PERGAMON

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POLYHEDRON

Haloaryl carbaboranes[☆]

2. Synthesis and characterisation of haloaryl-*closo*-carbaboranes. Crystal structures of 1-(4-BrC_6F_4)-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ (R=Me, Ph, Bu^t)

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Abstract

Reaction of C_6F_5Br with Li[1-R-1,2-*closo*-$C_2B_{10}H_{10}$] readily gives compounds 1-(4-BrC_6F_4)-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ [R=Me (**1**), Ph (**2**), Bu^t (**3**)]. Compounds **1**-**3** were characterised by NMR spectroscopy and single crystal X-ray diffraction studies. A significant lengthening of the C_{cage}–C_{cage} connectivity is seen as the steric demands of the cage bound substituents increase, from 1.712(7) Å in **1** to 1.736(7) and 1.743(8) Å in **2** and to 1.761(6) Å in **3**, the last being the longest C_{cage}–C_{cage} distance recorded for a carbaborane with alkyl or aryl substituents. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

We are currently interested in the effects of substituted aryl substituents on the properties of carbaboranes. Recent work has investigated the compounds, 1-R-12-R′-1,2-*closo*-$C_2B_{10}H_{10}$ (R=H, Ph; R′=Ph, *p*-Tol, *p*-$C_6H_4NO_2$) as potential non-linear optical (NLO) materials [1], and the use of electron-withdrawing and -donating aryl groups is expected to enhance such NLO properties. We are interested in polyfluorinated aryl rings as electron-withdrawing substituents to carbaboranes. The interdependence of electronic factors and structure for clusters is codified in Wade's rules [2] and, so, any significant electron withdrawal may have consequences for the structure of the cluster. Structural deformations in the cluster may also be induced as a result of the steric interactions of the exopolyhedral substituents.

Previous attempts to synthesise haloarylcarbaboranes, specifically pentafluorophenylcarbaboranes, by Zakharkin and Lebedev [3], involved the reaction of Li[1-R-1,2-*closo*-$C_2B_{10}H_{10}$] (R=Me, Ph) with C_6F_6. These reactions led to the isolation of the unexpected products 1,4-(2′-R-$C_2B_{10}H_{10}$)C_6F_4 even in the presence of excess C_6F_6, and no mono-cage products were identified.[1] In the present contribution we report the synthesis and characterisation of several haloarylcarbaboranes of general formula 1-(4-C_6F_4Br)-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ where R=Me, Ph, Bu^t. This group of compounds is considered in relation to the analogous compounds 1-Ph-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ (R=H [4], Br [5], Me [6], Ph [7]) in which the electron-withdrawing fluorine atoms are absent.

2. Experimental

2.1. General

All reactions were carried out under an atmosphere of dry, oxygen-free N_2 using standard Schlenk line techniques, with some subsequent manipulation in air. Solvents were dried and distilled under nitrogen immediately prior to use. Preparative thin-layer chromatography (TLC) employed Kieselgel 60 F_{254} plates (Merck), pre-washed in the

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[☆] For Part 1, see Ref. [14].

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[1] In all molecules, the haloaryl ring is attached to C(1), which involves a renumbering of the cluster from the starting material, where C(1) bears substituent R.

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Table 1
Crystallographic data and details of data collection and structure refinement for compounds **1–3**

	1	**2**	**3**
Formula	$C_9H_{13}B_{10}BrF_4$	$C_{14}H_{15}B_{10}BrF_4$	$C_{12}H_{19}B_{10}BrF_4$
Crystal size/mm	0.60×0.25×0.25	0.50×0.30×0.20	0.50×0.35×0.30
System	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	*Pbar1*	$P2_1/c$
a/Å	6.840(3)	10.901(3)	8.955(3)
b/Å	14.927(3)	13.263(2)	14.930(4)
c/Å	15.902(4)	13.823(3)	14.341(4)
α/°	90	97.83(9)	90
β/°	92.64(3)	97.12(11)	95.11(3)
γ/°	90	91.76(7)	90
V/Å^3	1621.9(9)	1962.3(7)	1909.7(10)
Z	4	4 (2 independent)	4
D_{calc}/g cm^{-3}	1.578	1.514	1.486
$\theta_{orientation}$/°	$8<\theta<11$	$9<\theta<11$	$9<\theta<11$
$\theta_{data\ collection}$/°	$1.87<\theta<24.97$	$1.50<\theta<24.97$	$1.97<\theta<24.97$
h range	$-8\rightarrow+8$	$-12\rightarrow+12$	$-10\rightarrow+10$
k range	$0\rightarrow+17$	$-15\rightarrow+15$	$0\rightarrow+17$
l range	$0\rightarrow+18$	$0\rightarrow16$	$0\rightarrow+17$
Data measured	2937	7291	3584
Unique data	2834	6890	3357
Data observed [$F<2\sigma(F)$]	1479	3466	1870
g_1	0.1026	0.1476	0.1033
R (all data)	0.1531	0.1695	0.1384
R (observed data)	0.0643	0.0828	0.0643
$wR(F^2)$	0.1708	0.2255	0.1770
S	0.932	0.988	1.003
Variables	251	561	285
Max. residue/eÅ^{-3}	0.316	0.938 (near Br)	0.348
Min. residue/eÅ^{-3}	−0.779	−1.639 (near Br)	−0.870

appropriate solvent. Infra-red spectra were recorded as solutions in CH_2Cl_2, referenced against the same solvent or as KBr discs, on a Perkin-Elmer 598 or a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded at room temperature on Bruker WP200 (^{11}B, ^{1}H) and WH360 (^{1}H, ^{19}F) spectrometers. Chemical shifts are reported relative to external $SiMe_4$ (^{1}H), CCl_3F (^{19}F) and $BF_3\cdot OEt_2$ (^{11}B), with positive shifts to high frequency. Microanalyses were performed by the Edinburgh University Chemistry Department. The starting materials 1-Me-$C_2B_{10}H_{11}$ [8], 1-Ph-$C_2B_{10}H_{11}$ [4] and 1-Bu^t-$C_2B_{10}H_{11}$ [9] were prepared by literature methods, and their purities confirmed by microanalysis and ^{1}H NMR spectroscopy.

2.2. Syntheses

2.2.1.1. 1-(4-BrC_6F_4)-2-Me-1,2-*closo*-$C_2B_{10}H_{10}$ (1)

To a solution of 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ (0.704 g, 4.45 mmol) in diethyl ether (25 ml) at 0°C was added a 1.6-M solution of BuLi in hexane (3.1 ml, 5 mmol). A solution of C_6F_5Br (1.1 g, 4.46 mmol) in a small amount of diethyl ether was then added. The mixture was stirred for 30 min at room temperature, until the solution turned dark orange. The solvents were removed under reduced pressure to leave a brown oily solid. This was extracted with hexane (3×10 ml) and the solvent was removed from the extract under reduced pressure. Recrystallisation from MeOH gave the product as a white solid, which was dried in vacuo. Yield=1.36 g, 81%.

Found: C, 28.63%; H, 3.91%. Calculated (for $C_9H_{13}B_{10}BrF_4$): C, 28.14%; H, 3.40%. IR (CH_2Cl_2): ν_{max} 2550 cm^{-1} (B–H). NMR ($CDCl_3$): ^{11}B-{^{1}H} δ 0.91 (1B), −4.74 (2B) and −8.38 (7B) ppm; ^{19}F δ −128.6 (br. s, 2F, *o*-F) and −130.5 (m, 2F, *m*-F) ppm; ^{1}H: δ 1.87 (s, 3H, CH_3) ppm.

2.2.1.2. Synthesis of 1-(4-BrC_6F_4)-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$ (2)

To 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ (2.20 g, 10.0 mmol) in diethyl ether (30 ml) at 0°C was added a BuLi solution (1.6 M, 6.8 ml, 11.0 mmol). A solution of C_6F_5Br (2.51 g, 11.0 mmol) in diethyl ether (5 ml) was then added to the stirring mixture. This was then warmed to room temperature and stirred for 20 h, giving a pale orange solution. The solvents were removed under reduced pressure to leave an orange oil, which was extracted with hexane (3×40 ml). The solvent was removed from the extract under reduced pressure to yield a pale, oily solid. Recrystallisation from warm MeOH gave a white solid, **2**, which was dried in vacuo. Yield=3.8 g, 85%.

Found: C, 38.16%; H, 4.01%. Calculated (for

$C_{14}H_{15}B_{10}BrF_4$): C, 37.60%; H, 3.38%. IR (CH_2Cl_2): ν_{max} 2545 cm^{-1} (B–H). NMR ($CDCl_3$): ^{11}B-{^{1}H} δ 1.84 (1B), −2.40 (1B) and −8.23 (8B) ppm; ^{19}F δ −129.7 (br. s, 2F, *o*-F) and −131.2 (m, 2F, *m*-F) ppm; ^{1}H δ 7.57 (d, 2H), 7.32 (m, 1H) and 7.25 (m, 2H) ppm.

2.2.1.3. Synthesis of 1-(4-BrC_6F_4)-2-Bu^t-1,2-closo-$C_2B_{10}H_{10}$ (**3**)

A diethyl ether (40 ml) solution of 1-Bu^t-1,2-*closo*-$C_2B_{10}H_{11}$ (0.51 g, 2.5 mmol) was treated with a solution of BuLi in hexane (1.8 ml, 2.9 mmol). C_6F_5Br (0.37 ml, 2.4 mmol) in a small amount of diethyl ether was then added. The mixture was stirred for 4 h at room temperature, until the solution turned orange, and then the solvents were removed under reduced pressure to leave a dark, oily solid. This was extracted with hexane (2×15 ml) and the solvent was removed from the extract under reduced pressure. Recrystallisation from warm MeOH gave the product, **3**, as a white solid, which was dried in vacuo. Yield=0.49 g, 49%. Found: C, 34.64%; H, 6.04%. Calculated (for $C_{12}H_{19}B_{10}BrF_4$): C, 33.93%; H, 5.48%. IR (CH_2Cl_2): ν_{max} 2575 cm^{-1} (B–H). NMR ($CDCl_3$): ^{11}B-{^{1}H} δ 1.00 (1B), −2.69 (2B), −7.86 (3B) and −9.24 (4B) ppm; ^{19}F: δ −129.7 (br. s, 2F, *o*-F) and −131.2 (m, 2F, *m*-F) ppm; ^{1}H: δ 1.22 (s, 9H, Bu^t) ppm.

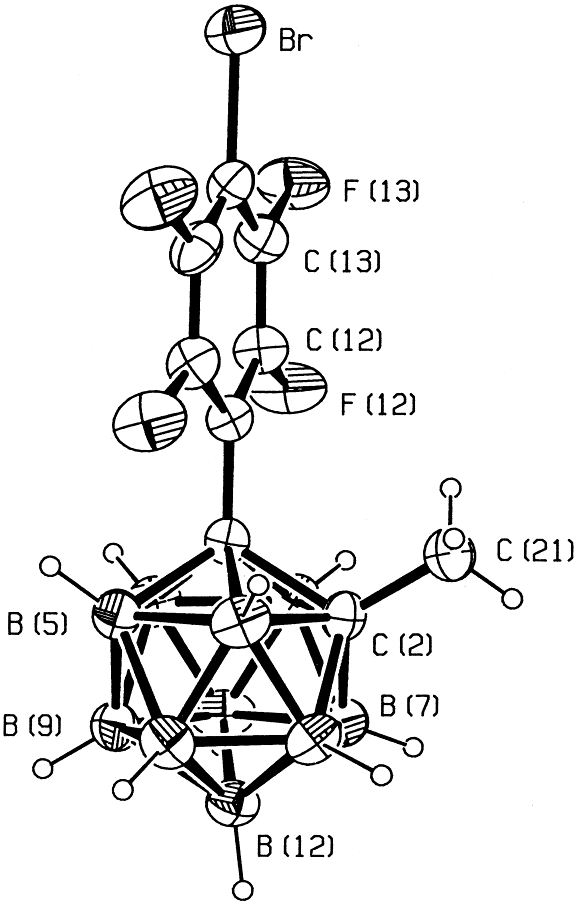


Fig. 1. Perspective view of a single molecule of compound **1** (30% thermal ellipsoids except for hydrogen atoms, which have an artificial radius of 0.1 Å for clarity). The aryl ring is numbered cyclically [C(11)–C(16)], and hydrogen atoms carry the same number as the atom to which they are attached.

2.2.2. Crystallography

All data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature using graphite monochromated Mo–K_α X-radiation, λ=0.71069 Å. Diffraction-quality crystals of the compounds were grown by slow evaporation of a methanol solution (compound **1**) or by diffusion between water and a methanol solution (compounds **2** and **3**), and were mounted in subsequently sealed Lindemann tubes.

In Table 1 are listed crystal data, as well as details of data collection and structure refinement, for crystals of compounds **1**, **2** and **3**. For each crystal, the unit cell parameters and orientation matrix for data collection were determined by the least-squares refinement of the setting angles of 25 strong, high-angle reflections. Data collection

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

C(11)–C(1)	1.515(7)	C(21)–C(2)	1.515(7)
C(1)–B(5)	1.695(8)	C(1)–B(4)	1.706(9)
C(1)–C(2)	1.712(7)	C(1)–B(6)	1.728(9)
C(1)–B(3)	1.743(9)	C(2)–B(11)	1.681(9)
C(2)–B(7)	1.685(9)	C(2)–B(3)	1.702(10)
C(2)–B(6)	1.707(9)	B(3)–B(8)	1.734(11)
B(3)–B(7)	1.735(10)	B(3)–B(4)	1.763(11)
B(4)–B(8)	1.749(11)	B(4)–B(5)	1.770(11)
B(4)–B(9)	1.770(11)	B(5)–B(9)	1.749(11)
B(5)–B(10)	1.769(10)	B(5)–B(6)	1.772(11)
B(6)–B(10)	1.741(10)	B(6)–B(11)	1.745(10)
B(7)–B(11)	1.739(11)	B(7)–B(12)	1.747(10)
B(7)–B(8)	1.759(11)	B(8)–B(9)	1.777(13)
B(8)–B(12)	1.784(11)	B(9)–B(10)	1.749(12)
B(9)–B(12)	1.765(10)	B(10)–B(11)	1.754(10)
B(10)–B(12)	1.760(12)	B(11)–B(12)	1.758(11)
C(16)–C(11)–C(1)	121.6(5)	C(12)–C(11)–C(1)	125.4(5)
C(11)–C(1)–B(5)	120.8(4)	C(11)–C(1)–B(4)	121.8(5)
B(5)–C(1)–B(4)	62.7(4)	C(11)–C(1)–C(2)	120.4(4)
C(11)–C(1)–B(6)	118.3(5)	B(5)–C(1)–B(6)	62.4(4)
C(2)–C(1)–B(6)	59.5(4)	C(11)–C(1)–B(3)	120.1(5)
B(4)–C(1)–B(3)	61.5(4)	C(2)–C(1)–B(3)	59.0(4)
C(21)–C(2)–B(11)	122.1(5)	C(21)–C(2)–B(7)	122.4(5)
B(11)–C(2)–B(7)	62.2(4)	C(21)–C(2)–B(3)	117.4(6)
B(7)–C(2)–B(3)	61.6(4)	C(21)–C(2)–B(6)	117.6(6)
B(11)–C(2)–B(6)	62.0(4)	C(21)–C(2)–C(1)	117.2(4)
B(3)–C(2)–C(1)	61.4(4)	B(6)–C(2)–C(1)	60.7(3)
C(2)–B(3)–B(7)	58.7(4)	B(8)–B(3)–B(7)	60.9(4)
C(2)–B(3)–C(1)	59.6(3)	B(8)–B(3)–B(4)	60.0(5)
C(1)–B(3)–B(4)	58.2(4)	C(2)–B(6)–C(1)	59.8(3)
C(2)–B(6)–B(11)	58.3(4)	B(10)–B(6)–B(11)	60.4(4)
C(1)–B(6)–B(5)	57.9(4)	B(10)–B(6)–B(5)	60.5(4)

was by $\omega-2\theta$ scans in 96 steps with an ω scan width $(0.8+0.34\ \tan\ \theta)$. Data were corrected for Lorentz and polarisation effects, and for decay (determined by remeasurement of the intensities of two chosen reflections every 8 X-ray h) using CADABS [10]. Only data for which $F>2.0\sigma(F)$ were retained for structure solution and refinement.

Each structure was solved by direct methods with all remaining non-hydrogen atoms found by difference Fourier methods and refined on F using full matrix least-squares (SHELXTL [11]). In compound **2**, the phenyl ring was constrained to be a regular hexagon (C–C, 1.395 Å). Hydrogen atoms were placed in idealised positions, riding on the atoms to which they were bonded. After isotropic convergence, data were corrected for absorption effects using empirical methods [12]. Non-hydrogen atoms were allowed anisotropic thermal parameters. In compounds **1** and **2**, the hydrogen atoms in each crystallographically independent molecule were given a common variable thermal parameter (U_H). In compound **3**, the hydrogen atoms were given isotropic thermal parameters set at $1.2U_{eq}$ for the atom to which they were bonded ($1.5U_{eq}$ for CH_3). In the final stages of refinement, data were weighted such that $w^{-1}=[\sigma^2(F_o^2)+(g_1P)^2+(g_2P)]$ where $P=[\max(F_o^2\ \text{or}\ 0)+2F_c^2]/3$.

3. Results and discussion

In 1970, Zakharkin and Lebedev [3] attempted to synthesise (polyfluorophenyl)carbaboranes by reaction of Li[1-R-1,2-*closo*-$C_2B_{10}H_{10}$] (R=Me, Ph) with C_6F_6, leading to the isolation of the unexpected product 1,4-(2′-R-$C_2B_{10}H_{10}$)C_6F_4 [4] and we have recently structurally characterised the compound where R=Ph (**4**) [13]. In an attempt to produce a mono-cage product, C_6F_5Br was used in place of C_6F_6 for reaction with Li[$RC_2B_{10}H_{10}$]. Recrystallisation from hot methanol gave analytically pure white crystalline products, 1-Ar_F-2-R-$C_2B_{10}H_{10}$ (R=Me [**1**], Ph [**2**], Bu^t [**3**]; Ar_F=4-C_6F_4Br) in good yields.

The identities of the products were confirmed by microanalysis, infra-red spectroscopy and by NMR studies. The ^{11}B-$\{^1H\}$ spectra obtained showed typical features for *closo* carbaboranes, with multiple peak coincidences in the spectrum due to the small range of ^{11}B resonances (+2 to −10 ppm) found. ^1H NMR spectroscopy showed that the weakly acidic cage CH atoms have been displaced, but the cage-bound substituents remain. ^{19}F NMR spectra contained only two resonances, for the *ortho*- and *meta*-fluorine environments, showing that the *para*-position was not occupied by a fluorine atom. It was noted in each case that one resonance showed significant fine structure, whilst

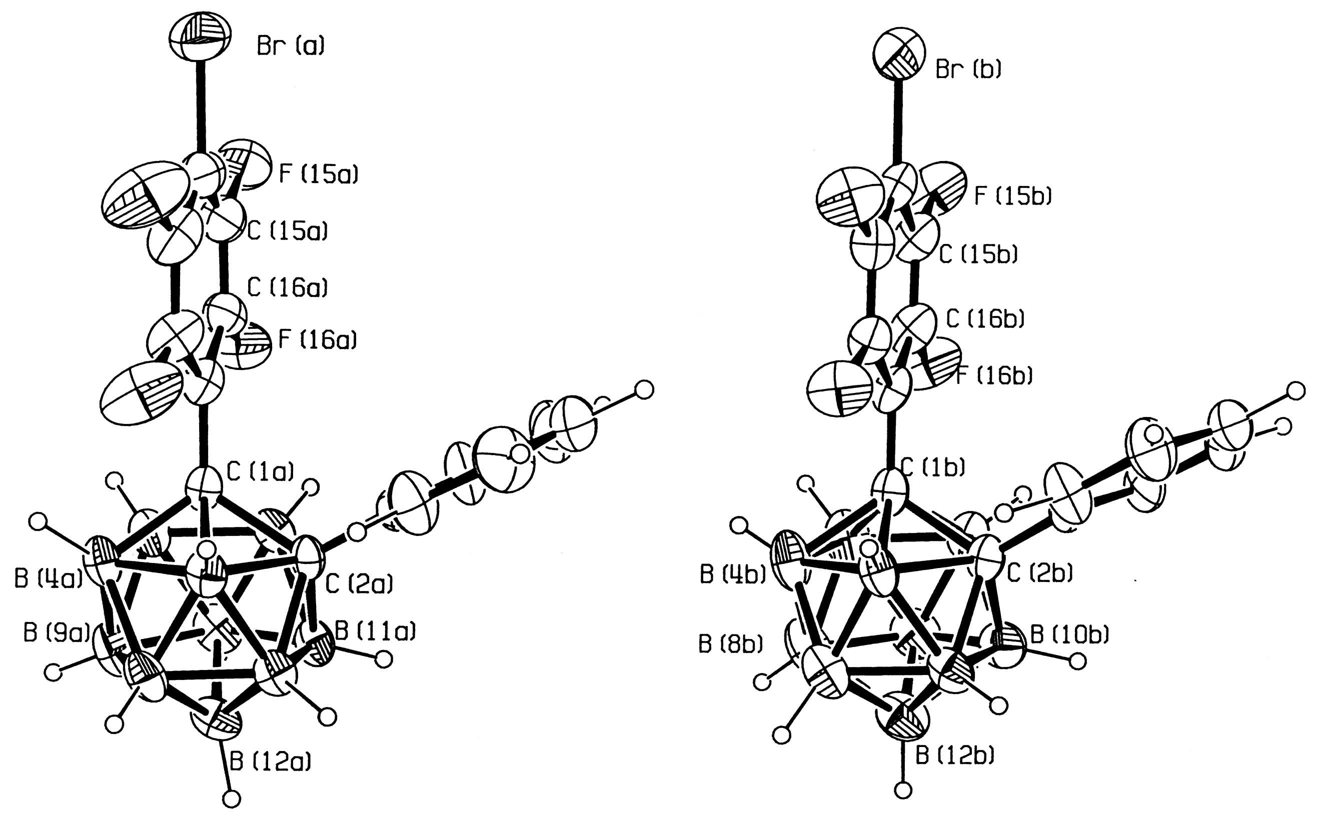


Fig. 2. Perspective views of each crystallographically independent molecule of compound **2** (30% thermal ellipsoids except for hydrogen atoms, which have an artificial radius of 0.1 Å for clarity). The aryl rings are numbered cyclically [C(11A)–C(16A), C(11B)–C(16B) for Ar_F and C(21A)–C(26A), C(21B)–C(26B) for Ph], and hydrogen and fluorine atoms carry the same number as the atom to which they are attached.

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

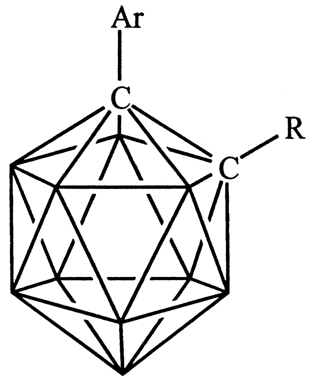
C(11A)–C(1A)	1.494(9)	C(11B)–C(1B)	1.469(9)
C(21A)–C(2A)	1.507(7)	C(21B)–C(2B)	1.496(7)
C(1A)–B(6A)	1.745(10)	C(1B)–B(6B)	1.725(10)
C(1A)–B(4A)	1.717(10)	C(1B)–B(4B)	1.736(11)
C(1A)–C(2A)	1.743(7)	C(1B)–C(2B)	1.736(8)
C(1A)–B(5A)	1.705(9)	C(1B)–B(5B)	1.740(11)
C(1A)–B(3A)	1.746(9)	C(1B)–B(3B)	1.775(10)
C(2A)–B(6A)	1.722(10)	C(2B)–B(6B)	1.709(10)
C(2A)–B(7A)	1.701(10)	C(2B)–B(7B)	1.711(10)
C(2A)–B(11A)	1.671(10)	C(2B)–B(11B)	1.715(12)
C(2A)–B(3A)	1.735(9)	C(2B)–B(3B)	1.738(10)
B(3A)–B(8A)	1.740(12)	B(3B)–B(8B)	1.748(13)
B(3A)–B(7A)	1.755(10)	B(3B)–B(7B)	1.756(12)
B(3A)–B(4A)	1.782(10)	B(3B)–B(4B)	1.787(11)
B(4A)–B(9A)	1.744(12)	B(4B)–B(9B)	1.74(2)
B(4A)–B(8A)	1.743(12)	B(4B)–B(8B)	1.76(2)
B(4A)–B(5A)	1.788(11)	B(4B)–B(5B)	1.793(13)
B(5A)–B(9A)	1.783(13)	B(5B)–B(9B)	1.75(2)
B(5A)–B(10A)	1.775(12)	B(5B)–B(10B)	1.76(2)
B(5A)–B(6A)	1.761(11)	B(5B)–B(6B)	1.787(12)
B(6A)–B(10A)	1.734(11)	B(6B)–B(11B)	1.758(12)
B(6A)–B(11A)	1.737(11)	B(6B)–B(10B)	1.778(14)
B(7A)–B(11A)	1.746(11)	B(7B)–B(11B)	1.778(13)
B(7A)–B(8A)	1.753(11)	B(7B)–B(8B)	1.782(13)
B(7A)–B(12A)	1.758(11)	B(7B)–B(12B)	1.821(14)
B(8A)–B(9A)	1.729(13)	B(8B)–B(9B)	1.75(2)
B(8A)–B(12A)	1.776(13)	B(8B)–B(12B)	1.78(2)
B(9A)–B(12A)	1.755(13)	B(9B)–B(12B)	1.73(2)
B(9A)–B(10A)	1.790(13)	B(9B)–B(10B)	1.75(2)
B(10A)–B(12A)	1.771(12)	B(10B)–B(12B)	1.73(2)
B(10A)–B(11A)	1.761(11)	B(10B)–B(11B)	1.76(2)
B(11A)–B(12A)	1.753(12)	B(11B)–B(12B)	1.771(14)
C(12A)–C(11A)–C(1A)	124.6(7)	C(12B)–C(11B)–C(1B)	124.1(6)
C(16A)–C(11A)–C(1A)	122.0(6)	C(16B)–C(11B)–C(1B)	123.8(6)
C(26A)–C(21A)–C(2A)	119.6(4)	C(26B)–C(21B)–C(2B)	121.1(4)
C(22A)–C(21A)–C(2A)	120.4(4)	C(22B)–C(21B)–C(2B)	118.9(4)
C(11A)–C(1A)–C(2A)	120.7(5)	C(11B)–C(1B)–C(2B)	119.6(5)
C(11A)–C(1A)–B(3A)	120.4(5)	C(11B)–C(1B)–B(3B)	122.0(5)
C(11A)–C(1A)–B(4A)	121.9(5)	C(11B)–C(1B)–B(4B)	124.3(6)
C(11A)–C(1A)–B(5A)	119.9(5)	C(11B)–C(1B)–B(5B)	120.5(6)
C(11A)–C(1A)–B(6A)	118.4(5)	C(11B)–C(1B)–B(6B)	116.5(5)
C(2A)–C(1A)–B(3A)	59.6(3)	C(2B)–C(1B)–B(3B)	59.4(4)
B(4A)–C(1A)–B(3A)	61.9(4)	B(4B)–C(1B)–B(3B)	61.2(4)
B(5A)–C(1A)–B(4A)	63.0(4)	B(5B)–C(1B)–B(4B)	62.1(5)
B(5A)–C(1A)–B(6A)	61.3(4)	B(5B)–C(1B)–B(6B)	62.1(5)
B(6A)–C(1A)–C(2A)	59.2(4)	B(6B)–C(1B)–C(2B)	59.2(4)
C(21A)–C(2A)–C(1A)	118.9(5)	C(21B)–C(2B)–C(1B)	119.2(5)
C(21A)–C(2A)–B(3A)	118.0(5)	C(21B)–C(2B)–B(3B)	118.2(5)
C(21A)–C(2A)–B(6A)	119.0(5)	C(21B)–C(2B)–B(6B)	119.0(5)
C(21A)–C(2A)–B(7A)	121.8(5)	C(21B)–C(2B)–B(7B)	120.4(5)
C(21A)–C(2A)–B(11A)	122.1(5)	C(21B)–C(2B)–B(11B)	121.7(5)
B(11A)–C(2A)–B(6A)	61.6(4)	B(11B)–C(2B)–B(6B)	61.8(5)
B(11A)–C(2A)–B(7A)	62.4(4)	B(11B)–C(2B)–B(7B)	62.5(5)
B(6A)–C(2A)–C(1A)	60.5(4)	B(6B)–C(2B)–C(1B)	60.1(4)
B(7A)–C(2A)–B(3A)	61.4(4)	B(7B)–C(2B)–B(3B)	61.2(5)
B(3A)–C(2A)–C(1A)	60.3(3)	B(3B)–C(2B)–C(1B)	61.4(4)
C(2A)–B(3A)–C(1A)	60.1(4)	C(2B)–B(3B)–C(1B)	59.2(4)
C(2A)–B(3A)–B(7A)	58.4(4)	C(2B)–B(3B)–B(7B)	58.6(4)
B(8A)–B(3A)–B(7A)	60.2(5)	B(8B)–B(3B)–B(7B)	61.1(5)
B(8A)–B(3A)–B(4A)	59.3(5)	B(8B)–B(3B)–B(4B)	59.6(6)
C(1A)–B(3A)–B(4A)	58.2(4)	C(1B)–B(3B)–B(4B)	58.3(4)
C(2A)–B(6A)–C(1A)	60.4(4)	C(2B)–B(6B)–C(1B)	60.7(4)
C(2A)–B(6A)–B(11A)	57.8(4)	C(2B)–B(6B)–B(11B)	59.3(5)
B(10A)–B(6A)–B(11A)	61.0(5)	B(10B)–B(6B)–B(11B)	59.8(6)
B(10A)–B(6A)–B(5A)	61.0(5)	B(10B)–B(6B)–B(5B)	59.1(6)
C(1A)–B(6A)–B(5A)	58.2(4)	C(1B)–B(6B)–B(5B)	59.4(4)

the higher frequency resonance was a very broad singlet. This latter resonance was assigned to the *ortho* fluorine atoms by analogy with the ^{19}F NMR spectra of **4**, which showed only one broad signal from its fluorine atoms, all of which are *ortho* to a carbaborane cage. The broadening is assumed to be due to long-range coupling to the boron nuclei in the cluster. The products were as expected for a S_NAr reaction, with substitution *para* to the least electronegative substituent, which was bromine in this case.

Compounds **1**–**3** form a series analogous to the 1-phenylcarbaboranes, with intersubstituent steric interactions growing as we increase the size of the C(2) substituent. A large series of carbaboranes, 1-Ph-2-R-1,2-$C_2B_{10}H_{10}$ [e.g. R=H (**5**) [4,14], Br [5], Me (**6**) [6], Ph (**7**) [7], Me_3Si (**8**) [15]] has been reported and compounds **1** and **2** are directly analogous to two of these. The non-fluorinated analogue of **3**, [1-Ph-2-Bu^t-$C_2B_{10}H_{10}$], however, has not been reported, although many attempts to synthesise it have been made [9]. Since the haloaryl carbaborane **3** forms easily, we can discount steric grounds for this failure.

The identity of compound **1** was confirmed by crystallographic study (Scheme 1). Fig. 1 views a single molecule and demonstrates the atomic numbering scheme adopted whilst Table 2 presents selected molecular parameters. In this molecule, intersubstituent steric effects are expected to be the smallest, and the C_{cage}–C_{cage} interatomic distance is 1.712(7) Å, which is not significantly longer than the 1.696(5) Å distance found in **6**, although both are greater than that found in the unsubstituted *ortho*-carbaborane, i.e., 1.630(6) Å [16]. Intersubstituent steric interactions will also affect the orientations adopted by the aryl rings. The orientation of phenyl rings attached to carbaboranes has previously been described by the parameter θ, the modulus of the average of the two C_{cage}–C_{cage}–C_{ring}–C_{ring} torsion angles, and we may use this parameter to describe the orientation of an aryl ring also. Thus, $\theta=90°$ when the aryl ring lies in the C_{cage}–C_{cage}–C_{ring} plane, and $\theta=0°$ when the ring lies perpendicular to this plane. Calculations have suggested that the electronically preferred orientation of the phenyl ring in **5**, where intersubstituent effects are small, is $\theta=68°$ [4]. In compound **1**, $\theta=6.8(9)°$, which is substantially reduced by the large intersubstituent effects and is even lower than that found in **6** ($\theta=16.7°$).

Compound **2** crystallises with two independent mole-



	Ar	R
1	Ar_F	Me
2	Ar_F	Ph
3	Ar_F	^{t}Bu
4	$4\text{-}(PhC_2B_{10}H_{10})C_6F_4$	Ph
5	Ph	H
6	Ph	Me
7	Ph	Ph
8	Ph	$SiMe_3$

Scheme 1.

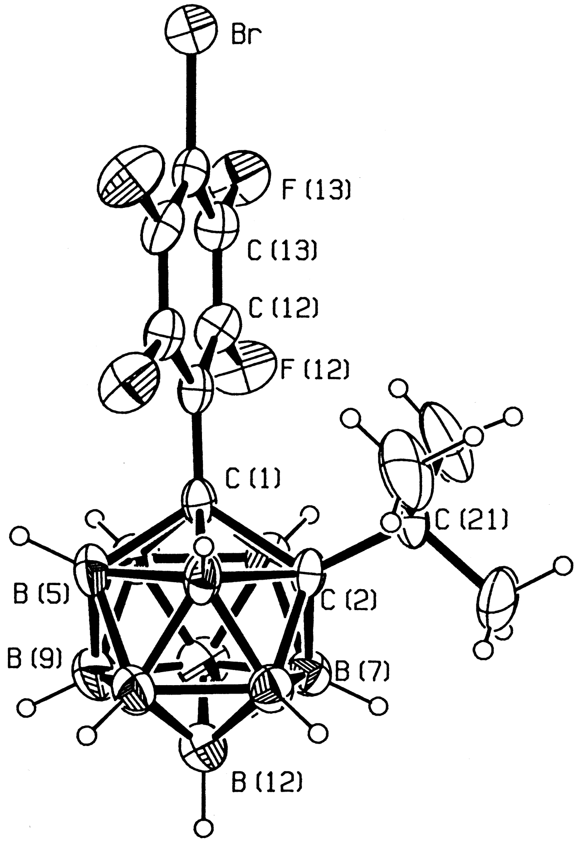


Fig. 3. Perspective view of a single molecule of compound **3** (30% thermal ellipsoids except for hydrogen atoms, which have an artificial radius of 0.1 Å for clarity). The aryl ring is numbered cyclically [C(11)–C(16)], and hydrogen atoms carry the same number as the atom to which they are attached.

Table 4
Selected interatomic distances (Å) and interbond angles (°) for compound **3**

C(11)–C(1)	1.501(6)	C(21)–C(212)	1.500(9)
C(21)–C(211)	1.497(8)	C(21)–C(2)	1.569(7)
C(21)–C(213)	1.518(9)	C(1)–C(2)	1.761(6)
C(1)–B(3)	1.737(8)	C(1)–B(4)	1.726(8)
C(1)–B(5)	1.719(9)	C(1)–B(6)	1.745(8)
C(2)–B(3)	1.731(8)	C(2)–B(6)	1.742(8)
C(2)–B(7)	1.702(8)	C(2)–B(11)	1.703(8)
B(3)–B(4)	1.773(11)	B(3)–B(7)	1.770(9)
B(3)–B(8)	1.756(10)	B(4)–B(5)	1.787(12)
B(4)–B(8)	1.756(10)	B(4)–B(9)	1.754(11)
B(5)–B(6)	1.766(10)	B(5)–B(9)	1.740(12)
B(5)–B(10)	1.752(9)	B(6)–B(10)	1.752(10)
B(6)–B(11)	1.752(8)	B(7)–B(8)	1.773(11)
B(7)–B(11)	1.740(10)	B(7)–B(12)	1.755(10)
B(8)–B(9)	1.776(14)	B(8)–B(12)	1.787(12)
B(9)–B(10)	1.747(13)	B(9)–B(12)	1.760(11)
B(10)–B(11)	1.773(10)	B(10)–B(12)	1.785(12)
B(11)–B(12)	1.768(10)		
(16)–C(11)–C(1)	123.4(4)	C(12)–C(11)–C(1)	123.4(4)
C(211)–C(21)–C(212)	106.9(6)	C(211)–C(21)–C(213)	106.3(7)
C(212)–C(21)–C(213)	107.2(6)	C(211)–C(21)–C(2)	110.4(5)
C(212)–C(21)–C(2)	112.7(5)	C(213)–C(21)–C(2)	112.9(5)
C(11)–C(1)–B(5)	119.3(4)	C(11)–C(1)–B(4)	118.9(4)
B(5)–C(1)–B(4)	62.5(4)	C(11)–C(1)–B(3)	120.2(4)
B(4)–C(1)–B(3)	61.6(4)	C(11)–C(1)–B(6)	120.8(4)
B(5)–C(1)–B(6)	61.3(4)	C(11)–C(1)–C(2)	123.3(4)
B(3)–C(1)–C(2)	59.3(3)	B(6)–C(1)–C(2)	59.6(3)
C(21)–C(2)–B(7)	121.3(4)	C(21)–C(2)–B(11)	121.3(4)
B(7)–C(2)–B(11)	61.5(4)	C(21)–C(2)–B(3)	119.4(4)
B(7)–C(2)–B(3)	62.1(3)	B(11)–C(2)–B(6)	61.1(3)
C(21)–C(2)–C(1)	120.9(4)	B(3)–C(2)–C(1)	59.7(3)
B(6)–C(2)–C(1)	59.7(3)	C(2)–B(3)–C(1)	61.0(3)
C(2)–B(3)–B(7)	58.1(3)	B(8)–B(3)–B(7)	60.4(4)
C(1)–B(3)–B(4)	58.9(4)	B(8)–B(3)–B(4)	59.7(4)
C(2)–B(6)–C(1)	60.7(3)	C(2)–B(6)–B(11)	58.4(3)
C(1)–B(6)–B(5)	58.6(3)	B(10)–B(6)–B(5)	59.7(4)
B(10)–B(6)–B(11)	60.8(4)		

cules in the asymmetric unit, and both are illustrated in Fig. 2. Selected interatomic distances and interbond angles are given in Table 3. The intersubstituent steric effects in **2** may be minimised by the two aryl rings both adopting low θ values. Such an effect is observed in both independent molecules, although to different extents, with the values of θ_{Ph} and θ_{Ar} being smaller in molecule A [$\theta_{Ar}=2.5(7)°$; $\theta_{Ph}=2.3(10)°$] than in molecule B [$\theta_{Ar}=6.8(7)°$; $\theta_{Ph}=10.3(10)°$]. Similar orientations of aryl rings are found in the structures of **4** and **7**, where the aryl rings are in similar environments to those in molecule **2**.

The C(1)–C(2) interatomic distances found in **2** are 1.743(7) Å (**2a**) and 1.736(8) Å (**2b**) and, although these are numerically larger, they are not significantly different from those in the non-halogenated analogue **7**, 1.733(4) and 1.720(4) Å. These values are larger than those found for carbaboranes where the C(2) substituent is a methyl group, due to increased steric interactions between the C(2) substituent and the aryl ring. Such interactions are indicated by the close approach (ca. 2.8 Å) of the fluorine atoms of the Ar$_F$ group to the plane of the non-fluorinated ring.

The structure of **3** was also determined by crystallographic study, and is shown in Fig. 3, with selected molecular parameters in Table 4. The extremely low value of θ [0.1(8)°] found is an expected consequence of the extremely bulky C(2) substituent. Intersubstituent steric effects are significant, and these may induce other distortions in addition to the lengthening of the C(1)–C(2) connectivity. Most noticeable is the ‘bend back’ of the aryl

Table 5
^{11}B chemical shifts in a series of carbaboranes, 1-Ar-2-R-$C_2B_{10}H_{10}$

	Ar	R	Range/ppm	Weighted mean/ppm
1	Ar$_F$	Me	$+0.91 \rightarrow -8.38$	−6.72
2	Ar$_F$	Ph	$+1.70 \rightarrow -8.40$	−5.21
3	Ar$_F$	^{t}Bu	$+1.00 \rightarrow -9.24$	−6.49
6	Ph	Me	$-2.36 \rightarrow -9.36$	−7.77
7	Ph	Ph	$-2.07 \rightarrow -8.60$	−6.97

ring away from the sterically demanding tertiary butyl group, giving a C(2)–C(1)–C(11) angle of 123.3(4)°, compared with ca. 120° in compounds **1**, **2** and **4**. The close contacts of the two substituents are also notable, with two butyl hydrogen atoms lying ca. 2.5 Å from the plane of the ring. A C(1)–C(2) distance of 1.761(6) Å is the result of these effects, which is considerably longer than in the previous haloaryl carbaboranes. Indeed, this distance is only known to be surpassed by that in three other *closo*-carbaboranes, all of which contain non-carbon atoms as substituents to the cage; oxygen in one case [17], and sulfur in the others [18]. The distance surpasses the length of the most similar carbaborane, 1-Ph-2-Me_3Si-1,2-*closo*-$C_2B_{10}H_{10}$, at 1.708(4) Å, which is as expected due to the smaller steric influence of the Me_3Si group relative to the Me_3C group, a consequence of the longer C_{cage}–Si bond.

The structural effects of replacing Ph by Ar_F do not appear to be significant in these molecules, suggesting either that the replacement has little electronic effect on the cluster or that any electronic changes do not affect the structure. Any electronic changes in this series of haloaryl carbaboranes may be identified by examining their ^{11}B chemical shifts, which are shown in Table 5, since significant reduction in electron density should lead to a deshielding of the ^{11}B nuclei. Only a change of 1.05–1.75 ppm is seen in the average ^{11}B resonances, although a more significant shift of ca. 3.5 ppm is seen in the highest frequency resonances. These are the integral one resonances, which identifies them as arising from B(9) or B(12), antipodal to C(2) and C(1), respectively. This large effect of substitution on these specific boron atoms, the so-called ‘antipodal effect’, has been well documented [19]. The small deshielding upon replacement of Ph by Ar_F does not represent a large transfer of the cluster electron density to the aryl ring, in agreement with the observed structures.

Although the use of Ar_F as a substituent for a carbaborane has no significant electronic effect on the cage relative to that produced by a phenyl ring, its use has allowed the synthesis of carbaboranes with significant steric interactions. These have produced extended C_{cage}–C_{cage} connectivities, including one of the longest yet reported. Carbametallaboranes derived from these sterically demanding carbaboranes may show interesting structural motifs, and will be the subject of further contributions.

Supplementary data

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E7, UK, and data may be obtained on request, quoting the deposition codes CCDC 111940, 111941 and 111942.

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