

# Syntheses and reactions of some new C-pentafluorophenyl and tetrafluorophenylene carborane systems

Andrei S. Batsanov, Mark A. Fox \*, Judith A.K. Howard, Kenneth Wade <sup>1</sup>

Department of Chemistry, Durham University Science Laboratories, South Road, Durham DH1 3LE, UK

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Dedicated with great affection and respect on the occasion of his 70th birthday to Professor Stanisław Pasynekiewicz, a prolific and original author on organometallic subjects who has kept the organometallic flag flying over Warsaw for four decades, notably by organising excellent regular organometallic conferences that ensured that the community remained in contact during difficult times.

## Abstract

The reaction of *para*-PhCB<sub>10</sub>H<sub>10</sub>CLi with excess C<sub>6</sub>F<sub>6</sub> produced *para*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (52%) and the tetrafluorophenylene bridged system 1,4-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (31%). The C-pentafluorophenyl compound *para*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> afforded good yields of 1,4-tetrafluorophenylene bridged carboranes with suitable nucleophilic reagents: 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-(*ortho*-HCB<sub>10</sub>H<sub>10</sub>C)C<sub>6</sub>F<sub>4</sub> from *ortho*-HCB<sub>10</sub>H<sub>10</sub>CLi, 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-HOC<sub>6</sub>F<sub>4</sub> from KOH and 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-EtOC<sub>6</sub>F<sub>4</sub> from KOEt. Addition of the monolithiated carborane, *meta*-PhCB<sub>10</sub>H<sub>10</sub>CLi, to excess C<sub>6</sub>F<sub>6</sub> produced *meta*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (19%) and the two-cage carborane 1,4-(*meta*-PhCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (70%). Reactions of the novel C-pentafluorophenyl *meta* carborane, *meta*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub>, with nucleophiles, *ortho*-HCB<sub>10</sub>H<sub>10</sub>CLi and <sup>n</sup>BuLi, gave 1-(*meta*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-(*ortho*-HCB<sub>10</sub>H<sub>10</sub>C)C<sub>6</sub>F<sub>4</sub> and 1-(*meta*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-<sup>n</sup>BuC<sub>6</sub>F<sub>4</sub>, respectively. The structure of 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-EtOC<sub>6</sub>F<sub>4</sub> was determined by a single crystal X-ray diffraction study. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Hexafluorobenzene; *ortho* Carborane; *meta* Carborane; *para* Carborane; Crystal structure; Multinuclear NMR

## 1. Introduction

There is much contemporary interest in compounds containing perfluorinated aryl groups bound to a variety of centres, notably in connection with their strongly electron-withdrawing properties. For example, Lewis acids like B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> are vital components of polymerisation catalysts derived from early transition metal metallocenes [1]. Perfluorinated aromatics are also known to form stacked arrays with their hydrocarbon analogues in which the C–F and C–H rings alternate in the stacks [2]. Interestingly, stacked arrays of aromatic ring systems bearing icosahedral carborane residues have been reported by Mingos and co-workers [3] and ourselves, and we have studied the electron-withdrawing properties of icosahedral carborane residues when attached to

substituents capable of dative π bonding [4]. Studies of systems containing perfluoroaryl residues attached to the carbon atoms of icosahedral carboranes appeared likely to be rewarding because of the competitive electron-withdrawing features such systems would present. We therefore embarked on such a study, only to find that though derivatives of the *ortho*, *meta* and *para* carboranes, 1,2-, 1,7- and 1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, respectively, are abundant in the open literature [5], derivatives containing C-attached pentafluorophenyl residues have proved elusive. They are presumably involved as intermediates in reactions between C-lithiocarboranes and C<sub>6</sub>F<sub>6</sub> from which, however, only tetrafluorophenylene (C<sub>6</sub>F<sub>4</sub>)-bridged bis(carborane) systems were isolated. For example, only the tetrafluorophenylene-bridged two-cage systems 1,4-(*ortho*-PhCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**1**), 1,4-(*ortho*-MeCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**2**) and 1,4-(*meta*-MeCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**3**) were isolated from reactions between an excess of hexafluorobenzene, C<sub>6</sub>F<sub>6</sub>, and the lithiocarboranes, *ortho*-PhCB<sub>10</sub>H<sub>10</sub>CLi, *ortho*-MeCB<sub>10</sub>H<sub>10</sub>CLi and *meta*-MeCB<sub>10</sub>H<sub>10</sub>CLi [6] (Scheme 1).

\* Corresponding author. Fax: +44-191-3861127.

E-mail addresses: m.a.fox@durham.ac.uk (M.A. Fox), kenneth.wade@durham.ac.uk (K. Wade)

<sup>1</sup> Also corresponding author.

It was suggested that the replacement of a fluorine atom by a carboranyl group leads to such strong activation of the fluorine atom in the *para* position of the ring as to cause the intermediates  $\text{RCB}_{10}\text{H}_{10}\text{CC}_6\text{F}_5$  (i.e. **4–6**) to react with the carboranyl lithium  $\text{RCB}_{10}\text{H}_{10}\text{CLi}$  much more rapidly than the starting hexafluorobenzene [6]. The intermediates **4–6** presumably involved were not isolated in the reported reactions even with a large excess of  $\text{C}_6\text{F}_6$ .

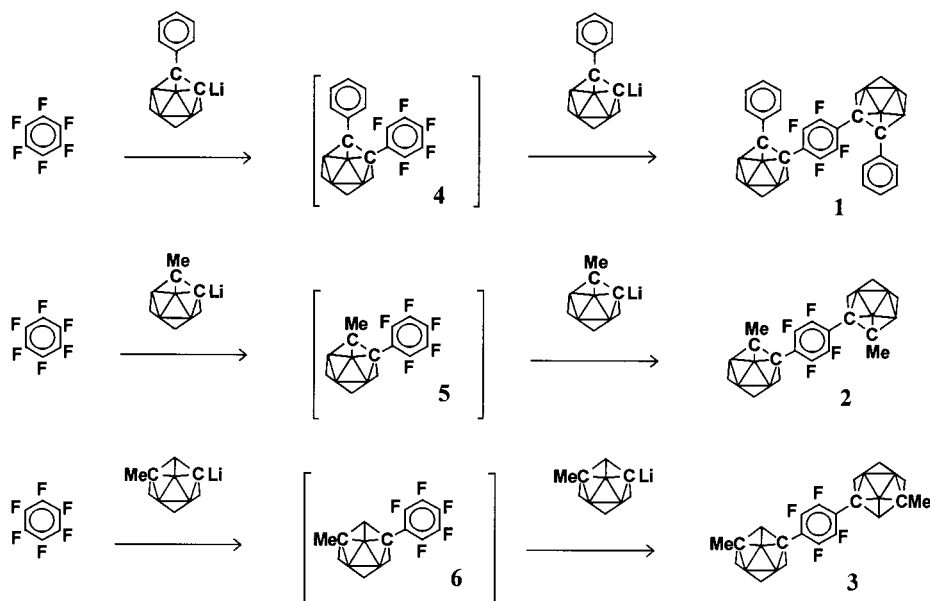
Generally the reaction rate of pentafluorobenzenes,  $\text{C}_6\text{F}_5\text{R}$ , with nucleophiles increases when the electron-withdrawing strength of R increases [7]. It is well known that the electron-withdrawing strength of the carboranyl group at the cage carbon decreases in the order *ortho*, *meta* and *para*. The isolation of a pentafluorophenyl carborane,  $\text{RCB}_{10}\text{H}_{10}\text{CC}_6\text{F}_5$ , was therefore considered more likely in the case of *para* carboranes.

Indeed, in this study we have isolated the first C-pentafluorophenyl *para* carborane 1,12- $\text{PhCB}_{10}\text{H}_{10}\text{CC}_6\text{F}_5$  (**7**) in good yield by the reaction of the *para*-carboranyl lithium, 1,12- $\text{PhCB}_{10}\text{H}_{10}\text{CLi}$ , with an excess of  $\text{C}_6\text{F}_6$ . The fluorine atom at the *para* position in  $\text{PhCB}_{10}\text{H}_{10}\text{CC}_6\text{F}_5$  (**7**) is readily substituted by nucleophiles to give the new tetrafluorophenyl derivatives **8–11**. Here we also describe the isolation of *meta* analogue 1,7- $\text{PhCB}_{10}\text{H}_{10}\text{CC}_6\text{F}_5$  (**12**) from the reaction of the *meta*-carboranyl lithium, 1,7- $\text{PhCB}_{10}\text{H}_{10}\text{CLi}$ , with excess  $\text{C}_6\text{F}_6$  and the reactions of the pentafluorophenyl carborane **12** with nucleophiles to yield new tetrafluorophenylene systems **13–16**.

## 2. Experimental

NMR spectra were recorded on a Bruker AC250 (250.1 MHz  $^1\text{H}$ , 235.3 MHz  $^{19}\text{F}$ , 80.3 MHz  $^{11}\text{B}$  and 62.9 MHz  $^{13}\text{C}$ ) instrument.  $\text{CDCl}_3$  was used as solvent in all NMR spectra recorded here and chemical shifts were referenced to  $\text{SiMe}_4 = 0.00$  ppm for  $^1\text{H}$  and  $^{13}\text{C}$ , externally to  $\text{BF}_3 \cdot \text{Et}_2\text{O} = 0.0$  ppm for  $^{11}\text{B}$  and externally to  $\text{CFCl}_3 = 0.0$  ppm for  $^{19}\text{F}$ . Infrared spectra were recorded as potassium bromide discs using a Perkin–Elmer 1720  $\times$  FTIR spectrometer. Mass spectra were recorded on a VG Micromass 7070E instrument operating in the EI mode at 70 eV. Calculated values of  $M_r$  show the full isotope range  $^{10}\text{B}_n$  to  $^{11}\text{B}_n$  including a  $^{13}\text{C}$  contribution where this is likely to have observable intensity; the less-probable combinations are seldom observed in practice.

Hexafluorobenzene, potassium hydroxide and *n*-butyllithium in hexanes were all obtained commercially (Aldrich) and used as received. *Ortho*-carborane, 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ , was purified by sublimation under high vacuum. 1-Phenyl-*meta*-carborane and 1-phenyl-*para*-carborane were made by our copper coupling method with iodobenzene and the related parent carborane [8,9]. Stirring refers to the use of a magnetic stirrer, washed to washing the organic layer with  $3 \times 20$  ml distilled water, dried to drying the organic layer with anhydrous magnesium sulphate and filtering off the solid and solvent-removed to removing solvent by rotary evaporator followed by pumping to dryness in vacuo at 0.1 mmHg.



Scheme 1.

### 2.1. Synthesis of *para*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (**7**) and 1,4-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**8**)

A total of 2.2 g (10 mmol) of 1-phenyl-*para*-carborane in 40 ml dry diethyl ether was added slowly with 10 mmol of *n*-butyllithium (4.8 ml of 2.1 M in hexanes) at 0°C under nitrogen. After warming to room temperature (r.t.) with stirring, the solution was then added dropwise to 3.5 g (20 mmol) of hexafluorobenzene in 20 ml of Et<sub>2</sub>O at 0°C. After stirring for 24 h at r.t., the resulting mixture was washed with 50 ml of dilute acid and the insoluble solid was filtered off. The ether layer was washed, dried and solvent-removed to give a white solid. This was combined with the insoluble solid and subjected to soxhlet extraction with hot acetonitrile. The extracted solvent on cooling gave 2.0 g (52%) of the pentafluorophenyl carborane (**7**). Found: C, 43.40; H, 3.90; *M<sub>r</sub>*, 379–389; Anal. Calc. for C<sub>14</sub>H<sub>15</sub>B<sub>10</sub>F<sub>5</sub>: C, 43.52; H, 3.89; *M<sub>r</sub>*, 380–391.  $\delta(^{11}\text{B})$ , -12.1;  $\delta(^{19}\text{F})$ , -133.3 (2F, *ortho* F), -152.6 (t, *J<sub>FF</sub>* = 21.4, 1F, *para* F), -161.5 (t, *J<sub>FF</sub>* ~ 19.5, 2F, *meta* F);  $\delta(^1\text{H})$ , 7.23 (m, 5H, phenyl CH), 4.0–1.0 (10H, BH);  $\delta(^{13}\text{C})$ , 145.7 (d, *J<sub>CF</sub>* = 261, *ortho* CF), 140.7 (d, *J<sub>CF</sub>* = 258, *para* CF), 137.8 (d, *J<sub>CF</sub>* = 256, *meta* CF), 135.9 (*ipso* phenyl C), 128.6 (*ortho* CH), 128.1 (*meta* CH), 126.8 (*para* CH), 110.9 (CCF), 88.1 (cage CPh), 71.4 (cage CC<sub>6</sub>F<sub>5</sub>). *v<sub>max</sub>* cm<sup>-1</sup> 3058w (phenyl CH stretch); 2683w, 2673w, 2626s, 2613s, 2603s (BH stretch); 1653m; 1531s, 1489s, 1481s (fluoroaryl skeletal ring stretch); 1446w, 1310w, 1090s, 1061w, 1041w, 1019w, 999s, 975w, 881w, 785w, 747w, 732w, 721w, 707w, 693m, 641w, 493w.

The insoluble solid in the thimble was identified as the tetrafluorophenylene-bridged two-cage compound **8** (0.9 g, 31%). Found: C, 45.01; H, 5.27; *M<sub>r</sub>*, 578–589; Anal. Calc. for C<sub>22</sub>H<sub>30</sub>B<sub>20</sub>F<sub>4</sub>: C, 45.05; H, 5.12; *M<sub>r</sub>*, 578–593.  $\delta(^{11}\text{B})$ , -11.3;  $\delta(^{19}\text{F})$ , -133.6;  $\delta(^1\text{H})$ , 7.21 (m, 10H, phenyl CH), 4.0–1.0 (20H, BH);  $\delta(^{13}\text{C})$ , 145.5 (d, *J<sub>CF</sub>* = 267, CF), 136.0 (*ipso* phenyl C), 128.6 (*ortho* CH), 128.1 (*meta* CH), 126.8 (*para* CH), 118.7 (CCF), 88.1 (cage CPh), 71.3 (cage CC<sub>6</sub>F<sub>4</sub>). *v<sub>max</sub>* cm<sup>-1</sup> 3061w (phenyl CH stretch); 2669w, 2611s (BH stretch); 1496m, 1477w, 1455s (fluoroaryl skeletal ring stretch); 1301w, 1117m, 1066w, 1045w, 998m, 975w, 878w, 782w, 749w, 719w, 687m, 644w, 491w, 415w.

### 2.2. Synthesis of 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-(*ortho*-HCB<sub>10</sub>H<sub>10</sub>C)C<sub>6</sub>F<sub>4</sub> (**9**)

A total of 0.86 g (6 mmol) of *ortho* carborane in 15 ml of Et<sub>2</sub>O was treated with 6 mmol of butyllithium (3 ml of 2.1 M in hexanes) under nitrogen with stirring. After 30 min, 2.32 g (6 mmol) of the pentafluoro carborane (**7**) was added slowly to the stirred mixture and then refluxed for 1 h. The cooled mixture was washed, dried and solvent-removed to give a white solid. The white solid was recrystallised from

methanol–acetonitrile to yield 2.08 g (68%) of the mixed cage compound **9**. Found: C, 37.38; H, 5.33; *M<sub>r</sub>*, 500–514; Anal. Calc. for C<sub>16</sub>H<sub>26</sub>B<sub>20</sub>F<sub>4</sub>: C, 37.65; H, 5.10; *M<sub>r</sub>*, 502–516.  $\delta(^{11}\text{B})$ , -1.6, -7.8, -11.7;  $\delta(^{19}\text{F})$ , -131.5 (2F, *ortho* F), -137.7 (2F, *meta* F);  $\delta(^1\text{H})$ , 7.21 (m, 5H, phenyl CH), 4.80 (s, 1H, cage CH), 4.0–1.0 (m, 20H, BH);  $\delta(^{13}\text{C})$ , 145.7 (d, *J<sub>CF</sub>* ~ 260, *ortho* CF), 145.5 (d, *J<sub>CF</sub>* ~ 260, *meta* CF), 135.8 (*ipso* phenyl C), 128.7 (*ortho* CH), 128.2 (*meta* CH), 126.8 (*para* CH), 116.8 (CCF), 113.5 (CCF), 88.7 (cage CPh), 70.8 (cage CC<sub>6</sub>F<sub>4</sub>), 66.4 (cage CC<sub>6</sub>F<sub>4</sub>), 60.5 (t, *J<sub>CF</sub>* = 13; cage CH). *v<sub>max</sub>* cm<sup>-1</sup> 3128m (carboranyl CH stretch); 3066w (phenyl CH stretch); 2613s (BH stretch); 1497w, 1480w, 1458s (fluoroaryl skeletal ring stretch); 1409w, 1383w, 1304w, 1261w, 1211w, 1160w, 1098m, 1041w, 1019w, 997s, 975w, 882w, 785w, 747w, 716m, 691m, 491w, 409w.

### 2.3. Synthesis of 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-HOC<sub>6</sub>F<sub>4</sub> (**10**)

A total of 0.77 g (2 mmol) of the pentafluorocarborane (**7**) was mixed with 1.4 g (25 mmol) of KOH in refluxing THF for 30 min. THF was vacuum-removed and the resulting solid was added with Et<sub>2</sub>O and dilute acid. The ether layer was separated, washed, dried and solvent-removed to leave the hydroxy compound **10** (0.55 g, 72%). Found: *M<sub>r</sub>*, 376–387; Anal. Calc. for C<sub>14</sub>H<sub>16</sub>B<sub>10</sub>F<sub>4</sub>O: *M<sub>r</sub>*, 378–389.  $\delta(^{11}\text{B})$ , -11.9;  $\delta(^{19}\text{F})$ , -135.0 (2F, *ortho* F), -162.4 (d, 12.5, 2F, *meta* F);  $\delta(^1\text{H})$ , 7.23 (m, 5H, phenyl CH), 5.69 (br, 1H, OH), 4.0–1.5 (m, 10H, BH);  $\delta(^{13}\text{C})$ , 145.6 (d, *J<sub>CF</sub>* = 240, *ortho* CF), 137.6 (d, *J<sub>CF</sub>* = 232, *meta* CF), 136.1 (*ipso* phenyl C), 135.3 (aromatic CO), 128.5 (*ortho* CH), 128.1 (*meta* CH), 126.9 (*para* CH), 106.1 (CCF), 87.3 (cage CPh), 72.3 (cage CC<sub>6</sub>F<sub>4</sub>). *v<sub>max</sub>* cm<sup>-1</sup> 3554m, 3440brm (OH stretch); 3066w (phenyl CH); 2680w, 2611s (BH stretch); 1655m, 1595w; 1527s, 1485s, 1446m (fluoroaryl skeletal ring stretch); 1332w, 1309w, 1260w, 1234m, 1173w, 1093s, 1030m, 984m, 970m, 880w, 801w, 783w, 744w, 729w, 707w, 689m, 646w, 596w, 491w.

### 2.4. Synthesis of 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-EtOC<sub>6</sub>F<sub>4</sub> (**11**)

A total of 0.77 g (2 mmol) of *para*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (**7**) was dissolved in 10 ml of 1:1 diethyl ether–ethanol and added with 1.4 g (25 mmol) of KOH in ethanol (10 ml). After heating the mixture with stirring at 50°C, the mixture was solvent-removed. The residue was dissolved in ether (10 ml), washed, dried and then solvent-removed to give a white solid. Recrystallisation of the solid with chloroform gave crystals of the ethoxy derivative **11**. (0.65 g, 79%) Found: *M<sub>r</sub>*, 406–415; Anal. Calc. for C<sub>16</sub>H<sub>20</sub>B<sub>10</sub>F<sub>4</sub>O: *M<sub>r</sub>*, 406–417.  $\delta(^{11}\text{B})$ , -12.0;  $\delta(^{19}\text{F})$ , -135.0 (2F, *ortho* F), -156.7 (d, *J<sub>FF</sub>* = 16.0, 2F, *meta* F);  $\delta(^1\text{H})$ , 7.22 (m, 5H, phenyl CH), 4.31 (q,

2H,  $J_{\text{HH}} = 7$  Hz, CH<sub>2</sub>), 4.0–1.0 (10H, BH), 1.37 (t, 3H,  $J_{\text{HH}} = 7$  Hz, CH<sub>3</sub>);  $\delta(^{13}\text{C})$ , 145.9 (d,  $J_{\text{CF}} = 259$ , *ortho* CF), 140.9 (d,  $J_{\text{CF}} = 250$ , *meta* CF), 136.7 (aromatic CO), 136.1 (*ipso* phenyl C), 128.5 (*ortho* CH), 128.1 (*meta* CH), 126.9 (*para* CH), 108.3 (CCF), 87.5 (cage CPh), 72.2 (cage CC<sub>6</sub>F<sub>4</sub>), 70.7 (CH<sub>2</sub>), 15.4 (CH<sub>3</sub>).  $v_{\text{max}}$  cm<sup>-1</sup> 3071w (phenyl CH stretch); 2978w, 2930w (alkyl CH stretch); 2680w, 2611s (BH stretch); 1646m, 1595w; 1511s, 1498m, 1470s, 1447m (fluorophenyl skeletal ring stretch); 1417w, 1391m, 1367w, 1261w, 1178w, 1099s, 1067w, 1041w, 1031w, 1015m, 992s, 927w, 884w, 800w, 783w, 745w, 709w, 691s, 625w, 601w, 493w, 461w.

## 2.5. Crystal structure study of

### 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-EtOC<sub>6</sub>F<sub>4</sub> (**11**)

The diffraction experiment was carried out at  $T = 150$  K, using a SMART 3-circle diffractometer with a 1K CCD area detector and a Cryostream open-flow N<sub>2</sub> cryostat with graphite-monochromated Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and a full hemisphere of reciprocal space scanned by  $\omega$  in 0.3° frames.

#### 2.5.1. Crystal data for **11**

C<sub>16</sub>H<sub>20</sub>B<sub>10</sub>F<sub>4</sub>O,  $M = 412.42$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 10.594(1)$ ,  $b = 19.072(1)$ ,  $c = 19.879(1)$  Å,  $V = 3989.3(5)$  Å<sup>3</sup> (from 512 reflections with  $12 < \theta < 23^\circ$ ),  $Z = 8$ ,  $D_{\text{calc.}} = 1.37$  g cm<sup>-3</sup>,  $F(000) = 1680$ ,  $\mu = 1.0$  cm<sup>-1</sup>, colourless crystal of  $0.4 \times 0.35 \times 0.35$  mm,  $2\theta \leq 48^\circ$ , 20847 total data, 6010 unique ( $R_{\text{int}} = 0.051$ ), 4557 observed with  $I \geq 2\sigma(I)$ . The structure was solved by direct methods and refined by full-matrix least-squares against  $F^2$  of all data (non-H atoms anisotropic, methyl group as rigid body, other H atoms riding, total of 597 variables) to  $wR$  ( $F^2$ , all data) = 0.169, goodness-of-fit 1.15,  $R$  ( $F$ , observed data) = 0.059, max/min residual electron density 0.20, -0.22 e Å<sup>-3</sup>, using SHELXTL (Version 5) software (G.M. Sheldrick, Bruker Analytical X-ray Instruments, Madison, WI, USA, 1995).

## 2.6. Synthesis of *meta*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (**12**) and

### 1,4-(*meta*-PhCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**13**)

A total of 2.2 g (10 mmol) of 1-phenyl-*meta*-carborane in 40 ml dry diethyl ether was added slowly with 10 mmol of *n*-butyllithium (4.8 ml of 2.1 M in hexanes) at 0°C under nitrogen. After warming to r.t. with stirring, the solution was then added dropwise to 3.5 g (20 mmol) of hexafluorobenzene in 20 ml of Et<sub>2</sub>O at 0°C. After stirring for 24 h at r.t., the mixture was washed, the ether layer separated, dried and the solvent-removed to leave a white solid. The solid was subjected to vacuum sublimation and 0.73 g (19%) of crystalline solid obtained was identified as the pentafluorophenyl compound **12**. Found: C, 43.86; H, 4.01;

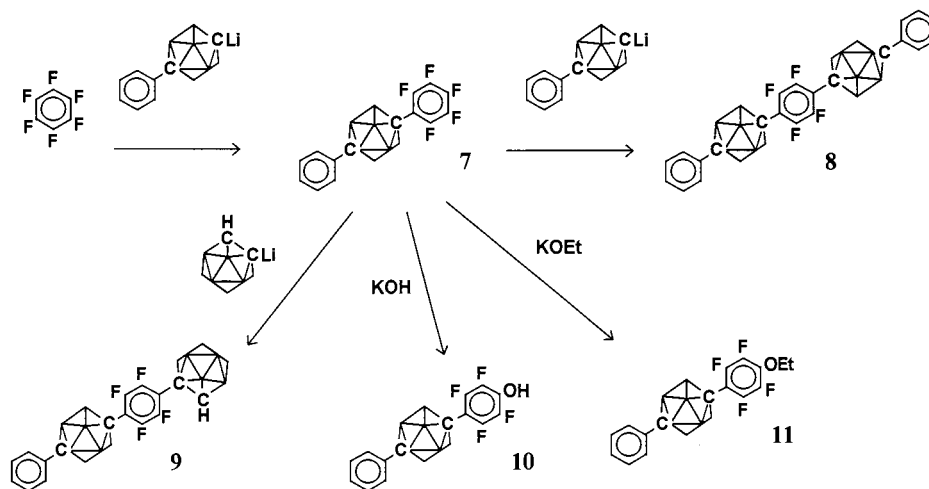
$M_r$ , 381–388; Anal. Calc. for C<sub>14</sub>H<sub>15</sub>B<sub>10</sub>F<sub>5</sub>: C, 43.52; H, 3.89;  $M_r$ , 380–391.  $\delta(^{11}\text{B})$ , -3.1 (1B), -5.9 (1B), -10.5 (6B), -13.5 (2B);  $\delta(^{19}\text{F})$ , -132.9 (2F, *ortho* F), -151.8 (t,  $J_{\text{FF}} = 21.2$ , 1F, *para* F), -161.0 (t,  $J_{\text{FF}} \sim 18.8$ , 2F, *meta* F);  $\delta(^1\text{H})$ , 7.47 (2H, d, *ortho* phenyl CH), 7.31 (m, 3H, *meta*, *para* phenyl CH), 4.0–1.0 (10H, BH);  $\delta(^{13}\text{C})$ , 146.2 (d,  $J_{\text{CF}} = 258$ , *ortho* CF), 141.1 (d,  $J_{\text{CF}} = 258$ , *para* CF), 138.0 (d,  $J_{\text{CF}} = 262$ , *meta* CF), 134.7 (*ipso* phenyl C), 128.9 (*ortho* CH), 128.4 (*meta* CH), 127.7 (*para* CH), 110.0 (CCF), 78.2 (cage CPh), 66.2 (cage CC<sub>6</sub>F<sub>5</sub>).  $v_{\text{max}}$  cm<sup>-1</sup> 3058w (phenyl CH stretch); 2693w, 2659m, 2615s, 2595s (BH stretch); 1650m, 1634w, 1601w; 1531s, 1481s (fluoroaryl skeletal ring stretch); 1447m, 1420w, 1373w, 1314w, 1261w, 1175w, 1139w, 1085s, 1056w, 1033m, 1013s, 1001s, 966w, 935w, 917w, 868w, 801w, 747m, 726m, 703w, 693m, 663w, 627w, 605w, 577w, 490w.

The unsublimed residue was recrystallised from hot acetonitrile to give the two-cage derivative **13** (2.05 g, 70%) Found: C, 44.69; H, 5.03;  $M_r$ , 581–589; Anal. Calc. for C<sub>22</sub>H<sub>30</sub>B<sub>20</sub>F<sub>4</sub>: C, 45.05; H, 5.12;  $M_r$ , 582–590.  $\delta(^{11}\text{B})$ , -4.7 (4B), -9.9 (16B);  $\delta(^{19}\text{F})$ , -132.7;  $\delta(^1\text{H})$ , 7.47 (4H, d, *ortho* phenyl CH), 7.31 (6H, m, *meta*, *para* phenyl CH), 4.0–1.0 (20H, BH);  $\delta(^{13}\text{C})$ , 146.0 (d,  $J_{\text{CF}} = 260$ , CF), 134.7 (*ipso* phenyl C), 128.9 (*ortho* CH), 128.4 (*meta* CH), 127.7 (*para* CH), 115.1 (CCF), 78.2 (cage CPh), 66.1 (cage CC<sub>6</sub>F<sub>4</sub>).  $v_{\text{max}}$  cm<sup>-1</sup> 3092w, 3066w (phenyl CH stretch); 2702w, 2652m, 2619s, 2609s, 2582s, 2571s (BH stretch); 1596w; 1495m, 1453s (fluoroaryl skeletal ring stretch); 1393w, 1306m, 1261w, 1241w, 1191w, 1120m, 1105w, 1076w, 1037w, 1016w, 1002s, 977w, 943w, 916w, 895w, 867w, 851w, 813w, 795w, 765w, 743m, 721s, 685s.

## 2.7. Synthesis of

### 1-(*meta*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-(*ortho*-HCB<sub>10</sub>H<sub>10</sub>C)C<sub>6</sub>F<sub>4</sub> (**14**)

A total of 0.43 g (3 mmol) of *ortho* carborane in 15 ml of Et<sub>2</sub>O was treated with 3 mmol of butyllithium (1.5 ml of 2.1 M in hexanes) under nitrogen with stirring. After 30 min, 1.16 g (3 mmol) of *meta*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (**12**) was added slowly to the stirred mixture and then refluxed for 1 h. The cooled mixture was washed, dried and solvent-removed to give a white solid. The solid was recrystallised from methanol to give 0.86 g (56%) of the mixed-cage derivative **14**. Found: C, 38.10; H, 5.19;  $M_r$ , 500–515; Anal. Calc. for C<sub>16</sub>H<sub>26</sub>B<sub>20</sub>F<sub>4</sub>: C, 37.65; H, 5.10;  $M_r$ , 502–516.  $\delta(^{11}\text{B})$ , -1.5, -8.3, -9.6, -11.7;  $\delta(^{19}\text{F})$ , -131.2 (2F, *ortho* F), -137.3 (2F, *meta* F);  $\delta(^1\text{H})$ , 7.45 (2H, d, *ortho* phenyl CH), 7.34 (1H, t, *para* phenyl CH), 7.32 (2H, t, *meta* phenyl CH), 4.83 (s, 1H, cage CH), 4.0–1.0 (m, 20H, BH);  $\delta(^{13}\text{C})$ , 146.3 (d,  $J_{\text{CF}} = 263$ , *ortho* CF), 145.3 (d,  $J_{\text{CF}} = 256$ , *meta* CF), 134.5 (*ipso* phenyl C), 129.0 (*ortho* CH), 128.5 (*meta* CH), 127.7 (*para* CH), 116.0 (CCF), 114.0 (CCF), 78.3 (cage CPh), 66.4 (cage



Scheme 2.

$\text{CC}_6\text{F}_4$ ), 65.7 (cage  $\text{CC}_6\text{F}_4$ ), 60.0 (t,  $J_{\text{CF}} = 13$ ; cage CH).  $\nu_{\text{max}} \text{ cm}^{-1}$  3139m (carboranyl CH stretch); 3065w (phenyl CH stretch); 2592s (BH stretch); 1495m, 1489m, 1458s (fluoroaryl skeletal ring stretch); 1306m, 1245w, 1210w, 1161w, 1121w, 1098m, 1035w, 998s, 969w, 938w, 871w, 853w, 809w, 737m, 715s, 691m, 663w, 641w, 628w, 603w.

### 2.8. Synthesis of 1-(*meta*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-*n*BuC<sub>6</sub>F<sub>4</sub> (**15**)

A total of 0.77 g (2 mmol) of the pentafluoro carborane (**12**) in dry ether was added with 2.1 mmol of *n*-butyllithium (1.0 ml of 2.1 M in hexanes) and refluxed for 20 min. The mixture was treated with water and the ether layer was separated, washed, dried and solvent removed to leave a clear oil identified as the butyl compound **15**. (0.72 g, 85%) Found:  $M_r$ , 419–427; Anal. Calc. for  $\text{C}_{18}\text{H}_{24}\text{B}_{10}\text{F}_4$ ;  $M_r$ , 418–429.  $\delta(^{11}\text{B})$ , –3.2 (1B), –5.3 (1B), –10.1 (6B), –12.0 (2B);  $\delta(^{19}\text{F})$ , –135.4 (2F, *ortho* F), –144.1 (2F, *meta* F);  $\delta(^1\text{H})$ , 7.51 (2H, d, *ortho* phenyl CH), 7.32 (3H, m, *meta*, *para* phenyl CH), 4.0–1.0 (10H, BH), 2.85 (t,  $J_{\text{HH}} = 7.5$ , 2H,  $\text{C}_6\text{F}_4\text{CH}_2$ ), 1.72 (quintet,  $J_{\text{HH}} \sim 7.5$ , 2H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.52 (quintet,  $J_{\text{HH}} \cong 7.5$ , 2H,  $\text{CH}_2\text{CH}_3$ ), 1.08 (t,  $J_{\text{HH}} = 7.5$ , 3H,  $\text{CH}_3$ );  $\delta(^{13}\text{C})$ , 145.4 (d,  $J_{\text{CF}} \cong 258$ , *ortho* and *meta* CF), 134.9 (*ipso* phenyl C), 128.7 (*ortho* CH), 128.4 (*meta* CH), 127.8 (*para* CH), 122.3 (CBu), 111.6 (CCF), 78.0 (cage CPh), 67.1 (cage  $\text{CC}_6\text{F}_4$ ), 31.0 (CCH<sub>2</sub>), 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 13.6 ( $\text{CH}_3$ ).  $\nu_{\text{max}} \text{ cm}^{-1}$  3062w (phenyl CH stretch); 2960m, 2929m, 2872m (alkyl CH stretch); 2605s (BH stretch); 1596m; 1496m, 1470s (fluoroaryl skeletal ring stretch); 1381w, 1289m, 1261w, 1210w, 1192w, 1159w, 1123m, 1108m, 1078m, 1056m, 1003w, 988m, 921w, 872w, 854w, 801w, 777w, 745m, 731m, 691s, 667w, 627w, 617w, 603w.

### 3. Results and discussion

Scheme 2 summarises the reactions of fluoroaryl *para* carboranes carried out here. The reaction of 1-phenyl-12-lithio-*para*-carborane and an excess of  $\text{C}_6\text{F}_6$  afforded *para*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (**7**) and *para*-1,4-(PhCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**8**) in 52 and 31% yields, respectively. Isolation of the two-cage compound 1,4-(PhCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**8**) suggests the fluorine atom at the *para* position of the pentafluorophenyl carborane PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (**7**) is activated by the carboranyl group. Reactions of **7** with nucleophiles gave tetrafluorophenylene derivatives bearing new substituents at the *para* position of the fluorophenyl ring. With **7**, the reagents *ortho*-HCB<sub>10</sub>H<sub>10</sub>CLi, KOH and KOEt gave 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-(*ortho*-HCB<sub>10</sub>H<sub>10</sub>C)C<sub>6</sub>F<sub>4</sub> (**9**), 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-HOC<sub>6</sub>F<sub>4</sub> (**10**) and 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-EtOC<sub>6</sub>F<sub>4</sub> (**11**), respectively in good yields.

A crystal of the ethoxy tetrafluorophenyl carborane (**11**) was subjected to an X-ray structural determination. The asymmetric unit of **11** comprises two molecules, A and B (see Fig. 1) in each of which the aromatic rings are nearly coplanar (dihedral angles of 2.5° in A and 8.4° in B). The (OC<sub>2</sub>) plane of the ethoxy group is inclined to the perfluorophenyl plane by 55.0° (A) and 59.2° (B). All aryl rings in the structure are parallel within 10° and pack in layers parallel to the crystallographic (1 0 2) plane. The independent molecules are related via an approximate (non-crystallographic) inversion centre at (1/2, 1/8, 1/4), but for slightly different conformations around the C(cage)–C(aryl) bonds [different relative orientation of aryl rings and the cage].

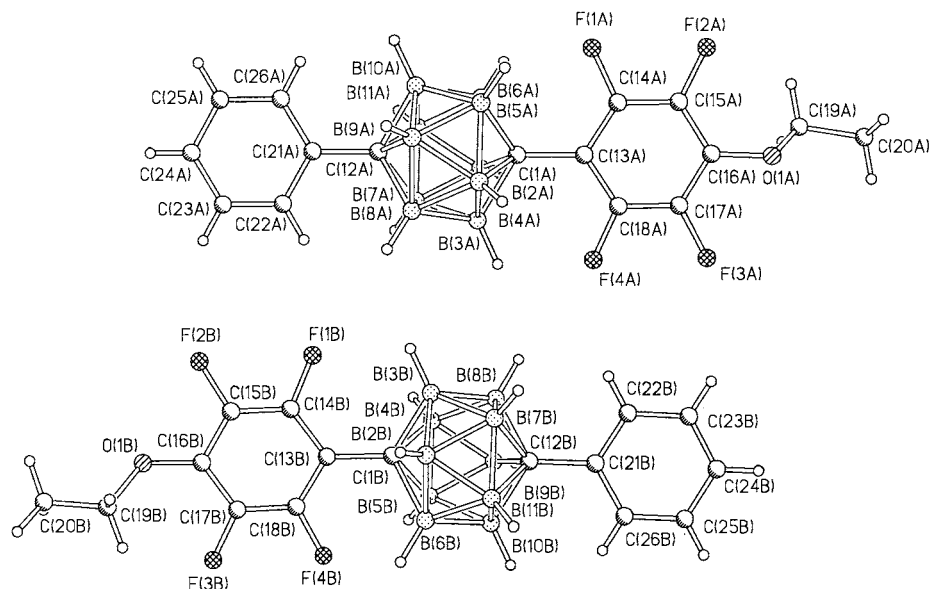
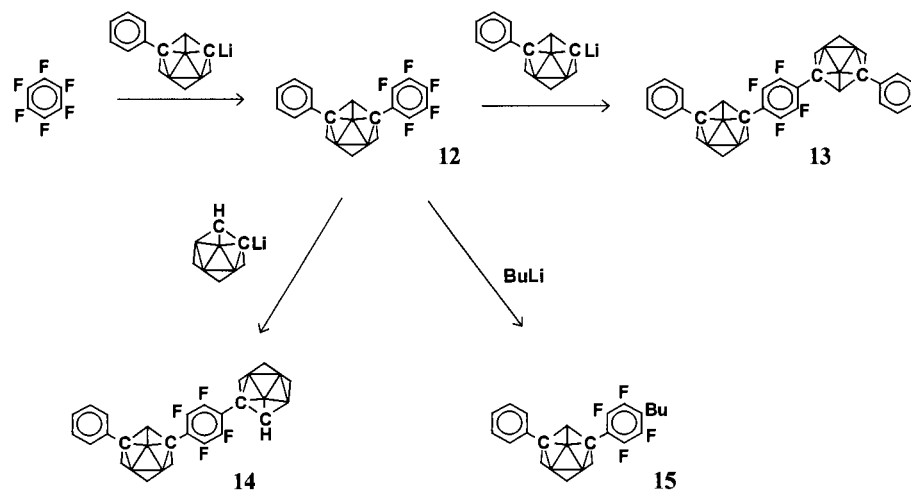


Fig. 1. Two independent molecules in the structure of 1-(*para*-PhCB<sub>10</sub>H<sub>10</sub>C)-4-EtOC<sub>6</sub>F<sub>4</sub> (**11**). Selected bond lengths in Å: C(1A)–C(13A) 1.527(4), C(12A)–C(21A) 1.514(4), C(16A)–O(1A) 1.365(3), C(1B)–C(13B) 1.520(4), C(12B)–C(21B) 1.521(4), C(16B)–O(1B) 1.360(3).



Scheme 3.

Scheme 3 shows visually the reactions of the new fluorophenyl *meta* carboranes that have taken place here. The reaction of the lithio-carborane *meta*-PhCB<sub>10</sub>H<sub>10</sub>CLi and excess C<sub>6</sub>F<sub>6</sub> gave a mixture of *meta*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (**12**) and 1,4-(*meta*-PhCB<sub>10</sub>-H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**13**) in 19 and 70% yields, respectively. The lower yield of **12** compared with the *para* analogue **7** is expected from the stronger electron-withdrawing character of the *meta* carboranyl carbon. The electron-withdrawing character of the phenyl-*meta*-carboranyl group at the cage carbon is comparable to a phenylethynyl group as the reactions of PhC≡CLi and C<sub>6</sub>F<sub>6</sub> produced PhC≡CC<sub>6</sub>F<sub>5</sub> and 1,4-(PhC≡C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> in 10–15% and 50% yields, respectively [10].

Since the tetrafluorophenylene-bridged two-cage compound 1,4-(*meta*-PhCB<sub>10</sub>H<sub>10</sub>C)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> (**13**) is formed in this reaction, the pentafluorophenyl compound **12** is clearly susceptible to nucleophiles at the *para* position of the C<sub>6</sub>F<sub>5</sub> ring. This is confirmed by the reactions of *ortho*-HCB<sub>10</sub>H<sub>10</sub>CLi and of <sup>n</sup>BuLi with *meta*-PhCB<sub>10</sub>H<sub>10</sub>CC<sub>6</sub>F<sub>5</sub> (**12**), which give 1-*meta*-PhCB<sub>10</sub>H<sub>10</sub>C-4-(*ortho*-HCB<sub>10</sub>H<sub>10</sub>C)C<sub>6</sub>F<sub>4</sub> (**14**) and 1-(*meta*-PhCB<sub>10</sub>-H<sub>10</sub>C)-4-<sup>n</sup>BuC<sub>6</sub>F<sub>4</sub> (**15**) in good yields, respectively.

All of the new carborane derivatives discussed in this study were characterised by <sup>19</sup>F-, <sup>1</sup>H-, <sup>13</sup>C- and <sup>11</sup>B-NMR, mass and FT-IR spectroscopy. Points of interest in the NMR data for carboranes **7**–**15** are

1. the substituent effects of a carboranyl group on the fluorine NMR chemical shifts of perfluorobenzenes are shown to be comparable to an ethynyl group ( $-134.2$  ppm (*ortho*),  $-149.9$  (*para*),  $-159.6$  (*meta*) for  $\text{HC}\equiv\text{CC}_6\text{F}_5$ ) [11],
2. the  $^{19}\text{F}$  peaks assigned to fluorines nearest to the carborane moiety are found to be broad which may be due to long-range boron–fluorine ( $^4J_{\text{BF}}$ ) couplings and
3. long-range carbon–fluorine ( $^4J_{\text{CF}}$ ) couplings are observed for peaks assigned to the unsubstituted *ortho* carboranyl carbons in the  $^{13}\text{C}$ -NMR spectra of **9** and **14**.

#### 4. Conclusions

Two C-pentafluorophenyl carboranes and some new  $\text{C}_6\text{F}_4$ -bridged species were made for the first time in this study. Both carboranes, *para*- and *meta*- $\text{PhCB}_{10}\text{H}_{10}\text{CC}_6\text{F}_5$ , were isolated from reactions between *para*- and *meta*- $\text{PhCB}_{10}\text{H}_{10}\text{CLi}$ , respectively with excess hexafluorobenzene. Reactions of the C-pentafluorophenyl carboranes with nucleophiles gave tetrafluorophenylene species in which the fluorine atom at the *para* position of the fluoroaryl group had been easily replaced by the nucleophile.

#### 5. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 132905 for compound **11**. Copies of the information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax +44-1223-336033 or e-mail: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>).

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