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Polyhedron 22 (2003) 1293–1301
POLYHEDRON
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Synthesis and characterisation of labelled diphenylcarboranes

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Received 27 November 2002; accepted 21 January 2003

Abstract

The synthesis, by either acid-catalysed electrophilic substitution or recapitation, and characterisation of four new B-labelled diphenyl carboranes is described. Two of these, 1,2-Ph_2-9,12-I_2-1,2-*closo*-$C_2B_{10}H_8$ (**1**) and 1,2-Ph_2-3-Me-1,2-*closo*-$C_2B_{10}H_9$ (**2**) were subjected to crystallographic study, whilst the 3-Et (**3**) and 3-F (**4**) analogues of **2** were studied spectroscopically. Decapitation of the mono-iodo analogue of **1** affords [5-I-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^-$, isolated as $[HNEt_3]^+$ (**5a**) $[HNMe_3]^+$ (**5b**) and $[C_6H_5CH_2NMe_3]^+$ (**5c**) salts, the last of which was subjected to crystallographic analysis. Decapitation of **3** and **4** selectively removes B6, yielding the 3-labelled *nido*-carboranes [3-Et-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^-$ and [3-F-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^-$, respectively, both isolated as $[HNMe_3]^+$ salts (**6a** and **7**). The ethyl species was also prepared as the $[HNEt_3]^+$ salt (**6b**), and was structurally characterised. Salts **5b**, **6a** and **7** are all afforded in good yield and the anions are ideal candidates for subsequent deprotonation and metallation, which should result in low-temperature isomerisation of the transient 3,1,2-MC_2B_9 species thereby produced, and thereby yield important, robust, mechanistic information on the rearrangement process.

Keywords: Carborane; Isomerisation; Synthesis; Spectroscopy; Crystallographic study; Vertex labelling

1. Introduction

The mechanism of isomerisation of carboranes has been of interest for many years [1–3]. However, the high temperatures usually involved have precluded experimental study of the mechanism via labelled vertices since the integrity of the vertex-label bond cannot be guaranteed under such conditions [4].

Some years ago we showed that metallation of [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^{2-}$ with a suitably bulky metal-ligand fragment could generate a 2,1,8-MC_2B_9 species at or near room temperature [5]. Assuming that the initial product of such metallation is a transient 3,1,2-MC_2B_9 species, this effectively represents low-temperature 1,2→1,7 C atom isomerisation of an icosahedral (hetero)carborane (Scheme 1). Moreover, we were fortunate additionally to be able to isolate reaction intermediates in some cases [6], with gross architectures identical to that predicted [7] in an ab initio computational study of the isomerisation of 1,2-*closo*-$C_2B_{10}H_{12}$, thus providing an important signpost for the isomerisation mechanism.

These findings have renewed interest in the feasibility of constructing a complete experimental mapping of the mechanism(s) of (hetero)carborane isomerisation from the sum of the results of a series of individual labelling experiments. Such experiments require access to derivatives of [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^{2-}$ carrying robust labels at each and every symmetry-independent boron vertex (Fig. 1). This paper describes some recent synthetic and structural results achieved in pursuit of that goal.

2. Experimental

2.1. Synthetic and spectroscopic studies

Experiments were performed under dry, oxygen-free, N_2 using standard Schlenk techniques, with some

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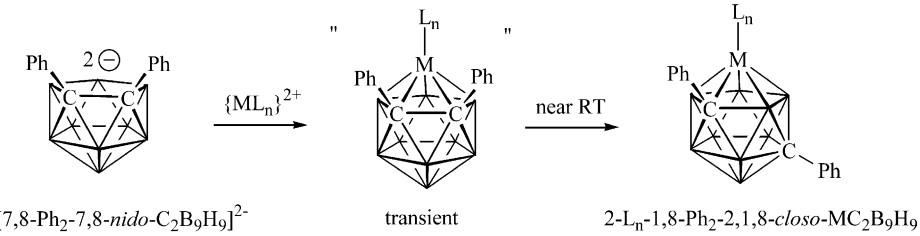
0277-5387/03/$ - see front matter
doi:10.1016/S0277-5387(03)00103-7



Scheme 1. Metallation of [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^{2-}$ with a bulky metal-ligand fragment ML_n generating a C-atom isomerised 2,1,8-MC_2B_9 species at or near room temperature via a notional 3,1,2-MC_2B_9 intermediate.

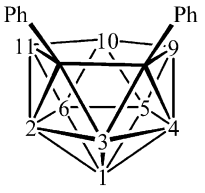


Fig. 1. Boron atom numbering in [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^{2-}$.

subsequent manipulation in the open laboratory. Solvents were freshly distilled over CaH_2 (CH_2Cl_2) or Na wire (THF, Et_2O, 40–60 petroleum ether) or stored over 4 Å molecular sieves (EtOH, $CDCl_3$). NMR spectra at 200.13 (^{1}H), 400.13 (^{1}H), 128.38 (^{11}B) or 161.98 MHz (^{19}F) were recorded on Bruker AC 200 or DPX 400 spectrometers from $CDCl_3$ solutions at ambient temperature, chemical shifts being recorded relative to $SiMe_4$ (^{1}H), $BF_3{\cdot}OEt_2$ (^{11}B) or $CFCl_3$ (^{19}F). IR spectra were recorded from CH_2Cl_2 solutions on a Perkin–Elmer Spectrum RX FTIR spectrophotometer. EI mass spectra were recorded using a Kratos Concept mass spectrometer. Elemental analyses were determined by the departmental service. The starting materials 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ [8], 1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$ [9], [$HNMe_3$][7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$] [10], $MeBBr_2$ and $EtBBr_2$ [11,12] were prepared by literature methods or slight variants thereof. All other reagents were used as supplied.

2.1.1. Synthesis of 1,2-Ph_2-9,12-I_2-1,2-*closo*-$C_2B_{10}H_8$ (*1*)

1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ (0.553 g, 1.85 mmol) and I_2 (2.366 g, 9.32 mmol) were heated to 50 °C in glacial acetic acid (7.5 ml). Whilst using a blast screen, a 1:1 mixture of conc. HNO_3 and conc. H_2SO_4 (4 ml) was added dropwise over 30 min and the mixture stirred for a further 2 h. The cooled solution was poured into H_2O (50 ml), filtered, and the residue washed with H_2O (3 × 10 ml). The purple solid was dissolved in Et_2O ($\approx$ 150 ml) and dried over $MgSO_4$. Recrystallisation from the minimum amount of 40–60 petroleum ether at −30 °C afforded 1,2-Ph_2-9,12-I_2-1,2-*closo*-$C_2B_{10}H_8$ (**1**) as a colourless solid. Yield 0.490 g, 48.2%. *Anal*. Found: C, 30.4; H, 3.55. Calc. for $C_{14}H_{18}B_{10}I_2$: C, 30.7; H, 3.31%. IR ν (cm^{-1}): 2613 (br). ^{1}H NMR δ (ppm): 7.1–7.5 (m, C_6H_5). ^{11}B{^{1}H} NMR δ (ppm): −3.99 (2B), −5.46 (4B), −7.58 (2B), −10.03 (2B, B9, B12).

2.1.2. Synthesis of 1,2-Ph_2-3-Me-1,2-*closo*-$C_2B_{10}H_9$ (*2*)

To a stirring solution of [$HNMe_3$][7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$] (0.233 g, 0.67 mmol) in Et_2O (15 ml) at 0 °C was added *n*-BuLi in hexanes (0.54 ml of 2.5 M solution $\equiv$ 1.35 mmol). The mixture was allowed to warm to room temperature then heated to reflux for 2 h. After cooling, Et_2O was removed in vacuo and the residue suspended in 40–60 petroleum ether and frozen to −196 °C. $MeBBr_2$ (0.15 ml, 0.225 g, 1.21 mmol) was added, and the mixture allowed to warm to room temperature with stirring. Volatiles were removed in vacuo, 40–60 petroleum ether (20 ml) added, and the mixture filtered. The filtrate was evaporated to yield a white solid, which was recrystallised from 40 to 60 petroleum ether at 3 °C to afford 1,2-Ph_2-3-Me-1,2-*closo*-$C_2B_{10}H_9$ (**2**) as a colourless solid. Yield 0.029 g, 14.0%. *Anal*. Found: C, 54.0; H, 7.63. Calc. for $C_{15}H_{22}B_{10}$: C, 53.0; H, 7.14%. IR ν (cm^{-1}): 2575 (br). ^{1}H NMR δ (ppm): 6.9–7.4 (m, 10H, C_6H_5), 0.73 (s, 3H, CH_3). ^{11}B{^{1}H} NMR δ (ppm): 2.03 (1B, B3), −0.11 (2B), −5.21 (3B), −6.62 (3B), −8.63 (1B).

2.1.3. Synthesis of 1,2-Ph_2-3-Et-1,2-*closo*-$C_2B_{10}H_9$ (*3*)

Similarly, from [$HNMe_3$][7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$] (2.598 g, 7.51 mmol) in Et_2O (70 ml), *n*-BuLi in hexanes (6.00 ml of 2.5 M solution $\equiv$ 15.0 mmol) and $EtBBr_2$ (2.50 ml, 3.755 g, 18.78 mmol) was synthesised 1,2-Ph_2-3-Et-1,2-*closo*-$C_2B_{10}H_9$ (**3**) as a colourless solid. Yield 0.820 g, 33.6%. *Anal*. Found: C, 57.8; H, 7.62. Calc. for $C_{16}H_{24}B_{10}$: C, 59.2; H, 7.46%. IR ν (cm^{-1}): 2576 (br). ^{1}H NMR δ (ppm): 7.0–7.3 (m, 10H, C_6H_5), 1.18 (t, 3H, CH_3), 1.04 (q, 2H, CH_2). ^{11}B{^{1}H} NMR δ (ppm): 3.77 (1B, B3), −0.26 (2B), −6.51 (6B), −8.45 (1B). MS *m*/*z*: 324 (M^+).

2.1.4. Synthesis of 1,2-Ph_2-3-F-1,2-*closo*-$C_2B_{10}H_9$ (*4*)

Similarly, from [$HNMe_3$][7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$] (0.430 g, 1.24 mmol) in Et_2O (20 ml), *n*-BuLi in hexanes (1.00 ml of 2.5 M solution $\equiv$ 2.50 mmol) and $BF_3{\cdot}OEt_2$ (0.08 ml, 0.62 mmol) was synthesised 1,2-Ph_2-3-F-1,2-*closo*-$C_2B_{10}H_9$ (**4**) as a white solid. Yield 0.126 g, 32.1%. *Anal*. Found: C, 53.4; H, 6.31. Calc. for $C_{14}H_{19}B_{10}F$: C,

53.5; H, 6.09%. IR ν (cm^{-1}): 2582 (br). ^1H NMR δ (ppm): 7.0–7.6 (m, C_6H_5). $^{11}B\{^1H\}$ NMR δ (ppm): 4.36 (d, $^1J_{BF} = 43$ Hz, 1B, B3), −2.64 (2B), −7.65 (2B), −9.22 (4B), −14.44 (1B). ^{19}F NMR δ (ppm): −185 (1:1:1:1 quar., $^1J_{BF} = 55$ Hz). MS m/z: 314 (M^+).

2.1.5. Synthesis of [$HNEt_3$][5-I-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (**5a**)

1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$ (1.472 g, 3.47 mmol) and KOH (0.488 g, 8.71 mmol) were heated to reflux in EtOH (50 ml) for 72 h. After removal of excess KOH by treatment with CO_2 gas, the volatiles were removed in vacuo leaving a colourless oil. This was dissolved in H_2O (20 ml), filtered, and treated with a slight excess of [$HNEt_3$]Cl (0.508 g, 3.69 mmol) in H_2O (10 ml). The solid thus precipitated was extracted into CH_2Cl_2 (30 ml + 3 × 10 ml), and dried over $MgSO_4$. Evaporation yielded [$HNEt_3$][5-I-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (**5a**) as a white solid. Yield 1.073 g, 60.2%. *Anal*. Found: C, 46.8; H, 6.95; N, 2.70. Calc. for $C_{20}H_{35}B_9IN$: C, 46.8; H, 6.87; N, 2.73%. IR ν (cm^{-1}): 2543 (br). ^1H NMR δ (ppm): 6.8–7.2 (m, 10H, C_6H_5), 3.28 (q, 6H, CH_2), 2.34 (t, 9H, CH_3). $^{11}B\{^1H\}$ NMR δ (ppm): −4.35 (1B), −5.38 (1B), −11.29 (1B), −13.30 (1B), −15.46 (2B), −20.88 (1B, B5), −27.65 (1B), −30.68 (1B).

The salts [$HNMe_3$][5-I-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (**5b**) and [$C_6H_5CH_2NMe_3$][5-I-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (**5c**) were prepared similarly in comparable yields.

2.1.6. Synthesis of [$HNMe_3$][3-Et-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (**6a**)

Similarly, from compound **3** (0.383 g, 1.18 mmol) and KOH (0.152 g, 2.71 mmol) in EtOH (20 ml), followed by treatment with [$HNMe_3$]Cl (0.163 g, 1.19 mmol) in H_2O (5 ml), was synthesised [$HNMe_3$][3-Et-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (**6a**) as a white solid. Yield 0.311 g, 51.3%. *Anal*. Found: C, 61.4; H, 9.37; N, 3.79. Calc. for $C_{19}H_{34}B_9N$: C, 61.1; H, 9.17; N, 3.75%. IR ν (cm^{-1}): 2523 (br). ^1H NMR δ (ppm): 6.8–7.1 (m, 10H, C_6H_5), 2.77 (t, 9H, CH_3), 1.15 (t, 3H, BCH_2CH_3), 0.82 (app. t, 2H, BCH_2CH_3). $^{11}B\{^1H\}$ NMR δ (ppm): −1.31 (1B, B3), −6.22 (2B), −14.74 (4B), −31.63 (2B).

The salt [$HNEt_3$][3-Et-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (**6b**) was prepared in similar yield in an entirely analogous manner.

2.1.7. Synthesis of [$HNMe_3$][3-F-7,8-Ph_2-7,8-nido-$C_2B_9H_9$] (7)

Similarly, from compound **4** (0.295 g, 0.93 mmol) and KOH (0.157 g, 2.80 mmol) in EtOH (20 ml), followed by treatment with [$HNMe_3$]Cl (0.112 g, 1.21 mmol) in H_2O (2 ml) and recrystallisation from CH_2Cl_2 was synthesised [$HNMe_3$][3-F-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (**7**) as a colourless crystalline material. Yield 0.325 g, 96.1%. *Anal*. Found: C, 56.7; H, 8.37; N, 3.76. Calc. for $C_{17}H_{29}B_9FN$: C, 56.1; H, 8.04; N, 3.85%. IR ν (cm^{-1}): 2524 (br). ^1H NMR δ (ppm): 6.8–7.2 (m, 10H, C_6H_5), 2.71 (s, 9H, CH_3). $^{11}B\{^1H\}$ NMR δ (ppm): 3.17 (d, $^1J_{BF} = 55$ Hz, 1B, B3), −7.58 (2B), −16.97 (4B), −34.48 (1B), −37.40 (1B). ^{19}F NMR δ (ppm): −198 (1:1:1:1 quar., $^1J_{BF} = 56$ Hz).

2.2. Crystallographic studies

Single, diffraction-quality, crystals of **1**, **2**, **5c** and **6b** were grown by diffusion of a CH_2Cl_2 solution of the compound and a fivefold excess of 40–60 petroleum ether at room temperature. Diffraction data were measured at 160(2) K on a Bruker AXS *P*4 diffractometer equipped with an Oxford Cryosystems Cryostream cooler. One asymmetric fraction of intensity data was collected [13] to θ_{max} 25° with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) using ω scans. Standard reflections were re-measured every 100 data and any crystal decay corrected. Data for **1**, **5c** and **6b** were corrected for absorption by ϕ scans. All structures were solved [14] by direct and difference Fourier methods and refined by full-matrix least-squares against F^2, with non-hydrogen atoms assigned anisotropic displacement parameters. The anion of **5c** is disordered with 50% occupancy of B3H and B12H fragments, this rendering the anion non-crystallographically-imposed C_s symmetry. A consequence of this disorder is that it proved impossible to locate the H atom associated with the open face. The crystal of **6b** contains 0.5 molecule of CH_2Cl_2 of solvation per ion pair, slightly disordered about a centre of symmetry, and C–Cl was restrained to 1.70(4) Å in the refinement. Phenyl, methylene and methyl H atom positions were calculated and treated as riding models (C–H distances 0.95, 0.99 and 0.98 Å, respectively), with displacement parameters calculated as 1.2, 1.2 and 1.5 times the bound carbon atom U_{eq}, respectively. Cage H atoms were either treated as riding on the appropriate B atom (B–H = 1.1 Å, **2** and **5c**) or were restrained to a B–H distance of 1.10(2) Å (**1** and **6b**) with U_H set at 1.2 times U_B in all cases. The only exception was in **6b** where H(10B) which was allowed positional refinement and the U values of the B-bound H atoms were freely refined. Table 1 lists details of unit cell data, intensity data collection and structure refinement.

3. Results and discussion

3.1. Labelled closo-carboranes

This paper describes new, labelled, derivatives of 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ prepared by two methods, electrophilic substitution and recapitation.

Electrophilic substitution has for many years been an established procedure by which carboranes may be

Table 1
Crystallographic data[a] for compounds **1**, **2**, **5c** and **6b**

	1	**2**	**5c**	**6b**
Formula	$C_{14}H_{18}B_{10}I_2$	$C_{15}H_{22}B_{10}$	$C_{24}H_{35}B_9IN$	$C_{22}H_{40}B_9N\cdot 0.5CH_2Cl_2$
M_r	548.18	310.43	560.71	458.30
Colour	Colourless	colourless	colourless	colourless
Habit	Block	needle	needle	block
Crystal system	Orthorhombic	monoclinic	monoclinic	triclinic
Space group	*Pnma*	*C*2/*c*	$P2_1/n$	$P\bar{1}$
a (Å)	15.356(3)	16.876(2)	11.673(3)	10.4960(10)
b (Å)	15.601(2)	7.835(4)	19.663(3)	10.5080(10)
c (Å)	8.5730(10)	27.063(4)	13.427(2)	14.544(2)
α (°)	90	90	90	74.940(10)
β (°)	90	107.553(9)	113.620(17)	72.290(10)
γ (°)	90	90	90	63.300(10)
U (Å^3)	2053.8(5)	3411.8(16)	2823.9(10)	1350.8(3)
Z	4	8	4	2
D_{calc} (Mg m^{-3})	1.773	1.209	1.319	1.127
μ(Mo Kα) (mm^{-1})	3.057	0.059	1.148	0.154
F(0 0 0)	1032	1296	1132	490
Crystal size (mm)	0.28 × 0.32 × 0.36	0.14 × 0.24 × 0.76	0.08 × 0.12 × 0.42	0.16 × 0.36 × 0.42
Transmission factors	0.75–0.83	–	0.75–0.99	0.875–0.902
Data collected	2472	3846	6117	5591
Ind. data, *n*	1867	2981	4971	4742
R_{int}	0.0321	0.0314	0.0672	0.0445
No. variables, *p*	138	227	329	346
R, wR_2, (all data)	0.0519, 0.0886	0.0791, 0.1859	0.1462, 0.1469	0.0935, 0.1751
S (all data)	1.023	1.115	1.012	1.052
E_{max}, E_{min} (e Å^{-3})	0.863, −0.499	0.369, −0.258	0.834, −0.550	0.499, −1.055

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o||$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}]$, (where $w^{-1} = [\sigma_c^2(F_o)^2+(aP)^2+bP]$ and $P = [0.333\,(F_o)^2+0.667(F_c)^2])$, $S = [\Sigma[w(F_o^2-F_c^2)^2(n-p)]^{1/2}$, (where *n* is the number of data and *p* the number of parameters).

halogenated. The Lewis acid-catalysed iodination of 1,2-*closo*-1,2-$C_2B_{10}H_{12}$ with elemental I_2 affords, successively, 9-I-1,2-*closo*-$C_2B_{10}H_{11}$ [15–17] and 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ [17,18], whilst an analogous reaction using the more strongly iodinating agent ICl also yields the di-iodo derivative in high yield but more quickly [18].

Iodination of 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ is more difficult to achieve because of the electron withdrawing influence of the phenyl groups. We [9] achieved a 70% yield of 1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$ by iodination (using 0.5 equiv. of I_2) catalysed by strong mineral acid, a method first reported by Vasil'eva and Khalfina [19]. The same procedure, but with 2.5 equiv. of I_2, gave only relatively small amounts of the di-iodo compound 1,2-Ph_2-9,12-I_2-1,2-*closo*-$C_2B_{10}H_8$, **1**, (as assessed by ^{11}B NMR spectroscopy) but using 5 equiv. of I_2 afforded **1** in nearly 50% yield.

Compound **1** was characterised by microanalysis and IR and NMR spectroscopies. Consistent with the expected C_{2v} molecular symmetry, there are only four resonances in the $^{11}B\{^1H\}$ NMR spectrum, with relative integrals 1:2:1:1 from high frequency to low frequency. Of these, only the lowest frequency resonance, at approximately −10 ppm, remains a singlet in the ^{11}B spectrum, identifying it as arising from the labelled vertices B9 and B12.

A crystallographic study of **1** confirmed its identity. Fig. 2 shows a perspective view of a single molecule and Table 2 lists selected interatomic distances and inter-

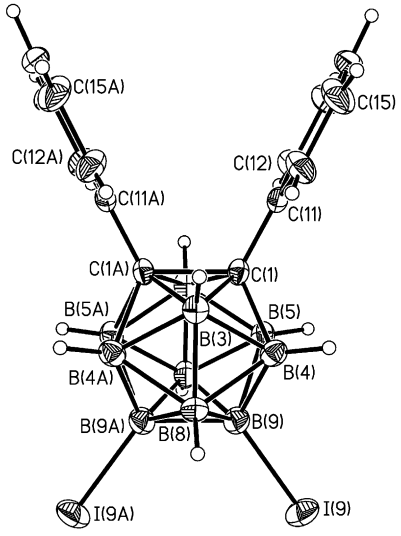


Fig. 2. Perspective view of compound **1** nearly perpendicular to the crystallographically-imposed mirror plane. Thermal ellipsoids are drawn at the 50% probability level, except for H atoms.

Table 2
Selected interatomic distances (Å) and interbond angles (°) for **1**

Distances			
C(1)–C(1A)	1.733(8)	C(1)–B(3)	1.746(7)
C(1)–B(4)	1.713(6)	C(1)–B(5)	1.708(7)
C(1)–B(6)	1.750(7)	B(3)–B(4)	1.783(7)
B(3)–B(8)	1.786(10)	B(4)–B(5)	1.780(7)
B(4)–B(8)	1.793(6)	B(4)–B(9)	1.787(7)
B(5)–B(6)	1.773(7)	B(5)–B(9)	1.778(7)
B(5)–B(10)	1.773(7)	B(6)–B(10)	1.752(11)
B(8)–B(9)	1.783(9)	B(9)–B(9A)	1.751(10)
B(9)–B(10)	1.797(9)	C(1)–C(11)	1.499(6)
B(9)–I(9)	2.175(5)		
Angles			
C(11)–C(1)–C(1A)	117.8(2)	C(11)–C(1)–B(3)	118.3(4)
C(11)–C(1)–B(4)	122.8(4)	C(11)–C(1)–B(5)	122.3(4)
C(11)–C(1)–B(6)	117.0(4)	I(9)–B(9)–B(9A)	125.54(14)
I(9)–B(9)–B(8)	122.4(3)	I(9)–B(9)–B(4)	118.2(3)
I(9)–B(9)–B(5)	118.2(3)	I(9)–B(9)–B(10)	122.4(4)

bond angles. Compound **1** resides on a crystallographic mirror plane through atoms B(3), B(6), B(8) and B(10). The C(1)–C(1A) distance in **1** is 1.733(8) Å, marginally longer than that [C(1)–C(2)] in 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ [20] [1.727(6) Å average for two crystallographically-independent molecules] and 1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$ [9] [1.724(4) Å]. The conformation of the phenyl groups in 1,2-Ph_2-1,2-*closo*-C_2B_{10} species is conveniently described by θ_{Ph}, defined [21] as the modulus of the average C_{cage}-C_{cage}-C_{Ph}-C_{Ph} torsion angles. In **1** θ_{Ph} is low, 4.1°, with the crystallographic mirror plane requiring that the rings are (slightly) twisted from 0° in a disrotatory fashion. Ab initio molecular orbital (MO) calculations on 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ [22] have shown that conformations with low values of θ_{Ph} are very similar in energy, whilst semi-empirical MO calculations on 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ [20], for which the average measured θ_{Ph} is only 5.5°, suggest that *con*rotation of the phenyl rings by up to 40° can be tolerated without significant destabilisation from Ph···Ph crowding.

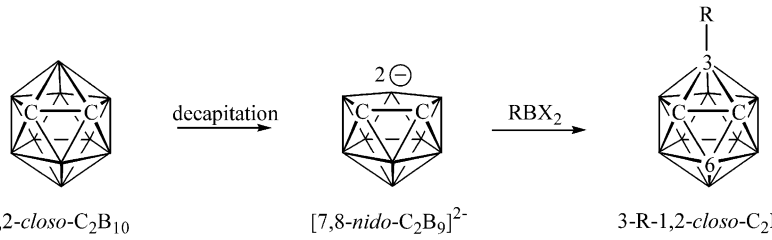
The B–I distance in **1** is 2.175(5) Å, in excellent agreement with that [2.178(4) Å] in 1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$ although longer than that [average 2.153(14) Å] in 9,10-I_2-1,7-*closo*-$C_2B_{10}H_{10}$ [18] where the I-labelled B atoms are not antipodal to C. In both 1,2-*closo*-C_2B_{10} compounds the B-I vector is not ideally radial to the polyhedron but inclined somewhat towards the B(4)–B(5) connectivity, as evidenced by inspection of the I–B–X angles (Table 2 for **1**).

Whilst electrophilic substitution is an ideal way of labelling a 1,2-*closo*-C_2B_{10} carborane at positions 9 and 12, reflecting the relatively high negative charge at these sites [23], an alternative strategy must be adopted for labelling positions 3 and 6, the most positive boron atoms. The approach here is one of *recapitation*, i.e., selective degradation (decapitation) of 1,2-*closo*-C_2B_{10} carborane to [7,8-*nido*-C_2B_9]$^{2-}$ carborane followed by reaction with RBX_2 (Scheme 2) whereupon the incoming B atoms is pre-labelled with group R. Both decapitation [24] and recapitation [25] were first described by Hawthorne et al. and have become standard procedures. We [26] have recently used the approach to prepare 1-R'-3-R-1,2-*closo*-$C_2B_{10}H_{10}$ species (R' = Me, Ph; R = Br, I) and subsequently shown [27] that these compounds can be decapitated with selective loss of the B6 vertex, as required to produce a 3-labelled *nido* species (vide infra).

Recapitation of [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$]$^{2-}$ (produced in situ from heating to reflux [$HNMe_3$][7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$] and 2 equiv. of *n*-BuLi in Et_2O) with {BMe^{2+}}, {BEt^{2+}} and {BF^{2+}} fragments afforded by $BMeBr_2$, $BEtBr_2$ and $BF_3{\cdot}Et_2O$, respectively, gave the new 3-labelled diphenylcarboranes 1,2-Ph_2-3-Me-1,2-*closo*-$C_2B_{10}H_9$, **2**, 1,2-Ph_2-3-Et-1,2-*closo*-$C_2B_{10}H_9$, **3**, and 1,2-Ph_2-3-F-1,2-*closo*-$C_2B_{10}H_9$, **4**, as colourless solids. Yields of **3** and **4** are reasonable, but that of **2** is relatively poor, which we attribute largely to the difficulty of handling $BMeBr_2$ relative to the other borane reagents.

Compounds **2**–**4** were characterised by microanalysis, IR and NMR spectroscopy, and, for **3**, mass spectrometry. The ^{1}H NMR spectra of all three compounds show the expected resonances arising from aromatic and, for **2** and **3**, alkyl protons. For **3** the signal arising from the –CH_2– group is a clear quartet at 400 MHz but an apparent broad triplet at 200 MHz as a result of the adjacency of the boron cage. The ^{11}B{^{1}H} spectra at 128 MHz show evidence of signal overlap, with only five (1:2:3:3:1, high frequency to low), four (1:2:6:1) and five (1:2:2:4:1) resonances, respectively, visible between +5 and −10 ppm (+5 and −15 for **4**). However, in all three cases, the highest frequency signal is assigned to B3 as it alone does not show additional coupling in the ^{11}B spectrum. For **2** and **3** the highest frequency ^{11}B{^{1}H} signal is a singlet, but for **4** it is a broad doublet due to B–F coupling with $^1J_{BF}$ measured as 43 Hz. The ^{19}F NMR spectrum of **4** shows the expected 1:1:1:1 quartet with $^1J_{BF}$ measured as 55 Hz, the apparent difference in coupling constants being ascribed to poor resolution arising from signal broadening.

A diffraction study of a single crystal of **2** (Fig. 3 and Table 3) confirmed its identity. The methyl-labelled boron atom has recapitated the *nido*-carborane and occupies vertex 3 (closo numbering scheme) adjacent to both cage C atoms. The molecule has effective C_s symmetry about a plane passing through B(3), B(6), B(8) and B(10), but this is not crystallographically-imposed. The steric influence of the methyl label has caused the Ph substituents to re-orient in a disrotatory manner relative to their conformation in 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ [20], as they now subtend θ_{Ph} angles of 21.6° [ring on C(1)] and 21.7° [ring on C(2)]. This



Scheme 2. Generalised decapitation/recapitation scheme affording 3-labelled *closo*-carboranes. Subsequent decapitation of the labelled carborane occurs preferentially at position 6.

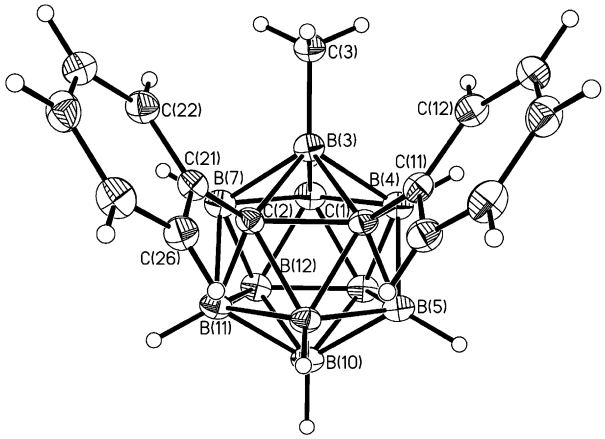


Fig. 3. Perspective view of compound **2**. Thermal ellipsoids are drawn at the 50% probability level, except for H atoms.

Table 3
Selected interatomic distances (Å) and interbond angles (°) for **2**

Distances			
C(1)–C(2)	1.734(3)	C(1)–B(3)	1.770(3)
C(1)–B(4)	1.713(3)	C(1)–B(5)	1.717(3)
C(1)–B(6)	1.736(3)	C(2)–B(6)	1.743(3)
C(2)–B(11)	1.719(3)	C(2)–B(7)	1.714(3)
C(2)–B(3)	1.770(3)	B(3)–B(7)	1.804(4)
B(3)–B(8)	1.781(4)	B(3)–B(4)	1.796(4)
B(4)–B(8)	1.776(4)	B(4)–B(9)	1.775(4)
B(4)–B(5)	1.779(3)	B(5)–B(6)	1.774(4)
B(5)–B(9)	1.781(4)	B(5)–B(10)	1.778(4)
B(6)–B(10)	1.766(4)	B(6)–B(11)	1.776(3)
B(7)–B(11)	1.775(3)	B(7)–B(12)	1.775(4)
B(7)–B(8)	1.774(4)	B(8)–B(9)	1.791(4)
B(8)–B(12)	1.783(4)	B(9)–B(10)	1.794(4)
B(9)–B(12)	1.787(4)	B(10)–B(11)	1.786(4)
B(10)–B(12)	1.799(4)	B(11)–B(12)	1.782(4)
C(1)–C(11)	1.509(3)	C(2)–C(21)	1.510(3)
B(3)–C(3)	1.583(3)		
Angles			
C(11)–C(1)–C(2)	121.38(18)	C(11)–C(1)–B(3)	117.86(18)
C(11)–C(1)–B(4)	119.76(18)	C(11)–C(1)–B(5)	119.74(18)
C(11)–C(1)–B(6)	119.44(17)	C(21)–C(2)–C(1)	121.11(17)
C(21)–C(2)–B(3)	118.21(18)	C(21)–C(2)–B(7)	120.36(18)
C(21)–C(2)–B(11)	120.06(17)	C(21)–C(2)–B(6)	119.08(17)
C(3)–B(3)–C(1)	123.30(19)	C(3)–B(3)–C(2)	123.01(19)
C(3)–B(3)–B(7)	123.6(2)	C(3)–B(3)–B(8)	125.47(18)
C(3)–B(3)–B(4)	123.9(2)		

apparently has no influence on the C(1)–C(2) distance in **2**, 1.734(3) Å, identical to that in 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$.

3.2. Labelled *nido*-carboranes

The utility of labelled diphenylcarboranes such as **1**–**4** in helping to establish an experimental mapping of the mechanism of (hetero)carborane isomerisation depends on retention of the labelled vertex when the *closo*-carborane is decapitated to the 7,8-Ph_2-7,8-*nido*-C_2B_9 anion prior to metallation. It is well established [24] that nucleophilic attack of 1,2-*closo*-C_2B_{10} carboranes by heating to reflux with ethanolic hydroxide results in decapitation of the B3 [≡B6] vertex. Thus in compound **1** and its analogue 1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$, the only potential problem is that the B–I bond could be broken under such conditions. For compounds **2**–**4** a further problem could be that the substituted vertex is that which is lost, although recent results obtained in collaboration with Teixidor and co-workers [27] show that compounds 1-R'-3-R-1,2-*closo*-$C_2B_{10}H_{10}$ (R' = Me, Ph; R = Br, I) selectively decapitate at vertex 6, leaving the labelled boron atom intact.

Because it is singly labelled, the mono-iodo diphenylcarborane 1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$ [9] is potentially more useful than **1** in mechanistic studies. Heating to reflux an ethanolic solution of 1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$ with 2.5 equiv. of OH^- converted the *closo*-carborane to [5-I-7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^-$, isolated as its $[HNEt_3]^+$, **5a**, $[HNMe_3]^+$, **5b**, and $[C_6H_5CH_2NMe_3]^+$, **5c**, salts. The salt **5** was characterised by microanalysis, IR spectroscopy, and ^1H and ^{11}B NMR spectroscopy. The $^{11}B\{^1H\}$ spectrum of **5a** reveals eight resonances (one accidental co-incidence) between −4 and −31 ppm, typical for a 7,8-*nido*-C_2B_9 species [28]. The third lowest frequency resonance (−20.9 ppm) remains a singlet in the ^{11}B spectrum and is thus identified as arising from the I-labelled boron atom.

Salt **5c** gave crystals suitable for crystallographic study, the results of which are shown in Fig. 4 (view of the anion only) and listed in Table 4. In the anion there is limited disorder, with vertices 3 and 12 each 50% occupied by {BH} to render the anion non-imposed C_s

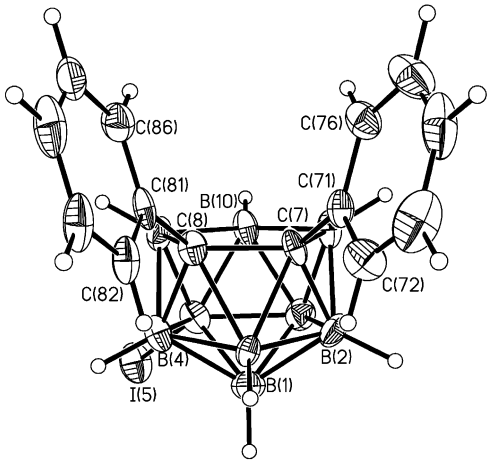


Fig. 4. Perspective view of the anion of **5c**. The partially-occupied 12th BH vertex is omitted for clarity, and, because of this partial disorder, the H atom associated with the open face was not located. Except for H atoms, thermal ellipsoids are drawn at the 50% probability level.

Table 4
Selected interatomic distances (Å) and interbond angles (°) for **5c**

Distances			
B(1)–B(2)	1.781(12)	B(1)–B(3)	1.68(2)
B(1)–B(4)	1.803(13)	B(1)–B(5)	1.773(12)
B(1)–B(6)	1.806(13)	B(2)–B(3)	1.71(2)
B(2)–B(6)	1.760(13)	B(2)–C(7)	1.676(12)
B(2)–B(11)	1.816(14)	B(3)–B(4)	1.761(17)
B(3)–C(7)	1.791(19)	B(3)–C(8)	1.849(19)
B(4)–B(5)	1.747(13)	B(4)–C(8)	1.674(11)
B(4)–B(9)	1.809(13)	B(5)–B(6)	1.808(13)
B(5)–B(9)	1.757(13)	B(5)–B(10)	1.776(13)
B(6)–B(10)	1.773(14)	B(6)–B(11)	1.769(13)
C(7)–C(8)	1.609(10)	C(7)–B(11)	1.680(11)
C(8)–B(9)	1.665(11)	B(9)–B(10)	1.806(13)
B(10)–B(11)	1.787(12)	B(6)–B(10)	1.773(14)
C(7)–B(12)	1.806(18)	C(8)–B(12)	1.81(2)
B(9)–B(12)	1.77(2)	B(10)–B(12)	1.746(19)
B(11)–B(12)	1.71(2)		
N(1)–C(90)	1.495(10)	N(1)–C(91)	1.488(10)
N(1)–C(92)	1.511(10)	C(92)–C(93)	1.501(10)
C(93)–C(94)	1.394(11)	C(94)–C(95)	1.401(12)
C(95)–C(96)	1.367(14)	C(96)–C(97)	1.350(13)
C(97)–C(98)	1.387(11)	C(98)–C(93)	1.408(12)
Angles			
I(5)–B(5)–B(1)	118.0(5)	I(5)–B(5)–B(4)	121.0(6)
I(5)–B(5)–B(9)	122.3(5)	I(5)–B(5)–B(10)	119.7(5)
I(5)–B(5)–B(6)	120.4(5)		
C(71)–C(7)–C(8)	117.4(6)	C(71)–C(7)–B(3)	117.0(8)
C(71)–C(7)–B(2)	120.4(6)	C(71)–C(7)–B(11)	119.7(6)
C(71)–C(7)–B(12)	115.4(8)	C(81)–C(8)–C(7)	116.4(6)
C(81)–C(8)–B(3)	117.8(8)	C(81)–C(8)–B(4)	121.3(6)
C(81)–C(8)–B(9)	120.4(6)	C(81)–C(8)–B(12)	115.2(8)

symmetry about the plane defined by C(7), C(8), B(5) and B(6). Such disorder is not uncommon in *nido*-7,8-C_2B_9 species and does not affect the major conclusions of the crystallographic study; the C(7)–C(8) distance, 1.609(10) Å, is very similar to that in the unlabelled analogue [7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}]^-$, 1.590(5) Å in the $[HNEt_3]^+$ salt and 1.602(3) Å in the $[C_6H_5CH_2NMe_3]^+$ salt [10]; the measured θ_{Ph} values, 1.1° [ring on C(7)] and 5.2° [ring on C(8)], again are fully comparable with those in [7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}]^-$ (average of 7.8° and 19.0°, respectively).

Analogous decapitation reactions were also performed on the 3-labelled *closo*-diphenylcarboranes **3** and **4**. In both cases a single product was formed in good to excellent yield, isolated in the former case as both $[HNMe_3]^+$ salt, **6a**, and $[HNEt_3]^+$ salt, **6b**, and in the latter case as the $[HNMe_3]^+$ salt, **7**, and characterised by spectroscopic and (for **6b**) crystallographic studies.

The ^1H NMR spectra of **6a** and **6b** at 200 MHz shows the expected resonances for Ph and (cation) Me or Et groups with the correct relative integrals. As with compound **3** the signal for the methylene protons of the (anion) Et group appear as a broad triplet. The highest frequency resonance in the $^{11}B\{^1H\}$ NMR spectrum remains a singlet in the ^{11}B spectrum and is thus assigned to the Et-labelled boron atom. Salt **6b** was also studied crystallographically. Fig. 5 shows a perspective view of the anion, and Table 5 hosts selected molecular dimensions. The key result is that the closo precursor **3** has been selectively decapitated at position 6, leaving the labelled boron 3 intact. The C(7)–C(8) connectivity is 1.602(3) Å, essentially identical to that in **5c** and [7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}]^-$ [10]. Relative to this latter unlabelled analogue, the Ph rings in **6b** are twisted in a disrotatory fashion, subtending θ_{Ph} values of 12.9° [ring on C(7)] and 24.1° [ring on C(8)], this asymmetry presumably a steric consequence of the orientation of the Et substituent. In spite of partially disordered solvent in the lattice, the crystallographic

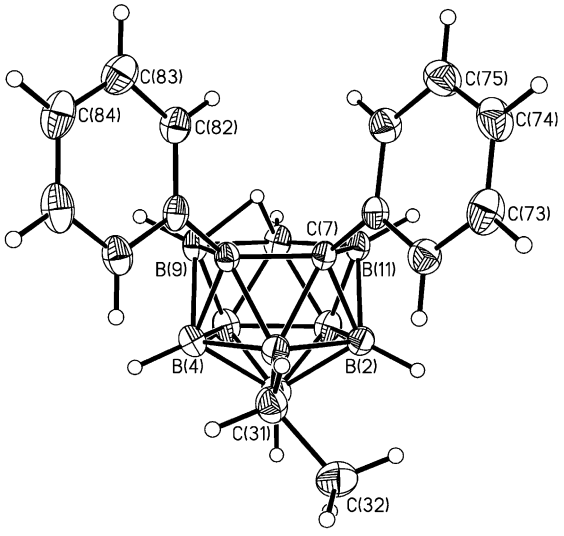


Fig. 5. Perspective view of the anion of **6b**. Except for H atoms, thermal ellipsoids are drawn at the 50% probability level.

Table 5
Selected interatomic distances (Å) and interbond angles (°) for **6b**

Distances			
B(1)–B(2)	1.773(4)	B(1)–B(3)	1.797(4)
B(1)–B(4)	1.750(4)	B(1)–B(5)	1.809(4)
B(1)–B(6)	1.798(4)	B(2)–B(3)	1.785(4)
B(2)–B(6)	1.760(4)	B(2)–C(7)	1.724(4)
B(2)–B(11)	1.784(4)	B(3)–B(4)	1.773(4)
B(3)–C(7)	1.768(4)	B(3)–C(8)	1.745(4)
B(4)–B(5)	1.769(4)	B(4)–C(8)	1.716(4)
B(4)–B(9)	1.798(4)	B(5)–B(6)	1.816(4)
B(5)–B(9)	1.774(4)	B(5)–B(10)	1.774(4)
B(6)–B(10)	1.781(4)	B(6)–B(11)	1.754(4)
C(7)–C(8)	1.602(3)	C(7)–B(11)	1.625(3)
C(8)–B(9)	1.642(3)	B(9)–B(10)	1.837(4)
B(10)–B(11)	1.815(4)	B(6)–B(10)	1.781(4)
B(9)–H(10B)	1.41(3)	B(10)–H(10B)	1.18(3)
N(1)–C(11)	1.500(4)	N(1)–C(13)	1.520(4)
N(1)–C(15)	1.498(4)	C(11)–C(12)	1.504(4)
C(13)–C(14)	1.507(6)	C(15)–C(16)	1.525(5)
Angles			
C(31)–B(3)–B(1)	125.0(2)	C(31)–B(3)–B(2)	125.0(2)
C(31)–B(3)–C(7)	127.4(2)	C(31)–B(3)–C(8)	124.5(2)
C(31)–B(3)–B(4)	122.0(2)	B(3)–C(31)–C(32)	114.3(2)
C(71)–C(7)–C(8)	121.30(19)	C(71)–C(7)–B(3)	119.03(19)
C(71)–C(7)–B(2)	118.80(19)	C(71)–C(7)–B(11)	115.05(19)
C(81)–C(8)–C(7)	121.16(19)	C(81)–C(8)–B(3)	120.35(19)
C(81)–C(8)–B(4)	121.2(2)	C(81)–C(8)–B(9)	114.85(19)
C(11)–N(1)–C(13)	111.8(2)	C(11)–N(1)–C(15)	113.5(3)
C(13)–N(1)–C(15)	112.6(3)	N(1)–C(11)–C(12)	113.4(3)
N(1)–C(13)–C(14)	114.4(3)	N(1)–C(15)–C(16)	114.2(3)

determination of **6b** is relatively precise—the facial H atom, H(10B), was successfully located and refined, and found to bridge the B(9)–B(10) edge asymmetrically, B(9)–H 1.41(3) Å, B(10)–H 1.18(3) Å.

Salt **7** was characterised by microanalysis, IR spectroscopy, and ^{1}H, ^{11}B and ^{19}F NMR spectroscopy. In the ^{11}B{^{1}H} spectrum the highest frequency resonance is a doublet, $^{1}J_{BF} = 55$ Hz, clearly arising from the labelled boron atom. This coupling is mirrored in the ^{19}F spectrum, which reveals a 1:1:1:1 quartet, $^{1}J_{BF} = 56$ Hz, at δ −198 in $CDCl_3$, 13 ppm to low frequency of the equivalent resonance in **4**. Clearly the {BF} vertex of **4** has been retained on decapitation. The symmetry apparent in the ^{11}B spectrum of **7** and its similarity to that of **6** unambiguously identify salt **7** as $[HNMe_3][3\text{-F-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]$.

4. Conclusions

We have described four new derivatives of $1,2\text{-Ph}_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ in which labels are appended to vertices 9 and 12, or to vertex 3. We have demonstrated that decapitation of the 9-iodo, 3-ethyl and 3-fluoro derivatives retains the vertex-label bond and, in the last two cases, also selectively removes the unlabelled vertex 6. Thus we now have access to good yields of the 5- and 3-labelled nido species $[5\text{-I-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$, $[3\text{-Et-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$, and $[3\text{-F-}7,8\text{-Ph}_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^-$, all conveniently available as $[HNMe_3]^+$ salts. Deprotonation of these, followed by metallation with a bulky metal-ligand fragment, should give rise to labelled C atom isomerised metallacarboranes, structural study of which will provide important information on the mechanism of rearrangement of (hetero)carboranes. The results of these studies will be the subject of subsequent publications [29].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 197923 (**1**), 197924 (**2**), 197925 (**5c**) and 197926 (**6b**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Leverhulme Trust (D.E.) and Heriot-Watt University (S.R., T.D.McG.) for support, Mr G. Evans and Mrs C. Graham for microanalysis, Dr A.S.F. Boyd for NMR spectra and Dr R. Ferguson for mass spectra. A.J.W. acknowledges the receipt of a Royal Society Leverhulme Trust Senior Research Fellowship, 2002–2003, and the hospitality of Prof. A. Laguna and colleagues at the Universidad de Zaragoza, Spain, where this manuscript was written.

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