_4$][2-Ph-*closo*-1-CB$_{11}$H$_{11}$] **1**, [PPh$_4$][2-(*p*-MeC$_6$H$_4$)-*closo*-1-CB$_{11}$H$_{11}$] **2**, [N(CH$_2$Ph)Me$_3$][2-F-*closo*-1-CB$_{11}$H$_{11}$] **3**, 2-Me$_3$N-*closo*-1-CB$_{11}$H$_{11}$ **4** and [PPh$_4$][2-Cl(CH$_2$)$_4$O-*closo*-1-CB$_{11}$H$_{11}$] **5** were characterised by ^{1}H, ^{11}B and ^{11}B–^{11}B correlation NMR spectroscopy. The crystal structure of **5** shows a cage distortion that is postulated to result from π interaction of the substituent with the cluster. Crystal data: triclinic, space group $P\bar{1}$, a = 10.672(2), b = 11.047(2), c = 14.203(3) Å, α = 75.97(2), β = 87.84(2), γ = 83.22(2)°, Z = 2. Final R = 0.042 for 3951 reflections with $I > 2\sigma(I)$.

The recent upsurge of interest in ^{10}B neutron capture therapy (BNCT) of cancer[1] has produced a renewed impetus for the synthesis of substituted boron clusters. The chemistry of monocarbon carboranes has experienced a similar resurgence.[2] In the past decade, however, substitution chemistry of cluster boron systems has been overshadowed by the effort to characterise novel primary skeletal arrangements of atoms in clusters. This is due, in part, to the paucity of general and controllable methods for the synthesis of such substituted systems and in part to a perception that *exo* substituents play only a minor role in the chemistry of the systems. In this and subsequent papers these suppositions will be addressed in detail. We report here systematic syntheses of 2-substituted dodecahydro-1-carba-*closo*-dodecaborate(1 −) derivatives, and their spectroscopic and structural characterisation.

Experimental

Materials and Intermediates.—Materials were reagent grade or better and were used as received from standard commercial vendors except where noted below. Tetrahydrofuran (thf) was distilled from sodium–benzophenone immediately prior to use. Dichloromethane was used as received for chromatography but was distilled from CaH$_2$ for preparations. The salt [NMe$_3$H][CB$_{10}$H$_{13}$] was prepared from freshly sublimed decaborane(14) (Callery Chemical Company) *via* Me$_3$NCB$_{10}$H$_{12}$.[3,4] Dichlorophenylborane was prepared from tetraphenyltin and boron trichloride.[5] Dichlorodimethylaminoborane was prepared by the method of Wiberg and Sütterlin.[6] Boron trifluoride–diethyl ether (1:1) and tin tetrachloride were distilled under vacuum prior to use. Column chromatography was performed either on untreated silica gel (SiO$_2$, 60–120 mesh, FSA Laboratory Supplies) or activated alumina (Al$_2$O$_3$, Laporte U.G.I., 100 mesh) washed with ethyl acetate.

NMR Spectra.—The ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded at 400.14, 128.38, 100.61 and 376.5 MHz respectively on a Bruker AMX400 spectrometer. Lock was maintained with deuterated solvents and shifts were referenced to the external standards SiMe$_4$ (^{13}C and ^{1}H), BF$_3$·OEt$_2$ (^{11}B) and CCl$_3$F (^{19}F). Some ^{11}B and ^{1}H data were recorded using the same referencing and lock procedures on a Varian 600 spectrometer operating at 599.94 (^{1}H) or 192.48 MHz (^{11}B).

Syntheses.—[NBu$^n{}_4$][2-Ph-*closo*-1-CB$_{11}$H$_{11}$] **1**. To a thf solution (6 cm^3) of [NMe$_3$H][CB$_{10}$H$_{13}$] (0.19 g, 0.98 mmol) was added a 1.6 mol dm^{-3} solution of LiBu^n in hexanes (2.0 cm^3). The flask was evacuated to remove butane and NMe$_3$. The resultant clear yellow solution of 'Li$_3$CB$_{10}$H$_{11}$' was cooled to 0 °C before adding BPhCl$_2$ (1 cm^3, 7.6 mmol) by syringe. This gave a paler solution which was allowed to stir at room temperature for 45 min before all volatiles were removed *in vacuo*. Boron-11 NMR spectral analysis of the crude product indicated essentially quantitative conversion into a *closo*-CB$_{11}$ species. Removal of monoboron and organic impurities was effected by digestion of the crude gum in hot 10% NaOH(aq) solution. The mixture was filtered and to the filtrate was added an aqueous solution of [NBu$^n{}_4$]Br (0.33 g, 1.02 mmol). A sticky precipitate was filtered off and further purified by column chromatography on silica gel eluted with 10% MeCN–90% CH$_2$Cl$_2$. Solvent was removed from the first fraction (R_f 0.8) to yield 0.113 g (25%) of white crystalline product, m.p. 108.5–109.8 °C (Found: C, 59.80; H, 11.80; N, 3.10. C$_{23}$H$_{52}$B$_{11}$N requires C, 59.85; H, 11.35; N, 3.05%).

[PPh$_4$][2-(*p*-MeC$_6$H$_4$)-*closo*-1-CB$_{11}$H$_{11}$] **2** *and* [NEt$_3$H][2-(*p*-MeC$_6$H$_4$)-*closo*-1-CB$_{11}$H$_{11}$].—A solution of 'Li$_3$CB$_{10}$H$_{11}$' in thf was prepared from [NMe$_3$H][CB$_{10}$H$_{13}$] (1.108 g, 5.72 mmol) and LiBu^n as above. To this solution at 0 °C was quickly added an excess of solid dichloro(*p*-tolyl)borane (*ca.* 15 mmol) under an argon back-flush. The exothermic dissolution and reaction occurred rapidly to give a pale brown solution which was allowed to stir for 90 min. The Schlenk tube was then evacuated to remove all volatiles. The white gum was digested with 10% NaOH(aq) (20 cm^3). A large amount of oil (1–2 cm^3) persisted in the mixture. Acidification (concentrated HCl) produced a white precipitate which occluded much of the oil when filtered. Addition of an aqueous solution of [NEt$_3$H]Cl (excess) to the filtrate produced a colloidal precipitate, which was extracted into dichloromethane. Removal of solvent produced an oil which was purified by chromatography on silica eluted with 10% MeCN–90% CH$_2$Cl$_2$. Removal of solvent from all fractions produced a series of pale brown oils which crystallised on prolonged standing. The ^{11}B NMR spectrum indicated that those fractions with the major component of R_f

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

0.75 were pure with respect to boron and consistent with the product being $[NEt_3H][2\text{-}(p\text{-}MeC_6H_4)\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$.

The material that remained on the filter-paper was redissolved in boiling water and cooled to give needles of white dihydroxy(*p*-tolyl)borane which was removed by filtration. The filtrate was treated with additional $[NEt_3H]Cl$ to give a fine, cloudy precipitate which was extracted into dichloromethane to give a further yield of $[NEt_3H][2\text{-}(p\text{-}MeC_6H_4)\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ upon removal of solvent. The remnants in the flask were again digested with hot water and NaOH. An excess of the salt $[PPh_4]Cl$ (*ca.* 3 mmol) was added, the solution boiled, filtered hot, and the gummy solid twice recrystallised from dichloromethane layered with hexane to give pure $[PPh_4][2\text{-}(p\text{-}MeC_6H_4)\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ without chromatography. The ^1H NMR spectra indicated dichloromethane in the crystal in a 1:1 molar ratio of solvent:product. The crystals underwent a phase change (loss of solvent?) at ≈90 °C and melted at 160.0–161.2 °C (Found: C, 61.25; H, 5.95; P, 4.80. $C_{32}H_{28}B_{11}P{\cdot}CH_2Cl_2$ requires C, 60.30; H, 6.15; P, 4.70%). Problems of twinning precluded a single-crystal diffraction study.

$[N(CH_2Ph)Me_3][2\text{-}F\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ **3**. A solution of '$Li_3CB_{10}H_{11}$' (0.635 mmol) in thf, prepared as before, was heated to boiling until the volume had reached approximately 4 cm³. Chilling to 0 °C produced very fine white needles of the lithiated carborane. To this stirred suspension was added $BF_3{\cdot}OEt_2$ (1.2 cm³, 9.75 mmol) dropwise. The crystals dissolved as the exothermic reaction proceeded to give a clear yellow solution. After stirring for 30 min the solution was heated to boiling, and all volatiles were evacuated to leave a yellowish solid. This was digested in 1 mol dm⁻³ aqueous NaOH. Addition of $[N(CH_2Ph)Me_3]Cl$ to the filtered aqueous solution gave a precipitate which was filtered off and purified by flash column chromatography on alumina eluted with 10% MeCN–90% CH_2Cl_2. Removal of solvent from the first fraction (R_f = 0.85) gave 0.133 g (67%) of product, melting at 225.8–227.1 °C (Found: C, 42.30; H, 8.95; N, 4.50. $C_{11}H_{27}B_{11}FN$ requires C, 42.45; H, 8.75; N, 4.50%).

$2\text{-}Me_3N\text{-}closo\text{-}1\text{-}CB_{11}H_{11}$ **4**. A thf solution of '$Li_3CB_{10}H_{11}$' (1.58 mmol) crystallised as above was stirred at 0 °C during dropwise addition of freshly distilled $BCl_2(NMe_2)$ (1.5 cm³). The solution was stirred for 120 min and then evacuated to remove all volatile components. Addition of 1 mol dm⁻³ NaOH(aq) (10 cm³) produced a turbid emulsion on stirring. Dichloromethane (10 cm³) and Me_2SO_4 (2 cm³) were added, the two-phase solution was rapidly stirred for 20 min and the organic layer separated. Removal of solvent from this produced a brown oil. Chromatography on silica gel eluted with 100% dichloromethane gave a range of fractions. The earliest of these (R_f = 0.85) was contaminated with $(Me_2NBCl_2)_2$ as assessed by the ^{11}B and ^1H NMR spectra. Later fractions were contaminated with organic impurities. Combination of all clean fractions yielded 0.113 g (35.5%) of pure compound **4** (Found: C, 24.20; H, 10.15; N, 6.70. $C_4H_{20}B_{11}N$ requires C, 23.90; H, 10.00; N, 6.95%). Its spectral properties were different from those reported,[7b] m.p. 280–360 °C (decomp.).

$[PPh_4][2\text{-}Cl(CH_2)_4O\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ **5**. A thf solution of '$Li_3CB_{10}H_{11}$' (1.11 mmol) was crystallised as above. To the stirred suspension at 0 °C was quickly added solid $Me_2S{\cdot}BCl_3$ (2.09 g, 11.6 mmol) under argon back-flush. A rapid exothermic reaction occurred, but a significant amount of fine solid remained. The mixture was sonicated for 10 min, stirred for 45 min, evacuated to dryness, and 1 mol dm⁻³ NaOH(aq) (20 cm³) was added. A large amount of oil persisted, which settled in the lower phase. Addition of $[PPh_4]Cl$ (0.526 g, 1.5 mmol) to the aqueous phase was followed by heating the mixture. It was then extracted into dichloromethane and purified by flash column chromatography on alumina eluted with 5%MeCN–95%CH_2Cl_2. Solvent was removed from the first band of product (R_f = 0.88) to yield an oil which crystallised on standing. Recrystallisation from $1,2\text{-}C_2H_4Cl_2$ layered with hexane and washing with diethyl ether afforded 0.241 g (37.0%) of colourless crystals (m.p. 113.5–114.2 °C) (Found: C, 59.25; H, 6.80; Cl, 6.00; P, 5.20. $C_{29}H_{39}B_{11}ClOP$ requires C, 59.15; H, 6.65; Cl, 6.00; P, 5.25%).

X-Ray Structural Determination.—Crystal data. Crystals of compound **5** were obtained by diffusion of hexane into a 1,2-dichloroethane solution. $[P(C_6H_5)_4]^+[C_5H_{19}B_{11}ClO]^-$, M = 588.9, triclinic, space group $P\bar{1}$, a = 10.672(2), b = 11.047(2), c = 14.203(3) Å, α = 75.97(2), β = 87.84(2), γ = 83.22(2)°, U = 1613.1(5) Å³, by least-squares refinement on the setting angles of 25 centred peaks in the range $48 < 2\theta < 52°$, T = 113(2) K, λ = 1.541 78 Å, Z = 2, D_c = 1.213 g cm⁻³, $F(000)$ = 616, μ(Cu-Kα) = 16.8 cm⁻¹.

Data collection and processing. A colourless prism of dimensions 0.3 × 0.5 mm was mounted on a Siemens P3f diffractometer equipped with a nitrogen-streaming low-temperature device, T = 113(2) K. Intensity data were collected using a Wycoff ω-scan mode with a 0.5° scan range and variable scan speeds of 3–20° min⁻¹. 4619 Data were collected ($4 \leqslant 2\theta \leqslant 114°$; $\pm h,k,\pm l$) of which 4350 were unique, R_{int} = 0.0259 after empirical absorption correction using azimuthal scans (minimum, maximum transmission factors = 0.207, 0.442), giving 3951 with $I > 2\sigma(I)$. Three peaks were remeasured in every 100 data and showed no significant variations.

Structure analysis and refinement. Direct methods yielded the positions of all non-hydrogen atoms. The structure was refined by full-matrix least squares on F with all non-hydrogen atoms refined anisotropic. Phenyl and ethylene hydrogen positions were calculated; other hydrogens were located on a difference map. Hydrogens were refined with a riding model using grouped isotropic thermal parameters [$0.035(2) \leqslant U_{iso} \leqslant 0.042(3)$ Å²]. The 391 variables refined to give final R, R' and S values of 0.042, 0.068 and 1.97 using weights of $w = 1/[\sigma^2(F) + 0.0008F^2]$. The final difference map had maximum and minimum densities of 0.20 and −0.43 e Å⁻³. The SHELXTL[8] programs were used on a DEC MicroVAXII computer for all calculations. Scattering factors were taken from ref. 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis.—(i) General. A variety of products $[2\text{-}R\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^{q-}$ (q = 1 or 0) were obtained by insertion of a dihalogenoboron reagent BRX_2 into $[nido\text{-}7\text{-}CB_{10}H_{11}]^{3-}$ as shown in Scheme 1. In this way both anionic and neutral (zwitterionic) clusters were obtained, isolated by metathesis with large cations or by quaternisation of the substituent. Products are listed in Table 1.

$$\begin{tikzcd}
{[NMe_3H][CB_{10}H_{13}] + 3LiBu^n} \arrow[r] & {Li_3[CB_{10}H_{11}] + NMe_3 + 3BuH} \arrow[d, "(i)"] \\
 & {Li[2\text{-}R\text{-}closo\text{-}1\text{-}CB_{11}H_{11}] + 2LiX}
\end{tikzcd}$$

Scheme 1 (*i*) BRX_2

There are reports of the use of this 'functionalised boron insertion' reaction to produce substituted $closo\text{-}1,2\text{-}C_2B_{10}$[10] and $1,2\text{-}C_2B_5$[11] clusters, but this is the first report which includes examples of substituents from across the p block to emphasise the potential of this route as a *general* synthetic method. The application of the reaction to the monocarbon carborane structural class constitutes a new, general synthesis of the CB_{11} icosahedron which was only previously accessible *via* thermal disproportionations[12] and high-temperature insertions of ligand borane adducts.[13]

The 2 isomer produced by insertion into $[7\text{-}CB_{10}H_{11}]^{3-}$ is

Table 1 Reagents and products of functionalised boron insertion into [*nido*-7-$C_{10}H_{11}$]$^{3-}$

BRX_2	Metathesis/ quaternisation reagent	Product
$BPhCl_2$	[NBu^n_4]Br	**1** [NBu^n_4][2-Ph-*closo*-1-$CB_{11}H_{11}$]
$B(C_6H_4Me\text{-}p)Cl_2$	[PPh_4]Cl	**2** [PPh_4][2-(*p*-MeC_6H_4)-*closo*-1-$CB_{11}H_{11}$]
$BF_3{\cdot}OEt_2$	[$N(CH_2Ph)Me_3$]OH	**3** [$N(CH_2Ph)Me_3$][2-F-*closo*-1-$CB_{11}H_{11}$]
$BCl_2(NMe_2)$	Me_2SO_4–NaOH	**4** 2-Me_3N-*closo*-1-$CB_{11}H_{11}$
$Cl(CH_2)_4OBCl_2$	[PPh_4]Cl	**5** [PPh_4][2-$Cl(CH_2)_4O$-*closo*-1-$CB_{11}H_{11}$]

Table 2 Measured multielement NMR data[a] for compounds **1**–**5**, together with data for [$N(CH_2Ph)Me_3$][$CB_{11}H_{12}$]

Compound	2 Substituent	B(2)	B(3,6)	B(4,5)	B(7,11)	B(8,10)	B(9)	B(12)	C(1)	
[$CB_{11}H_{12}$]$^-$		−16.1	−16.1	−16.1	−13.2	−13.2	−13.1	−6.9		δ(^{11}B)
		1.61	1.61	1.61	1.46	1.46	1.46	1.59	2.35	δ(^{1}H)
		160	160	160	130	130	130	135		*J*(^{11}B–^{1}H)
1[b]	Ph[c]	−6.8	−14.5	−15.6	−12.3	−13.1	−15.6	−6.8		δ(^{11}B)
		—	1.80	1.75	1.75	1.55	1.43		2.68	δ(^{1}H)
		—	145	145	121	121	145	130		*J*(^{11}B–^{1}H)
		3,6; 7,11	4,5,9; 8,10; 7,11; 2	3,6; 8,10; 12	8,10; 3,6; 2; 12	12; 7,11; 3,6; 4,5,9	3,6; 8,10; 12	7,11; 8,10; 9		[^{11}B–^{11}B] COSY correlations
2[d]	C_6H_4Me[e]	−6.7	−14.5	−15.7	−12.3	−13.2	−15.7	−6.7		δ(^{11}B)
		—	1.76	1.72	1.72	1.53	1.40	1.68	2.60	δ(^{1}H)
		—	160	147	125	140	147	115		*J*(^{11}B–^{1}H)
3[f]	F[g]	3.3	−16.2	−17.9	−15.2	−16.2	−22.5	−9.1		δ(^{11}B)
		—	1.77	1.57	1.66	1.29	1.08	1.49	2.75	δ(^{1}H)
		—	145	150	132	145	137	141		*J*(^{11}B–^{1}H)
		7,11; 3,6[g]	7,11; 12; 2; 4,5; 9	3,6; 9	8,10; 3,6; 12; 2	7,11; 12; 2; 4,5; 9	4,5; 3,6; 12	7,11; 8,10; 9		[^{11}B–^{11}B] COSY correlations
5[h]	$O(CH_2)_4Cl$[i]	2.6	−16.3	−17.9	−15.0	−16.3	−21.9	−9.1		δ(^{11}B)
			1.71	1.53	1.61	1.26	1.06	1.47	2.50	δ(^{1}H)
			169	170	140	160	137	137		*J*(^{11}B–^{1}H)
		7,11; 3,6	2; 12; 7,11; 4,5; 9	3,6; 9	2; 12; 8,10; 3,6	2; 12; 7,11; 4,5; 9	12; 3,6; 4,5	7,11; 8,10; 9		[^{11}B–^{11}B] COSY correlations
4	NMe_3[j]	−2.6	−16.7	−15.9	−13.8	−13.2	−15.9	6.9		δ(^{11}B)
		—	—	—	—	—	—	—	3.09	δ(^{1}H)
			145	130	−130	126	−130	138		*J*(^{11}B–^{1}H)
		3,6; 7,11	2; 8,10	3,6; 8,10	2; 12; 8,10	12; 7,11; 4,5,9; 3,6	12; 3,6	8,10; 7,11; 9		[^{11}B–^{11}B] COSY correlations

[a] Unequivocal assignments based on [^{11}B–B^{11}] COSY correlations and [^{1}H–{^{11}B selective}] experiments; other assignments by analogy. *J* in Hz. [b] Resonances due to the cation [NBu_4]$^+$: δ(^{1}H) 0.97 (t, Me), 1.35 (sxt, $MeCH_2$), 1.60 (m, $CH_2CH_2CH_2$) and 3.07 (m, CH_2N). [c] Resonances due to the 2-Ph group: δ(^{1}H) 7.17 (complex m, *m*- and *p*-H) and 7.5 (br m, *o*-H); δ(^{13}C) 133.9 (*o*-H), 128.0 (*p*-H) and 127.2 (*m*-H). [d] Resonances due to the cation [PPh_4]$^+$: δ(^{1}H) 7.66–7.69 (complex m, *o*- and *m*-H) and 7.92 (t, *p*-H). [e] Resonances due to the 2-MeC_6H_4 group: δ(^{1}H) 2.26 (CH_3), 6.98 (*m*-H) and 7.40 (*o*-H). [f] Resonances due to the cation [$N(CH_2Ph)Me_3$]$^+$: δ(^{1}H) 4.38 (CH_2), 3.00 (NMe_3) and 7.6 (m, Ph); δ(^{13}C) 133.9, 131.9, 130.3 (Ph), 70.5 (CH_2) and 53.5 (NMe_3). [g] Doublet splitting of B(2) unresolved in one-dimensional NMR, but resolved in cross-peaks of two-dimensional COSY NMR, with apparent *J*(^{11}B–^{19}F) 130 Hz. Direct measurement of ^{19}F spectrum gave δ(^{19}F) −209.5, *J*(^{11}B–^{19}F) 55 Hz (1:1:1:1 quartet). [h] Resonances due to the cation [PPh_4]$^+$: δ(^{1}H) 7.6 (m), 7.78 (m) and 7.91 (m) (in CD_3CN); significant solvent shifts were noted in $CDCl_3$. [i] Resonances due to the $Cl(CH_2)_4O$ group: δ(^{1}H) 1.68 (tt, OCH_2CH_2), 1.85 (tt, $ClCH_2CH_2$), 3.55 (t, $ClCH_2$) and 3.67 (t, OCH_2); the couplings were established by [^{1}H–^{1}H] COSY correlations. [j] Resonance due to the NMe_3 substituent: δ(^{1}H) 3.02 (CH_3).

important for several reasons. First this geometry is rare, as prior substitution methodologies invariably result in 7 or 12 substitution in the few cases where it may be controlled.[2a,7] Recent work in our laboratories established 2 substitution in 1-Me_2N-2-Me_2S-*closo*-1-$CB_{11}H_{10}$, but this was attained by a serendipitous thermal rearrangement.[2e] A previous report of compound **4**[7b] is questionable since the NMR spectra differed from those of this work. Secondly 2 substitution provides the closest analogy to the well studied 1,2-carborane series, and allows structural comparisons to be made. Finally, 2 substitution provides a method of probing interactions between substituent- and cluster-based orbitals since the effects are likely to be more pronounced in a site adjacent to a cage heteroatom where the symmetry is lower. This point will be dealt with more fully in subsequent papers.

(*ii*) [NBu^n_4][2-Ph-*closo*-1-$CB_{11}H_{11}$] **1**. Insertion of $BPhCl_2$ into the trilithium salt of [7-$CB_{10}H_{11}$]$^{3-}$ gave undecahydro-2-phenyl-1-carba-*closo*-dodecaborate with the elimination of 2 mol of lithium chloride. Compound **1** is significant in being the first aryl-substituted derivative of [$CB_{11}H_{12}$]$^-$, and the first anionic *closo*-carborane with an *exo*-B–C linkage of any sort. Functionalising the phenyl group may offer a convenient route to produce compounds relevant to BNCT. The ^{11}B and ^{11}B-{^{1}H} NMR spectra exhibit some accidentally coincident resonances but may be interpreted in conjunction with the two-dimensional ^{11}B–^{11}B NMR spectrum (which resolves one such coincidence in its cross-peaks) as a 1:1:2:2:2:1 intensity pattern consistent with the substituted 11-boron icosahedral cluster fragment. The correlation spectroscopy (COSY) correlations also unambiguously discriminate between the alternative 2- or 7-substituted geometries, and allow full spectral assignment as shown in Table 2. The effect of phenyl substitution on the cluster is manifested in a downfield shift of 9.3 ppm of B(2) relative to the corresponding resonance for [$CB_{11}H_{12}$]$^-$. This shift probably results from superposition of deshielding effects induced by a combination of ring current in the phenyl substituents and electronic effects. A small antipodal shift[14,15] is also induced, but overall changes in the ^{11}B NMR envelope are small and the spectra are readily recognised as derived from that of $[CB_{11}H_{12}]^-$.

The ^1H NMR spectra exhibited phenyl resonances only slightly shifted from those of benzene, split in a manner consistent with polarisation of the π cloud away from the negatively charged cluster. More subtle interactions between the two π systems were observed in the UV/VIS spectrum of compound **1** which showed a 10 nm bathochromic shift relative to benzene in the λ_{max} of the phenyl ring.

(*iii*) $[PPh_4][2\text{-}(p\text{-}MeC_6H_4)\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ **2**. The method of preparation of compound **2** was analogous to that of **1**, and **2** showed very similar spectral features. A possibility of specific functionalisation exists through oxidation of the benzylic carbon atom.

(*iv*) $[N(CH_2Ph)Me_3][2\text{-}F\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ **3**. The functionalised boron insertion of $BF_3{\cdot}OEt_2$ into $[CB_{10}H_{11}]^{3-}$ afforded **3**, the first example of a 2-halogeno-CB_{11} cluster and the first fluoro-CB_{11} cluster. Conventional halogenations are reported to give only products multiply substituted at B(7)–B(12).[7a]

The ^{11}B and $^{11}B\text{-}\{^1H\}$ NMR spectra show substantial changes from those of $[CB_{11}H_{12}]^-$. It may even be said that the *exo* substituent is challenging the cluster heterovertex in the extent to which it dictates the shielding pattern of the cluster. The fluorinated boron appears as a broad singlet in the one-dimensional ^{11}B and $^{11}B\text{-}\{^1H\}$ NMR and in the diagonal peak of the two-dimensional $^{11}B\text{-}\{^1H\}\text{–}^{11}B\text{-}\{^1H\}$ NMR spectrum but as a clear doublet in its cross-peaks. Furthermore, the apparent magnitude of the $^1J(^{11}B\text{–}^{19}F)$ coupling assumed to generate the doublet is ≈130 Hz. However, the ^{19}F NMR spectrum exhibited a 1:1:1:1 quartet with $J(^{11}B\text{–}^{19}F)$ of 55 Hz, more consistent with previously observed values for cluster systems.[16] It therefore appears that the $^{11}B\text{–}^{11}B$ two-dimensional NMR spectrum facilitates the observance of couplings not visible in a one-dimensional spectrum, but the *J* values measured from them are unreliable.

In the case of the anion of compound **3** extensive disorder thwarted attempts to obtain accurate X-ray diffraction information. Consequently the only tools available to probe structure and bonding other than NMR spectroscopy were molecular orbital calculations,[17] the details of which will be published later.

(*v*) $2\text{-}Me_3N\text{-}closo\text{-}1\text{-}CB_{11}H_{11}$ **4**. The functionalised boron insertion of $BCl_2(NMe_2)$ into $[7\text{-}CB_{10}H_{11}]^{3-}$ presumably gave $[2\text{-}Me_2N\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$, but the product was not characterised as such. Instead, a tractable product was obtained by methylation to yield $2\text{-}Me_3N\text{-}closo\text{-}1\text{-}CB_{11}H_{11}$. A prior claim for the synthesis of this compound, in addition to its 7- and 12-substituted isomers, has been made but the spectral data reported[7b] are at variance with those presented in Table 2, which are more consistent with data for other isomers of **4** reported, and with the other data reported herein. For example, the singlet at δ −2.55 attributed to the trimethylamine-substituted boron compares with a value of δ +2.57 for $7\text{-}Me_3N\text{-}closo\text{-}1\text{-}CB_{11}H_{11}$. A value of δ +19.02 for B(2) was previously reported[7b] for $2\text{-}Me_3N\text{-}closo\text{-}1\text{-}CB_{11}H_{11}$. The value for B(2) (in **4**) would be expected to be at higher field than for $7\text{-}Me_3N\text{-}closo\text{-}1\text{-}CB_{11}H_{11}$ since the corresponding resonances of unsubstituted $[CB_{11}H_{12}]^-$ are in this order. Assignment of the remaining resonances of **4** was straightforward from the two-dimensional $^{11}B\text{–}^{11}B$ NMR data.

Compound **4** is of interest since it is isostructural with $1\text{-}Bu^t\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11}$ through replacement of a *exo*-cluster C with B and its bonded substituent C by N (C–C = B–N) and as such may be expected to be the least stable of the three B-substituted isomers. It thus offers an opportunity to probe thermal rearrangements in monocarbon carborane clusters, a subject in need of systematic investigation in the light of two such reactions already found by serendipity.[2e,7]

(*vi*) $[PPh_4][2\text{-}Cl(CH_2)_4O\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ **5**. Addition of $Me_2S{\cdot}BCl_3$ to a thf solution of $[7\text{-}CB_{10}H_{11}]^{3-}$ did not result in a Cl-substituted *closo* product but in an alkoxy-substituted one, presumably since the $Me_2S{\cdot}BCl_3$ underwent Me_2S/thf ligand exchange and subsequent ether-cleavage reaction much faster than the functionalised boron insertion. The identity of the

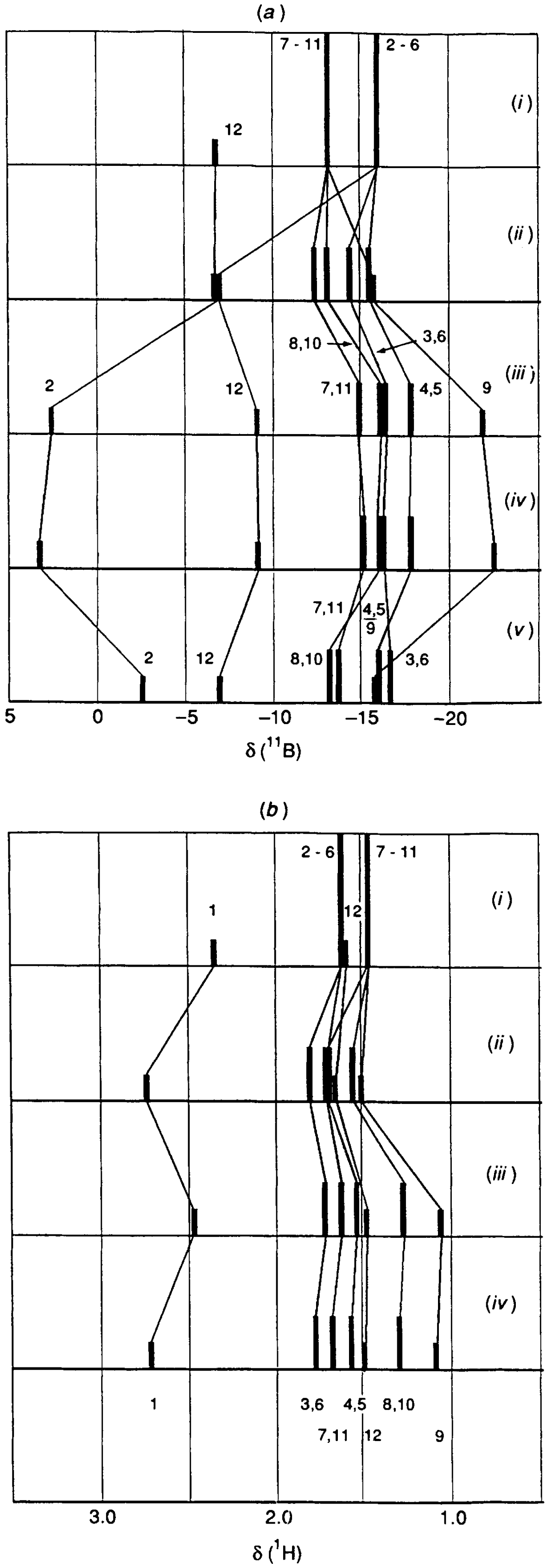

Fig. 1 Correlation of ^{11}B (*a*) and ^1H (*b*) chemical shifts for 2-substituted icosahedral monocarbon carboranes. Compounds: (*i*) $[CB_{11}H_{12}]^-$, (*ii*) **1**, (*iii*) **5**, (*iv*) **3** and (*v*) **4**

Table 3 Atomic coordinates (× 10^4) for compound **5**

Atom	*x*	*y*	*z*
C(1)	6 241(2)	5 274(2)	13 534(2)
B(2)	5 790(3)	4 990(3)	12 457(2)
B(3)	7 321(3)	5 401(3)	12 605(2)
B(4)	7 794(3)	4 790(3)	13 828(2)
B(5)	6 564(3)	3 968(3)	14 463(2)
B(6)	5 337(3)	4 083(3)	13 625(2)
B(7)	7 158(3)	4 131(3)	12 077(2)
B(8)	8 394(3)	4 022(3)	12 914(2)
B(9)	7 921(3)	3 123(3)	14 068(2)
B(10)	6 383(3)	2 687(3)	13 944(2)
B(11)	5 912(3)	3 313(3)	12 711(2)
B(12)	7 520(3)	2 713(3)	12 985(2)
O	4 934(2)	5 889(2)	11 855(1)
C(13)	3 895(2)	5 468(2)	11 473(2)
C(14)	3 098(2)	6 592(2)	10 859(2)
C(15)	3 829(2)	7 332(2)	10 016(2)
C(16)	3 026(3)	8 306(2)	9 288(2)
Cl	2 275(1)	9 546(1)	9 798(1)
P	2 263(1)	475(1)	2 604(1)
C(21)	1 850(2)	1 137(2)	3 626(2)
C(22)	1 975(2)	2 400(2)	3 538(2)
C(23)	1 743(3)	2 900(2)	4 339(2)
C(24)	1 384(2)	2 163(2)	5 211(2)
C(25)	1 270(2)	907(2)	5 298(2)
C(26)	1 501(2)	387(2)	4 505(2)
C(27)	1 897(2)	1 689(2)	1 522(2)
C(28)	665(2)	2 278(2)	1 391(2)
C(29)	366(2)	3 202(2)	559(2)
C(30)	1 289(2)	3 553(2)	−137(2)
C(31)	2 524(2)	3 004(2)	9(2)
C(32)	2 832(2)	2 061(2)	835(2)
C(33)	1 453(2)	−872(2)	2 619(2)
C(34)	1 892(2)	−2 009(2)	3 249(2)
C(35)	1 338(2)	−3 085(2)	3 266(2)
C(36)	353(2)	−3 037(2)	2 642(2)
C(37)	−86(2)	−1 915(2)	2 009(2)
C(38)	455(2)	−827(2)	1 997(2)
C(39)	3 913(2)	−81(2)	2 652(2)
C(40)	4 392(2)	−830(2)	2 031(2)
C(41)	5 643(2)	−1 316(2)	2 085(2)
C(42)	6 420(2)	−1 060(2)	2 756(2)
C(43)	5 945(2)	−313(2)	3 367(2)
C(44)	4 689(2)	184(2)	3 315(2)

product was unambiguously established by ^1H and ^{11}B NMR spectroscopy and by elemental analysis. The appearance of the ^{11}B NMR spectrum is strikingly similar to that of compound **3**, with the obvious exception of the fluorine coupling or broadening. The dispersion of the resonances is marginally smaller for **5** however.

Good X-ray diffraction data were obtained for compound **5** since the bulk of the substituent fixed one axis of the cluster in the solid state, whereas the small fluorine atom in **3** failed to do so.

Spectroscopy.—Comparison of the ^{11}B and ^1H NMR shielding patterns of compounds **1**–**4** [Fig. 1(*a*) and 1(*b*)] is worthwhile since all have ostensibly identical cluster frameworks. The spectra of $[CB_{11}H_{12}]^-$ are included as reference points, and **2** is omitted because of its similarity to **1**. This series of compounds offers an opportunity to compare the primary shift on the substituted boron atom (S shift) with the 'antipodal effect shift'[14] (A shift) on the atom antipodal to the substituent. Such detailed studies of the A-shift phenomenon as have already appeared in the case of heteroboranes[15] are beyond the scope of this paper, and may not be statistically justified. Qualitative trends are, however, apparent. Fig. 1(*a*) shows marked changes in the spectral pattern upon variation of substituent, suggesting significant perturbations in intracluster bonding. While **1** shows only moderately large A and S shifts, the spectrum is still broadly similar to that of $[CB_{11}H_{12}]^-$, indicating only minor perturbations with the aromatic substituent. The much larger perturbations, in both A and S shift, for F and OR substituents establish a positive correlation between the magnitude of the A and S shift, both effects being greatest with the most potent σ-withdrawing, π-donating substituents. A notable exception is **4** for which there is a very modest A shift in the presence of a comparatively large S shift. This confirms the importance of back donation in the mechanism of the effect.[18] A perturbation so large as that seen in the spectra of **3** and **5** suggests that the bonding may be altered sufficiently to induce a structural change, consistent with the 'isobonding'/'isospectral' relations suggested in the work of Heřmánek and others.[19]

X-Ray Structural Determination.—The atomic coordinates for compound **5** are presented in Table 3, selected bond lengths and angles in Tables 4 and 5. The data confirm the 2-substituted pseudo-icosahedral geometry of the anion (Fig. 2) deduced from the NMR data. The tetraphenylphosphonium cation shows no abnormal features, and merits little comment. While a cursory glance at the anion might provoke a similar level of comment, it is precisely the apparent absence of novel or unusual structural features that gives the data their value. Perhaps the most regular, familiar and inflexible cluster shape, the icosahedron, is here perturbed only by the presence of one carbon atom heterovertex (the best known of all heterovertices) and an alkoxy ligand. Such ligands are often ignored in the discussion of more complicated structures, presumably because any subtle effects they have on cluster geometry go unnoticed among the unsymmetric structures dominated by the effects of metal atoms and bulky ligands.[20]

Table 4 Selected bond lengths (Å) of compound **5**

C(1)–B(2)	1.730(4)	C(1)–B(3)	1.709(4)
C(1)–B(4)	1.715(4)	C(1)–B(5)	1.713(3)
C(1)–B(6)	1.699(4)	B(2)–B(3)	1.780(4)
B(2)–B(6)	1.799(4)	B(2)–B(7)	1.786(4)
B(2)–B(11)	1.789(4)	B(2)–O	1.409(3)
B(3)–B(4)	1.773(4)	B(3)–B(7)	1.773(4)
B(3)–B(8)	1.767(4)	B(4)–B(5)	1.777(4)
B(4)–B(8)	1.777(4)	B(4)–B(9)	1.779(4)
B(5)–B(6)	1.775(4)	B(5)–B(9)	1.777(4)
B(5)–B(10)	1.779(4)	B(6)–B(10)	1.767(4)
B(6)–B(11)	1.772(4)	B(7)–B(8)	1.783(4)
B(7)–B(11)	1.787(4)	B(7)–B(12)	1.784(3)
B(8)–B(9)	1.787(4)	B(8)–B(12)	1.793(4)
B(9)–B(10)	1.791(4)	B(9)–B(12)	1.785(4)
B(10)–B(11)	1.788(4)	B(10)–B(12)	1.787(4)
B(11)–B(12)	1.786(4)	O–C(13)	1.425(3)
C(13)–C(14)	1.520(3)	C(14)–C(15)	1.522(3)
C(15)–C(16)	1.507(3)	C(16)–Cl	1.796(3)

Compound **5** exhibits the expected flattening of the C-capped pentagonal pyramid relative to B-capped ones, in common with other crystallographically determined CB_{11} clusters. The most reliable data for comparison come from $[CB_{11}H_{12}]^-$ co-ordinated through H(12) to a metal centre,[21] since this fixes the carbon atom in position so avoiding the crystallographic disorder that makes other data sets less reliable.[2d] In the non-disordered case of $[CB_{11}H_{12}]^-$ the C–B distances average to ≈1.70 Å. Only one other anionic CB_{11} cluster has been crystallographically determined. It possesses a dimethylamino substituent bound to carbon, which overall seems to increase

Table 5 Selected bond angles (°) of compound **5**

B(2)–C(1)–B(3)	62.3(2)	B(2)–C(1)–B(4)	114.6(2)	B(2)–B(7)–B(8)	108.5(2)	B(3)–B(7)–B(8)	59.6(2)
B(3)–C(1)–B(4)	62.4(1)	B(2)–C(1)–B(5)	115.4(2)	B(2)–B(7)–B(11)	60.1(2)	B(3)–B(7)–B(11)	107.5(2)
B(3)–C(1)–B(5)	114.0(2)	B(4)–C(1)–B(5)	62.4(1)	B(8)–B(7)–B(11)	108.2(2)	B(2)–B(7)–B(12)	108.5(2)
B(2)–C(1)–B(6)	63.3(2)	B(3)–C(1)–B(6)	114.0(2)	B(3)–B(7)–B(12)	107.6(2)	B(8)–B(7)–B(12)	60.3(2)
B(4)–C(1)–B(6)	114.2(2)	B(5)–C(1)–B(6)	62.7(2)	B(11)–B(7)–B(12)	60.0(1)	B(3)–B(8)–B(4)	60.0(2)
C(1)–B(2)–B(3)	58.3(2)	C(1)–B(2)–B(6)	57.5(2)	B(3)–B(8)–B(7)	59.9(2)	B(4)–B(8)–B(7)	108.1(2)
B(3)–B(2)–B(6)	106.1(2)	C(1)–B(2)–B(7)	103.9(2)	B(3)–B(8)–B(9)	107.8(2)	B(4)–B(8)–B(9)	59.9(2)
B(3)–B(2)–B(7)	59.6(2)	B(6)–B(2)–B(7)	106.6(2)	B(7)–B(8)–B(9)	107.9(2)	B(3)–B(8)–B(12)	107.5(2)
C(1)–B(2)–B(11)	103.3(2)	B(3)–B(2)–B(11)	107.1(2)	B(4)–B(8)–B(12)	107.7(2)	B(7)–B(8)–B(12)	59.9(2)
B(6)–B(2)–B(11)	59.2(2)	B(7)–B(2)–B(11)	60.0(2)	B(9)–B(8)–B(12)	59.8(2)	B(4)–B(9)–B(5)	59.9(2)
C(1)–B(2)–O	118.9(2)	B(3)–B(2)–O	118.1(2)	B(4)–B(9)–B(8)	59.8(2)	B(5)–B(9)–B(8)	107.8(2)
B(6)–B(2)–O	122.3(2)	B(7)–B(2)–O	126.7(2)	B(4)–B(9)–B(10)	107.7(2)	B(5)–B(9)–B(10)	59.8(2)
B(11)–B(2)–O	129.3(2)	C(1)–B(3)–B(2)	59.4(2)	B(8)–B(9)–B(10)	108.1(2)	B(4)–B(9)–B(12)	107.9(2)
C(1)–B(3)–B(4)	59.0(1)	B(2)–B(3)–B(4)	109.4(2)	B(5)–B(9)–B(12)	107.8(2)	B(8)–B(9)–B(12)	60.2(2)
C(1)–B(3)–B(7)	105.3(2)	B(2)–B(3)–B(7)	60.3(2)	B(10)–B(9)–B(12)	60.0(2)	B(5)–B(10)–B(6)	60.1(2)
B(4)–B(3)–B(7)	108.7(2)	C(1)–B(3)–B(8)	105.4(2)	B(5)–B(10)–B(9)	59.7(2)	B(6)–B(10)–B(9)	107.6(2)
B(2)–B(3)–B(8)	109.4(2)	B(4)–B(3)–B(8)	60.2(2)	B(5)–B(10)–B(11)	107.9(2)	B(6)–B(10)–B(11)	59.8(2)
B(7)–B(3)–B(8)	60.5(2)	C(1)–B(4)–B(3)	58.7(1)	B(9)–B(10)–B(11)	107.8(2)	B(5)–B(10)–B(12)	107.6(2)
C(1)–B(4)–B(5)	58.7(1)	B(3)–B(4)–B(5)	107.9(2)	B(6)–B(10)–B(12)	107.5(2)	B(9)–B(10)–B(12)	59.9(2)
C(1)–B(4)–B(8)	104.8(2)	B(3)–B(4)–B(8)	59.7(1)	B(11)–B(10)–B(12)	60.0(2)	B(2)–B(11)–B(6)	60.7(2)
B(5)–B(4)–B(8)	108.3(2)	C(1)–B(4)–B(9)	104.7(2)	B(2)–B(11)–B(7)	59.9(2)	B(6)–B(11)–B(7)	107.7(2)
B(3)–B(4)–B(9)	107.8(2)	B(5)–B(4)–B(9)	60.0(2)	B(2)–B(11)–B(10)	108.7(2)	B(6)–B(11)–B(10)	59.5(2)
B(8)–B(4)–B(9)	60.3(2)	C(1)–B(5)–B(4)	58.8(1)	B(7)–B(11)–B(10)	107.9(2)	B(2)–B(11)–B(12)	108.2(2)
C(1)–B(5)–B(6)	58.3(1)	B(4)–B(5)–B(6)	107.6(2)	B(6)–B(11)–B(12)	107.4(2)	B(7)–B(11)–B(12)	59.9(1)
C(1)–B(5)–B(9)	104.9(2)	B(4)–B(5)–B(9)	60.1(2)	B(10)–B(11)–B(12)	60.0(1)	B(7)–B(12)–B(8)	59.8(2)
B(6)–B(5)–B(9)	107.9(2)	C(1)–B(5)–B(10)	104.6(2)	B(7)–B(12)–B(9)	108.0(2)	B(8)–B(12)–B(9)	59.9(2)
B(4)–B(5)–B(10)	108.4(2)	B(6)–B(5)–B(10)	59.7(2)	B(7)–B(12)–B(10)	108.1(2)	B(8)–B(12)–B(10)	108.0(2)
B(9)–B(5)–B(10)	60.5(2)	C(1)–B(6)–B(2)	59.2(2)	B(9)–B(12)–B(10)	60.2(2)	B(7)–B(12)–B(11)	60.1(1)
C(1)–B(6)–B(5)	59.0(2)	B(2)–B(6)–B(5)	109.0(2)	B(8)–B(12)–B(11)	107.8(2)	B(9)–B(12)–B(11)	108.1(2)
C(1)–B(6)–B(10)	105.7(2)	B(2)–B(6)–B(10)	109.2(2)	B(10)–B(12)–B(11)	60.1(2)	B(2)–O–C(13)	118.4(2)
B(5)–B(6)–B(10)	60.3(2)	C(1)–B(6)–B(11)	105.4(2)	O–C(13)–C(14)	109.2(2)	C(13)–C(14)–C(15)	113.1(2)
B(2)–B(6)–B(11)	60.2(2)	B(5)–B(6)–B(11)	108.8(2)	C(14)–C(15)–C(16)	114.6(2)	C(15)–C(16)–Cl	112.3(2)
B(10)–B(6)–B(11)	60.7(2)	B(2)–B(7)–B(3)	60.0(2)				

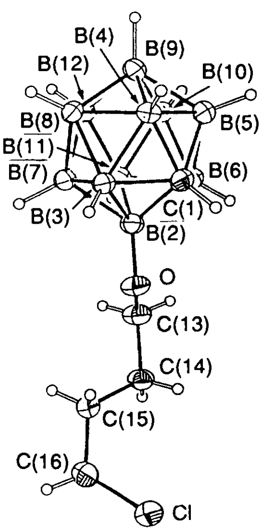

Fig. 2 Thermal ellipsoid plot (50% ellipsoids) of the anion of compound **5**

the C–B length, though very large estimated standard deviations make comparison unhelpful.[2d] The position of the carbon in compound **5** was selected because the bonds to this one location were consistently shorter than were the bonds to any of the other atoms in the icosahedron. This position for the carbon was confirmed by the fact that all of the thermal parameters of the atoms in the icosahedron refined to similar values.

The mean C–B length in compound **5** (excluding that of the substituted boron) of 1.709(4) Å agrees with the value in $[CB_{11}H_{12}]^-$ quoted above. However, C(1)–B(2), at 1.730(4) Å, is more than five standard deviations larger than the average of the other C–B lengths. This small but real lengthening is perhaps unexpected in such a 'normal' cluster, but in fact has some precedent. In $[1\text{-O-2-Ph-}closo\text{-}1,2\text{-}C_2B_{10}H_{10}]^-$ this type of structural feature was even more pronounced,[22] where the lengthening was rationalised as arising from poor donation from the carbon of a *nido*-shaped $[RCB_{10}H_{10}]^-$ (R = H) ligand into the π* orbitals of a μ_5 bridging carbonyl group. However, the description of **5** as a complex of $[RCB_{10}H_{10}]^-$ (R = H) with $BO(CH_2)_4Cl$ replacing CO seems inappropriate. More plausible is partial donation of p-electron density from the lone pairs of oxygen into the surface orbitals of the cluster, producing a partial opening towards an *iso-nido* geometry. Such distortions have also been seen in $Me_2C_2B_9(OH)_2H_7$, with the more flexible 11-vertex geometry.[23]

Since the oxygen lone pairs seem to be causing the opening, it is possible that the same specific interaction of the lone pairs was responsible for locking the cage carbon in one position in the solid state, allowing accurate diffraction data to be collected. One may therefore speculate that, in solution under free rotation of the alkoxy substituent relative to the rest of the molecule, the cluster 'breathes' in concert with the orientation of the lone pairs relative to the cluster carbon. This point, among others, is the subject of molecular orbital calculations to be reported in a subsequent paper.[17]

The fact that the B–O bond length in compound **5** (1.409 Å) is quite long [*cf.* 1.36 Å in $(Ph_3P)_2RuB_{10}H_8(OEt)_2$], and that the C–O–B angle is unremarkable suggests that any O→B π donation is very slight. This makes the observed distortion of greater relevance; the inference is that such interactions between substituent and cluster are more general than previously thought.

Conclusion

The functionalised boron-insertion reaction provides a viable synthesis of 2-substituted icosahedral monocarbon carboranes, and shows promise as a general substitution strategy.

A large antipodal shift was observed for fluoro- and alkoxy-substituents, substantiating claims that such shifts are produced by π-interacting substituents.[18] For the alkoxy-substituted compound, a distortion also attributable to such interactions was observed crystallographically, thus producing the first documented *structural* manifestation of the 'antipodal shift' NMR phenomenon. Similar distortions are to be expected for $[2\text{-F-}closo\text{-}1\text{-CB}_{11}\text{H}_{11}]^-$ consistent with it being isospectral with $[2\text{-Cl(CH}_2)_4\text{O-}closo\text{-}1\text{-CB}_{11}\text{H}_{11}]^-$ and isoelectronic with $[1\text{-O-2-Ph-}closo\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_8]^-$, the other icosahedral carborane to exhibit such distortions and gross spectral changes.[24]

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