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Model compounds and monomers for phenylene ether carboranylene ketone (PECK) polymer synthesis: preparation and characterization of boron-arylated *ortho*-carboranes bearing carboxyphenyl, phenoxyphenyl or benzoylphenyl substituents

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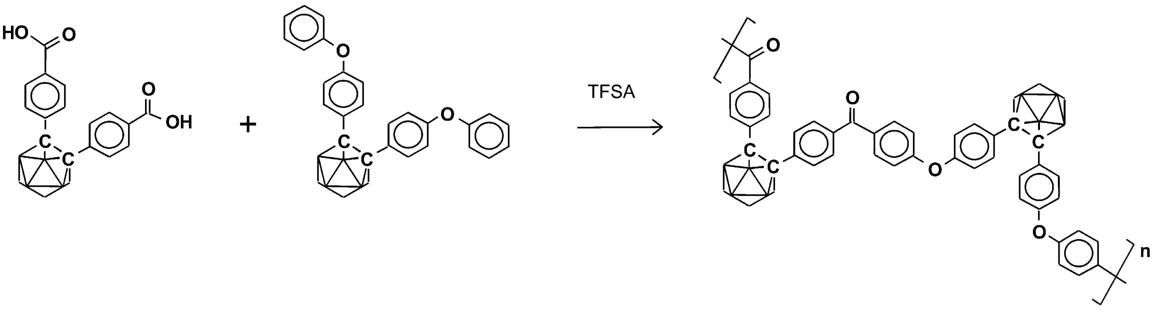
Fourteen new derivatives of *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, have been prepared containing functionalized aryl groups attached to one or both of the boron atoms (B9 and B12) antipodal to the carbon atoms, in order to test the suitability of such species for use in the preparation of new categories of phenylene ether carboranylene ketone (PECK) polymers. Model compounds prepared from 9-iodo-*ortho*-carborane **1** to test synthetic procedures and reactions included the mono-substituted carboranes 9-R^1-1,2-$C_2B_{10}H_{11}$ in which the boron attached group R^1 was *p*-tolyl (**2**), *p*-$HO_2CC_6H_4$ **3**, *p*-$MeOC_6H_4COC_6H_4$ **4**, *p*-$PhOC_6H_4$ **5** or *p*-$PhCOC_6H_4OC_6H_4$ **PhCOC**$_6H_4OC_6H_4$ $PhCOC_6H_4OC_6H_4$ **6** (C_6H_4 represents *para*-phenylene throughout). Formation of **3** from **2** by CrO_3 oxidation showed the capacity of the boron–aryl link to withstand strongly oxidizing conditions. Formation of **4** from **3** and anisole, PhOMe, in trifluoromethane sulfonic acid (TFSA), and of **6** from **5** and benzoic acid, $PhCO_2H$, in TFSA showed such systems could undergo the acylation reactions that would allow polymer formation from suitable diarylcarborane monomers. Compound **7**, 9-(3-PhCO-4-PhO-C_6H_3)-1,2-$C_2B_{10}H_{11}$ an isomer of **6**, was also obtained during the synthesis of **6** from **5** and benzoic acid. The diarylcarboranes 9,12-R^2_2-1,2-$C_2B_{10}H_{10}$ with R^2 = *p*-tolyl **9**, *p*-$HO_2CC_6H_4$ **10** or *p*-$MeOC_6H_4COC_6H_4$ **11**, bearing identical functionalised aryl groups attached to both antipodal boron atoms, were prepared from 9,12-I_2-1,2-$C_2B_{10}H_{10}$ **8**. Further series of diarylcarboranes 1,9- and 1,12-R^3_2-1,2-$C_2B_{10}H_{10}$, bearing identical aryl groups R^3 on one carbon atom (C1) and on the antipodal boron atom (B12), or on the boron atom (B9) antipodal to the unsubstituted carbon atom (C2), have also been prepared and characterized, with R^3 = *p*-tolyl **12**, **13**, *p*-$HO_2CC_6H_4$ **14**, **15** or *p*-$MeOC_6H_4COC_6H_4$ **16**, **17**.

Introduction

Over the last three decades, several research groups have prepared polymers containing remarkably stable icosahedral carboranes ($C_2B_{10}H_{12}$) using various well established polymer linking reactions.[1] These polymers include carborane units as pendant groups (*i.e.* -$CB_{10}H_{10}CR$) or as part of the backbone linked by the two carboranyl carbons (*i.e.* -$CB_{10}H_{10}C$-). Inclusion of carborane units in polymers generally leads to enhanced thermal stability but only carboranesiloxane elastomers (*e.g.* Olin's DEXSIL and Union Carbide's UCARSIL) have found specialist applications sufficient to offset the cost of the carborane.

Polyether ketones containing carboranes in chains of aromatic units have been synthesized by electrophilic condensation with trifluoromethanesulfonic acid (TFSA).[2,3] An example of phenylene ether carboranylene ketone (PECK) polymerization is shown where both the dicarboxylic acid and diether monomers contain a diarylcarborane unit (Scheme 1). PECK polymers were found to lose a much smaller proportion of their weight on pyrolysis at temperatures up to 1000 °C compared to conventional aromatic ether-ketones (*e.g.* ICI's VICTREX).

Two model reactions for PECK polymerization, that between the ether 1-(4-$PhOC_6H_4$)-1,2-$C_2B_{10}H_{11}$ and benzoic acid, or that between the carboxylic acid 1-(4-$HO_2CC_6H_4$)-2-Ph-1,2-$C_2B_{10}H_{10}$ and anisole (Scheme 2), gave carboranyl ether ketones in TFSA.[2,4] Carborane monomers that have been used to produce PECK polymers are all *C*-aryl carboranes, 1,2-(4-$HO_2CC_6H_4$)$_2$-1,2-$C_2B_{10}H_{10}$, 1,2-(4-$PhOC_6H_4$)$_2$-1,2-$C_2B_{10}H_{10}$,



Scheme 1 Example of PECK polymerisation from *C*-diaryl carboranes.

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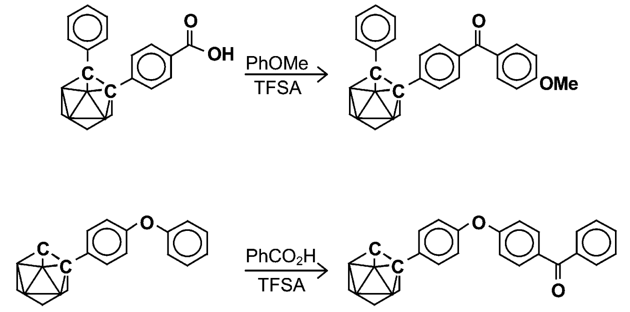


Scheme 2 Model acylations of *C*-aryl carboranes.

1,7-(4-$PhOC_6H_4)_2$-1,7-$C_2B_{10}H_{10}$ and 1,12-(4-$PhOC_6H_4)_2$-1,12-$C_2B_{10}H_{10}$.[2,3]

The high thermal strength of a cage boron–aryl carbon bond is demonstrated by the gas-phase rearrangement of 3-aryl-1,2-carborane at 550–600 °C to 2- and 4-aryl-1,7-carboranes.[5] By contrast, 1-phenyl-1,2-carborane gave aryl-C(cage) cleavage at 300 °C.[6] Although other comparisons of thermal stabilities between *B*- and *C*-aryl carboranes have not been investigated, it was nevertheless felt that carborane polymers with B–C links might have thermoplastic properties superior even to those reported for analogous high temperature carborane polymers with cage carbon–aryl carbon bonds.[7]

We therefore embarked on the present study, which had the following aims and objectives: (i) using model systems, to establish routes by which functionalised aryl groups such as $PhOC_6H_4$ or $HO_2CC_6H_4$ (*i.e.* of a type to permit formation of $C_6H_4OC_6H_4COC_6H_4$ linkages between carborane cages using acylation reactions in TFSA) could be attached to one or more of the boron atoms of an icosahedral carborane cage; (ii) to explore the chemical stability and relevant reactivity of such carborane derivatives; and (iii) to prepare suitable monomers for polymer formation by attaching two such functional aryl groups either to two boron atoms of a carborane cage, or to one boron and one carbon atom of a carborane cage.

For convenience, we chose *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, as the most suitable carborane for this study, and focused on substitution at boron atoms 9 and 12, *i.e.* those antipodal to the two carbon atoms.[8]

Experimental

Stirring refers to the use of a Teflon magnetic stirrer. Solutions were dried over anhydrous magnesium sulfate and evaporated under reduced pressure on a rotary evaporator or by stirring under vacuum using a cold trap. Melting points were measured using capillary tubes and an electrically heated block and are uncorrected. Thin layer chromatography (TLC) was conducted on Merck DC-Plastifolien Kieselgel 60 F_{254} (Art. 5735).

Preparative chromatography was carried out by dissolving the substrate in warm hexane and adding approximately twice its weight of chromatographic silica (Merck silica gel 60, particle size 0.04–0.063 mm Art. 9385). The resulting slurry was placed on top of a wet column (length six to eight times its diameter) of silica gel in hexane and eluted at atmospheric pressure. Fractions of quarter of column volume were analysed by TLC before recombination.

Infrared spectra were recorded as potassium bromide discs using a Perkin Elmer 377 spectrometer. Mass spectra were recorded on a VG Micromass 7070E instrument operating in the EI or negative CI (isobutane or NH_3) mode at 70 eV. Calculated values of M_r show the full isotope range $^{10}B_n$ to $^{11}B_n$; the less probable combinations are seldom observed in practice.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ solution, unless otherwise stated, on a Bruker AC250 multinuclear spectrometer operating at 250.13 MHz for ^1H, 80.24 MHz for ^{11}B and 62.89 MHz for ^{13}C. ^1H NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm, $(CD_3)_2CO$, 2.05 ppm). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$ 77.0 ppm, $(CD_3)_2CO$, 28.0 ppm). ^{11}B NMR were referenced externally to $Et_2O{\cdot}BF_3$, $\delta = 0.0$ ppm. Certain ^{11}B NMR assignments were determined with the aid of 2D ^{11}B–$^{11}B\{^1H\}$ COSY and proton-coupled spectra. The ^{13}C peak corresponding to the aryl carbon attached to boron were not detected above the noise level for *B*-aryl carboranes in this study.

Ether refers to diethyl ether dried, where necessary, by standing over sodium wire. Tetrahydrofuran (THF) was dried by refluxing and distillation over potassium and storage over sodium wire. Acid refers to hydrochloric acid unless otherwise noted. Butyllithium solution was used as supplied (Aldrich), or after storage, standardised by titration with butan-2-ol in toluene using 4,5-diazaphenanthrene as indicator. 1,2-$C_2B_{10}H_{12}$ and iodine were obtained commercially and purified by sublimation (70 °C, 0.01 mmHg). Dichlorobis(triphenylphosphine)palladium was purchased commercially and used as supplied. The following materials were prepared by published methods: purified copper(I) chloride;[9] 4-methylbenzenediazonium tetrafluoroborate;[10] 1-(*p*-MeC_6H_4)-1,2-$C_2B_{10}H_{11}$ (63% yield,[11] mp 151–153 °C: lit.[12] 68%, mp 154–155 °C); 9-I-1,2-$C_2B_{10}H_{11}$ **1** (89% yield,[13–15] mp 123 °C: lit.[16] 117–118 °C); 9-(4-MeC_6H_4)-1,2-$C_2B_{10}H_{11}$ **2** (47%, 127–128 °C: lit.[17] 87%, 129–129.5 °C); 9,12-I_2-1,2-$C_2B_{10}H_{10}$ **8** (82% yield,[13] mp 190–191°C: lit.[13] 193–194 °C); 4-iododiphenyl ether;[4] 4,4′-bis(phenoxy)diphenyl.[18]

NMR data for 1-(*p*-MeC_6H_4)-1,2-$C_2B_{10}H_{11}$. δ_C: 140.2 (*para C*-aryl - attached to methyl group), 130.7 (*ipso C*-aryl - attached to C1), 129.4 (*meta C*-aryl), 127.5 (*ortho C*-aryl), 76.7 (C1), 60.4 (C2), 20.9 (CH_3 *C*-aryl). δ_H: 7.29 (d; 8.0 Hz; *C*-aryl *ortho CH*); 7.05 (d; 8.0 Hz; *C*-aryl *meta* CH); 3.84 (C2H); 2.26 (CH_3 *C*-aryl); 4.1–1.0 (BH).

NMR data for 9-(*p*-MeC_6H_4)-1,2-$C_2B_{10}H_{11}$ **2**. δ_C: 136.9 (*para B*-aryl), 132.4 (*ortho B*-aryl), 128.3 (*meta B*-aryl), 53.1 (C1), 48.7 (C2), 21.2 (CH_3 *B*-aryl). δ_H: 7.30 (d; 7.5 Hz; *B*-aryl *ortho* CH); 7.08 (d; 7.5 Hz; *B*-aryl *meta* CH); 3.54 (C1H); 3.43 (C2H); 2.32 (CH_3 *B*-aryl); 4.1–1.0 (BH).

NMR data for 4-iododiphenyl ether; δ_C: 157.4 (CO of C_6H_4), 156.5 (CO of C_6H_5), 138.6 (OCC*C* of C_6H_4), 129.9 (OCC*C* of C_6H_5), 123.8 (OCCC*C* of C_6H_5), 120.8 (OC*C* of C_6H_5), 119.1 (OC*C* of C_6H_4), 85.8 (CI); δ_H: 7.62 (d; $^3J_{HH} = 8.5$ Hz; ICCH), 7.36 (t; 8.0 Hz; OCCCH of C_6H_5), 7.14 (t; 7.5 Hz; OCCCCH of C_6H_5), 7.02 (d; 8.5 Hz; OCCH of C_6H_5), 6.78 (d; 8.5 Hz; OCCH of C_6H_4).

NMR data for 4,4′-bis(phenoxy)diphenyl; δ_C: 157.2 (CO of C_6H_5), 156.7 (CO of C_6H_4), 135.7 (OCCC*C* of C_6H_4), 129.8 (OCC*C* of C_6H_5), 128.1 (OCC*C* of C_6H_5), 123.3 (OCCC*C* of C_6H_5), 119.1 (OC*C* of C_6H_4), 118.9 (OC*C* of C_6H_5); δ_H: 7.54 (d; $^3J_{HH} = 8.7$ Hz; OCCCH of C_6H_4), 7.38 (t; 7.9 Hz; OCCCH of C_6H_5), 7.17 (t; 7.5 Hz; OCCCCH of C_6H_5), 7.10 (d; 8.5 Hz; OCCH of C_6H_5), 7.08 (d; 8.5 Hz; OCCH of C_6H_4).

Synthesis of 9-(4-$HO_2CC_6H_4$)-1,2-$C_2B_{10}H_{11}$ 3

Chromium trioxide (3 g; 30 mmol) was gradually added to a stirred solution of 9-(*p*-MeC_6H_4)-1,2-$C_2B_{10}H_{11}$ **2** (0.47 g; 2 mmol), acetic anhydride (7.5 cm^3) and conc. sulfuric acid (1.5 cm^3) in glacial acetic acid (30 cm^3) at 20 °C. After 2 h, the green mixture was poured into ice-cold water (250 cm^3) and the precipitate was removed, washed with distilled water and dried. The white powder was characterized as the carborane acid (0.40 g; 76%), mp 251–252 °C. [Found: C, 40.2; H, 6.1%; M_r (mass spectrum), 260–266. $C_9H_{16}B_{10}O_2$ requires: C, 40.9; H, 6.1%; M_r, 255–266], δ_C ($(CD_3)_2CO$): 167.4 (*C*O); 132.4 (*C*CO); 131.6, 127.8 (aryl *C*H); 53.9 (carboranyl *C*1); 50.0 (carboranyl *C*2); δ_B ($(CD_3)_2CO$): 7.0 (s; B9); −2.1 (d; B12); −8.4

(d; B8,B10); −13.7 (d; B4,B5,B7,B11); −14.4 (d; B3, B6); δ_H ($(CD_3)_2CO$): 7.88 (d; 7.9 Hz; aryl C*H*); 7.46 (d; 7.9 Hz; aryl C*H*); 7.18 (s; O*H*); 4.68 (s; carboranyl C1*H*), 4.60 (s; carboranyl C2*H*); 4.1–1.0 (B*H*).

Condensation of 9-(4-$HO_2CC_6H_4$)-1,2-$C_2B_{10}H_{11}$ 3 with anisole

The carborane **3** (0.264 g; 1.0 mmol) and anisole (0.12 g; 1.1 mmol) were dissolved in TFSA (3.0 cm^3). A red solution was formed after one hour and left to stand for 24 h under nitrogen. The dark red solution was poured into water, the precipitate was extracted into ether and the extract was washed with 10% aqueous sodium hydroxide and water, dried and evaporated. The residue was recrystallized from hexane to give the anisoyl derivative, 9-[4-(4′-$MeOC_6H_4CO)C_6H_4$]-1,2-$C_2B_{10}H_{11}$ **4** (0.23 g; 65%) [Found: C, 62.1; H, 6.0%; M_r (mass spectrum), 412–418. $C_{21}H_{24}B_{10}O_2$ requires: C, 60.6; H, 5.7%; M_r, 408–419] ν_{max}/cm^{-1} 3064, 3048 (carboranyl CH); 2651, 2620s, 2598s, 2585s, 2577s (BH); 1642s (C=O); 1285s, 1253s (C-O-C), 848s (*p*-C_6H_4). δ_C: 195.7 (*C*=O); 165.8 (*C*OCH_3); 136.8, 132.4, 132.1, 130.3, 128.6 (other aryl carbon resonances); 113.4 (*C*$COCH_3$); 55.4 (O*C*H_3); 53.3 (carboranyl *C*1); 49.5 (carboranyl *C*2); δ_B: 8.2 (s; B9); −0.8 (d; B12); −7.4 (d; B8,10); −12.8 (B3–7,B11); δ_H: 7.82 (d; 8.5 Hz; aryl C*H*); 7.61 (d; 7.6 Hz; aryl C*H*); 7.47 (d; 7.6 Hz; aryl C*H*); 6.95 (d; 8.5 Hz; aryl C*H*); 3.88 (s; CH_3); 3.69 (s; carboranyl C2*H*); 3.59 (s; carboranyl C1*H*); 4.1–0.9 (B*H*).

Synthesis of 9-(*p*-$PhOC_6H_4$)-1,2-$C_2B_{10}H_{11}$ 5

4-Iododiphenyl ether (11.84 g; 40 mmol) in dry ether (25 cm^3) was added dropwise to magnesium filings (1.5 g; 60 mmol) and an iodine crystal in ether (15 cm^3) at 0 °C. After 2 h, the filings were removed and the solution added to a stirred solution of 9-I-1,2-$C_2B_{10}H_{11}$ **1** (2.70 g; 10 mmol) and dichlorobis(triphenylphosphine)palladium (0.04 g; 0.0568 mmol) in anhydrous ether (30 cm^3). After refluxing for 36 h, the mixture was added with water (100 cm^3). The organic layer was washed with dilute hydrochloric acid and water, dried and evaporated. The residue was subjected to column chromatography with hexane as eluent to give the carborane 9-(*p*-$PhOC_6H_4$)-1,2-$C_2B_{10}H_{11}$ **5** (1.88 g; 60%), mp 177–178 °C. [Found: C, 54.9; H, 6.7%; M_r (mass spectrum), 308–314. $C_{14}H_{20}B_{10}O$ requires: C, 53.9; H, 6.4%; M_r, 303–314] ν_{max}/cm^{-1} 3055s (carboranyl CH); 2640s, 2628s, 2611s, 2596s, 2571s (BH); 1586s (Ar-skel.); 1269s (C-O-C); 842, 831 (*p*-C_6H_4); 732s, 696s (C_6H_5). δ_C: (with proton coupling) 157.3 (t; *C*-O of C_6H_5), 156.9 (t; *C*-O of C_6H_4); 133.8 (dd; OCC*C* of C_6H_4), 129.6 (dd; OCC*C* of C_6H_5), 123.0 (dt; *para* OCCC*C* of C_6H_5); 118.9 (dt; OC*C* of C_6H_5), 117.8 (OC*C* of C_6H_4); 53.1 (d; carboranyl *C*1); 48.7 (d; carboranyl *C*2); δ_B: 7.3 (s; B9); −2.5 (d; B12); −9.0 (d; B8,10); −14.5 (m; B4,5,7,11); −15.5 (d; B3,6); δ_H: 7.35 (d; 8.4 Hz; OCCC*H* of C_6H_4); 7.33 (t; ~7.7 Hz; OCCC*H* of C_6H_5); 7.09 (t; 7.5 Hz; OCCCC*H* of C_6H_5); 7.02 (d; 8.0 Hz; OCC*H* of C_6H_5); 6.89 (d; 8.4 Hz; OCC*H* of C_6H_4); 4.1–1.0 (B*H*). The carbon and proton NMR assignments were deduced by comparing with NMR data of 4-iododiphenyl ether and 4,4′-bis(phenoxy)diphenyl.

Condensation of 9-(*p*-$PhOC_6H_4$)-1,2-$C_2B_{10}H_{11}$ 5 with benzoic acid

TFSA (8 cm^3) was added to a powdered mixture of 9-(*p*-$PhOC_6H_4$)-1,2-$C_2B_{10}H_{11}$ **5** (0.312 g; 1 mmol) and benzoic acid (0.122 g; 1 mmol) under nitrogen with stirring. The red solution was left standing for 24 hours and then poured into water (30 cm^3). The precipitate was washed with 5% sodium hydroxide solution and distilled water and dried. The solid was a 55 : 45 mixture of the benzoyl derivatives, 9-(4′-PhCO-4-$C_6H_4OC_6H_4$)-1,2-$C_2B_{10}H_{11}$ **6** and 9-(3-PhCO-4-$PhOC_6H_3$)-1,2-$C_2B_{10}H_{11}$ **7** (0.26 g; 62.5%) [Found: C, 62.1; H, 6.0%; M_r (mass spectrum), 412–418. $C_{21}H_{24}B_{10}O_2$ requires: C, 60.6; H, 5.7%; M_r, 408–419] ν_{max}/cm^{-1} 3065 (carboranyl CH); 2605s (BH); 1653s (C=O); 1280s, 1265s (C-O-C); 855, 832 (*p*-C_6H_4); 758, 738 (C_6H_5). δ_C: 202.0, 195.8 (*C*=O); 162.2, 159.6; 157.0; 154.3 (*C*O*C*); 139.2, 138.0, 137.3, 136.8, 134.0, 132.4, 132.0, 131.5, 130.5, 129.7, 129.0, 128.2, 125.2, 124.1, 123.4, 120.4, 119.3, 118.9, 117.1, 116.8 (aryl carbon resonances), 53.3 (carboranyl C1 of **6** and **7**); 50.6 (carboranyl C2 of **7**); 49.3 (carboranyl C2 of **6**).

Synthesis of 9,12-(*p*-$MeC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ 9

4-Iodotoluene (17.44 g; 80 mmol) in dry ether (40 cm^3) was added dropwise under nitrogen to magnesium turnings (3 g; 120 mmol) in ether (20 cm^3) at 0 °C. After 2 h the excess turnings were removed and the filtrate added to a solution of 9,12-I_2-1,2-$C_2B_{10}H_{10}$ **8** (3.96 g; 10 mmol) and palladium catalyst (0.04 g; 0.0568 mmol) in ether (20 cm^3). After 24 h refluxing the black mixture was decomposed with water (100 cm^3). The precipitate formed in the organic layer was washed with dilute acid, water and ether. The solid was recrystallized from hot toluene to give the diaryl carborane (1.04 g; 32%), mp 277–278 °C. [Found: C, 59.1; H, 7.3%; M_r (mass spectrum), 320–326. $C_{16}H_{24}B_{10}$ requires: C, 59.3; H, 7.4%; M_r, 315–326] ν_{max}/cm^{-1} 3056s (carboranyl CH); 2629s, 2594s, 2556s (BH); 1602s (Ar-skel.). δ_C: 136.4 (*C*CH_3); 132.8, 128.0 (aryl *C*H); 48.8 (carboranyl *C*); 21.2 (*C*H_3); δ_B: 8.5 (s; B9,12); −8.6 (d; B8,10); −13.3 (d; B4,5,7,11); −15.5 (d; B3,6); δ_H: 7.11 (d; 6.8 Hz; aryl *ortho*-C*H*); 6.93 (d; 6.8 Hz; aryl *meta*-C*H*); 3.62 (s; carboranyl C*H*); 2.23 (s; CH_3); 4.1–1.0 (B*H*).

Synthesis of 9,12-(*p*-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ 10

A stirred solution of 9,12-(*p*-$MeC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **9** (0.648 g; 2 mmol), acetic anhydride (7.5 cm^3), conc. sulfuric acid (1.5 cm^3) and glacial acetic acid (30 cm^3) was treated slowly with chromium(IV) trioxide at 20 °C. After 2 h, the mixture was poured into cold distilled water. The organic products were extracted into ether, dried and evaporated to leave a pale green solid. The solid was dissolved in boiling sodium hydrogen carbonate solution and acidified with dilute acid to give a precipitate. The white solid was washed with water and dried over phosphorus pentoxide to give 9,12-(*p*-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **10** (0.49 g; 64%), mp 312–313 °C. [Found: C, 49.7; H, 5.4%; M_r (mass spectrum), 380–386. $C_{16}H_{20}B_{10}O_4$ requires: C, 50.0; H, 5.2%; M_r, 375–386], ν_{max}/cm^{-1} 3650–2330 (OH); 3061 (carboranyl CH); 2596s (BH); 1687s (C=O); δ_C ($(CD_3)_2CO$): 165.9 (*C*=O); 131.8, (*C*CO); 128.2, 127.3 (aryl *C*H); 50.8 (carboranyl *C*); δ_B ($(CD_3)_2CO$): 7.6 (s; B9,12); −8.7 (d; B8,10); −12.6 (B3–7,11); δ_H ($(CD_3)_2CO$): 7.76 (d; 8.0 Hz; aryl C*H*); 7.33 (d; 8.0 Hz; aryl C*H*); 4.81 (s; carboranyl C*H*); 2.92 (s; O*H*); 4.0–1.0 (B*H*).

Condensation of 9,12-(*p*-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ 10 with anisole

The diacid, 9,12-(*p*-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **10** (0.384 g; 1 mmol), and anisole (0.24 g; 2.2 mmol) were dissolved in TFSA (4 cm^3) and left to stand for 24 h under nitrogen. The dark red solution was poured into water and the precipitate was extracted into ether. The organic layer was washed with 10% sodium hydroxide and water, dried and evaporated. The residue was recrystallized from hexane to give 9,12-(4′-MeO-4-$C_6H_4COC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **11** (0.41 g; 73%), mp 209–210 °C. [Found: C, 59.5; H, 5.6%; M_r (mass spectrum), 560–566. $C_{30}H_{32}B_{10}O_4$ requires: C, 59.6; H, 5.7%; M_r, 555–566] ν_{max}/cm^{-1} 3061 (carboranyl CH); 2599 (BH); 1647s (C=O); 1260s (C-O-C). δ_C: 195.9 (*C*=O); 163.1 (*C*OCH_3); 136.8, 132.7, 132.5, 130.3, 128.7 (other aryl *C* resonances); 113.5 (COC*C*H); 55.5 (*C*H_3); 50.1 (carboranyl *C*); δ_B: 8.0 (s; B9,12); −8.6

(d; B8,10); −13.0 (B3–7,B11); δ_H: 7.79 (d; 8.5 Hz; aryl C*H*); 7.54 (d; 7.5 Hz; aryl C*H*); 7.34 (d; 7.5 Hz; aryl C*H*); 6.94 (d; 8.5 Hz; aryl C*H*); 3.88 (s; C*H*$_3$); 3.79 (s; carboranyl C*H*); 4.1–1.0 (B*H*).

Synthesis of 1,9-(*p*-MeC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ 12 and 1,12-(*p*-MeC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ 13

A stirred solution of 9-(4-MeC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ **2** (2.34 g; 10 mmol) in ether (20 cm^3) at 0 °C was treated with butyllithium in hexane (7.1 cm^3; 1.61 mol dm^{-3}; 10 mmol). After 15 min the mixture was refluxed for 15 min, cooled to 0 °C, anhydrous copper(I) chloride (1.24 g; 12.5 mmol) was added and then slowly THF (30 cm^3) at 5 °C. The solution was stirred at 20 °C for 30 min then at 40 °C for 10 min. At 0 °C, 4-methylbenzenediazonium tetrafluoroborate (2.57 g; 12.5 mmol) was added in small portions, with gas evolution, to the solution with vigorous stirring. The mixture was stirred at 0 °C for 15 min, 20 °C for 15 min and finally 40 °C for 15 min. At ambient temperature, methanol was added then the precipitate was washed with benzene and ether. The organic liquid was washed with dilute acid, dried and evaporated. The residue was fractionally sublimed (170 °C at 0.01 mmHg). The fractions containing the desired carboranes (checked by TLC) were combined and recrystallized from hexane to give a 1 : 1 mixture of 1,9-(*p*-MeC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ **12** and 1,12-(*p*-MeC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ **13** (1.07 g; 33%). A small amount (0.12 g) of pure 1,12-diaryl carborane **13** was obtained by fractional recrystallization. Data for **12** and **13**, ν_{max}/cm^{-1} 3058 (carboranyl CH); 2627, 2592s, 2561s (BH); 1512 (Ar-skel.). **13**, mp 205–206 °C; [Found: C, 59.3; H, 7.6%; M_r (mass spectrum), 320–326. C$_{16}$H$_{24}$B$_{10}$ requires: C, 59.3; H, 7.4%; M_r, 315–326] δ_C: 140.2 (*para C*-aryl), 136.8 (*para B*-aryl), 132.5 (*ortho B*-aryl), 130.2 (*ipso C*-aryl), 129.5 (*meta C*-aryl), 128.2 (*meta B*-aryl), 127.6 (*ortho C*-aryl), 70.9 (C1), 59.3 (C2), 21.2 (CH$_3$ *B*-aryl), 20.9 (CH$_3$ *C*-aryl). δ_H: 7.52 (d; 7.9 Hz; *C*-aryl *ortho* CH); 7.35 (d; 7.2 Hz; *B*-aryl *ortho* CH); 7.16 (d; 7.9 Hz; *C*-aryl *meta* CH); 7.09 (d; 7.3 Hz; *B*-aryl *meta* CH); 4.00 (C2H); 2.38 (CH$_3$ *B*-aryl); 2.34 (CH$_3$ *C*-aryl). δ_B: 6.0 (s; B12); −1.5 (d; B9); −8.1 (d; B8,10); −11.3 (B3–7,11); **12**, δ_C: 140.2 (*para C*-aryl), 136.8 (*para B*-aryl), 132.3 (*ortho B*-aryl), 130.6 (*ipso C*-aryl), 129.5 (*meta C*-aryl), 128.2 (*meta B*-aryl), 127.5 (*ortho C*-aryl), 75.3 (C1), 54.7 (C2), 21.2 (CH$_3$ *B*-aryl), 20.9 (CH$_3$ *C*-aryl). δ_H: 7.52 (d; 7.9 Hz; *C*-aryl *ortho* C*H*); 7.40 (d; 7.3 Hz; *B*-aryl *ortho* CH); 7.16 (d; 7.9 Hz; *C*-aryl *meta* CH); 7.10 (d; 7.3 Hz; *B*-aryl *meta* CH); 3.88 (C2H); 2.38 (CH$_3$ *B*-aryl); 2.34 (CH$_3$ *C*-aryl), δ_B: 8.1 (s; B9), −4.2 (d; B12), −8.2 (d; B8,10), −11.3 (B3–7,11). The carbon and proton peaks were assigned on the basis of NMR data for 1-(*p*-MeC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ and 9-(*p*-MeC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ **2**.

Synthesis of 1,9-(*p*-HO$_2$CC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ 14 and 1,12-(*p*-HO$_2$CC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ 15

Chromium trioxide (3 g; 30 mmol) was added in small portions to a stirred mixture of the 1,9- and 1,12-ditolyl carboranes **12** and **13** (0.65 g; 2 mmol), glacial acetic acid (50 cm^3), acetic anhydride (20 cm^3) and conc. sulfuric acid (3 cm^3). The dark green mixture was stirred at 20 °C for 2 h then poured into water (300 cm^3). A precipitate appeared which was removed, and washed with distilled water to remove the green chromium residues. The off-white solid was dissolved in boiling sodium hydrogen carbonate solution then acidified with dilute acid. The white precipitate was filtered off and recrystallized from a 5 : 1 acetone : water mixture and dried over P$_2$O$_5$ to produce the diacid isomers (0.42 g; 55%). Data for 1,9-(*p*-HO$_2$CC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ **14** *and* 1,12-(*p*-HO$_2$CC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ **15**: [Found: C, 49.7; H, 5.1%; M_r (mass spectrum), 380–386. C$_{16}$H$_{20}$B$_{10}$O$_4$ requires: C, 50.0; H, 5.2%; M_r, 375–386] ν_{max}/cm^{-1} 3420–2100 (OH); 3070 (carboranyl CH); 2607s (BH); 1700s (C=O). δ_B ((CD$_3$)$_2$CO): 6.9 (s; B9 of **14**); 4.7 (s; B12 of **15**); −3.3 (B9 of **14**); −5.5 (B12 of **15**); −9.2 (B8,B10); −12.1 (B3,B6,B4,B5,B7,B11); δ_H ((CD$_3$)$_2$CO): 10.24 (br s; O*H*); 8.07 (d; 8.3 Hz; C*H* of aryl group at carboranyl C); 7.91 (d; 8.1 Hz; aryl C*H* at carboranyl B); 7.86 (d; 8.3 Hz; aryl C*H* at carboranyl C); 7.50 (d; 8.1 Hz; aryl C*H* at carboranyl B); 7.36 (br s; O*H*); 5.50 (s; carboranyl C*H*); 4.0–1.0 (B*H*).

Condensation of 1,9-(*p*-HO$_2$CC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ 14 and 1,12-(*p*-HO$_2$CC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ 15 with anisole

A mixture of the carborane diacids, **14** and **15**, and anisole was dissolved in TFSA and left to stand for 32 h. The dark red solution was poured into water (20 cm^3) affording a white precipitate. The solid was removed, washed with water and 10% sodium hydroxide and dried to give the anisoyl compounds 1,9-(4′-MeO-4-C$_6$H$_4$COC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ **16** and 1,12-(4′-MeO-4-C$_6$H$_4$COC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ **17**. (0.17g; 60%) [Found: C, 58.2; H, 5.4%; M_r (mass spectrum), 560–566. C$_{30}$H$_{32}$B$_{10}$O$_4$ requires: C, 59.6; H, 5.7%; M_r, 555–566] ν_{max}/cm^{-1} 3063 (carboranyl CH); 2586 (BH); 1653 (C=O); 1259s (C-O-C). The insolubility of the products in common solvents prevented use of solution-state NMR spectroscopy.

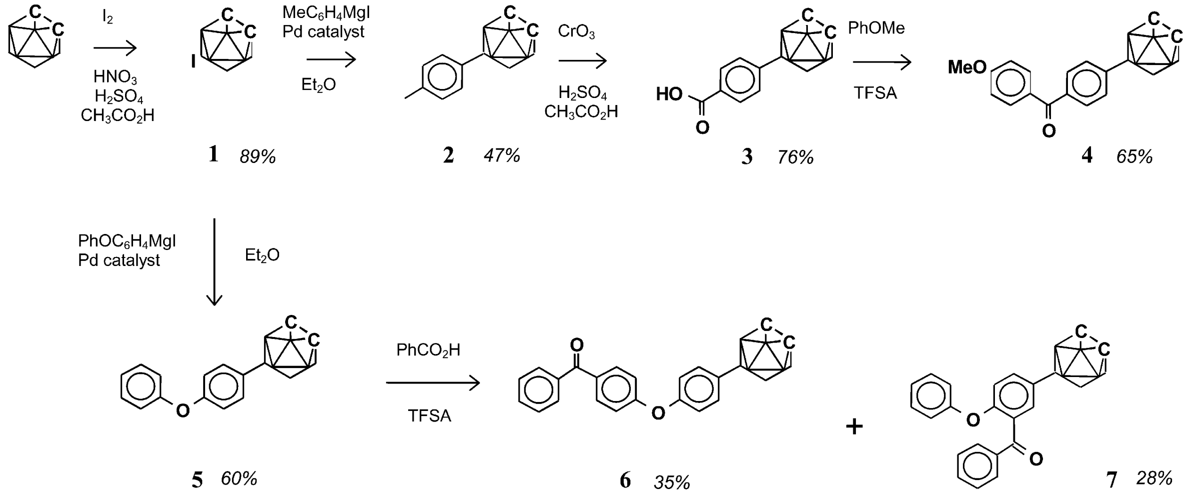
Results and discussion

Syntheses and yields of *B*-monoaryl carboranes from the parent carborane 1,2-C$_2$B$_{10}$H$_{12}$ in this study are summarized in Scheme 3. Compound 9-(*p*-MeC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ **2** was converted into the new acid 9-(*p*-HO$_2$CC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ **3** using the procedure reported for the related derivative 4-(*p*-HO$_2$CC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ from 4-(*p*-MeC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ and chromium trioxide in acid.[5,19] The reaction of the iodo carborane 9-I-1,2-C$_2$B$_{10}$H$_{11}$ **1** and *p*-phenoxyphenylmagnesium iodide in the presence of a palladium catalyst gave the novel ether 9-(*p*-PhOC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ **5**.

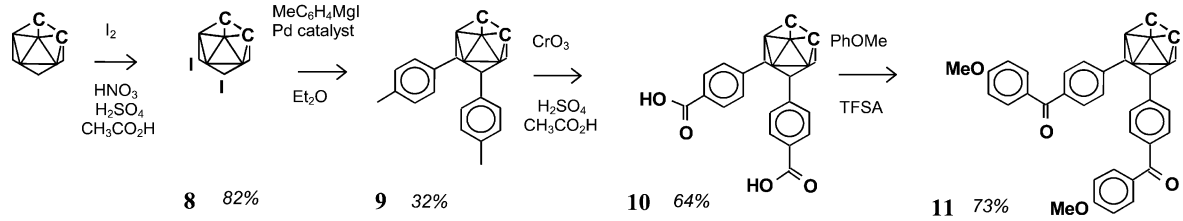
The ether ketone, 9-(4′-MeO-4-C$_6$H$_4$COC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ **4**, was obtained from anisole and *B*-aryl carborane 9-(*p*-HO$_2$CC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ **3** in TFSA. The reported reaction between the *C*-aryl carborane 1-(*p*-HO$_2$CC$_6$H$_4$)-2-Ph-1,2-C$_2$B$_{10}$H$_{10}$ and anisole in TFSA required 18 h for complete condensation to the ether ketone with the orange solution slowly turning red (Scheme 2).[4] Here, the rapid colour change in the *B*-aryl carborane reaction suggests most of the carboxylic acid **3** had already been converted in one hour. At the 9- position, the electron-donating ability of the cage favours the formation of the acyl ion, 4-(9′-(1′,2′-C$_2$B$_{10}$H$_{11}$))C$_6$H$_4$CO$^+$, whereas at the cage carbon the electron-withdrawing ability of the cage hinders the formation of the acyl ion 4-(1′-(2′-Ph-1′,2′-C$_2$B$_{10}$H$_{10}$))C$_6$H$_4$CO$^+$.[4] This is the most likely explanation for the faster rate of condensation in the formation of the *B*-aryl carborane **4** compared to the formation of the *C*-aryl carborane ether ketone.

Ether carborane **5** was treated with benzoic acid in TFSA to give two carboranyl ether ketones, 9-(4′-PhCO-4-C$_6$H$_4$OC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ **6** and 9-(3-PhCO-4-PhOC$_6$H$_3$)-1,2-C$_2$B$_{10}$H$_{11}$ **7**. Unlike the *C*-aryl carborane 1-Ph-1,2-C$_2$B$_{10}$H$_{11}$, the *B*-aryl carborane 9-Ph-1,2-C$_2$B$_{10}$H$_{11}$ can be acylated at the aromatic ring and showed a tendency to form *meta*-directing products with acylation.[20] In **5** the two positions susceptible to attack by the benzoyl ion, C$_6$H$_5$CO$^+$, are the *para* position of the phenyl group and the *meta* position of the aromatic ring attached to the cage. By contrast, the *C*-aryl carborane, 1-(4-PhOC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ is exclusively attacked at the *para* position of the phenyl group by the benzoyl ion to give 1-(4′-PhCO-4-C$_6$H$_4$OC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ (Scheme 2).[4]

In view of the success of the model reaction between the carboxylic acid **3** and anisole, the diacid monomer, 9,12-(*p*-HO$_2$CC$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{10}$ **10**, was synthesized *via* the ditolyl



Scheme 3 Syntheses of *B*-monoaryl carboranes.



Scheme 4 Syntheses of *B*-diaryl carboranes.

precursor **9** (Scheme 4). The new diaryl carborane 9,12-(p-$MeC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **9** was produced from the diiodo carborane 9,12-I_2-1,2-$C_2B_{10}H_{10}$ **8** and 4-methylbenzenemagnesium iodide in low yield. Chromium trioxide–sulfuric acid oxidation of the ditolyl derivative **9** afforded the dicarboxylic acid 9,12-(4-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **10**. The model reaction of the diacid monomer **10** with anisole in TFSA gave 9,12-(4′-MeO-4-$C_6H_4COC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **11** as the sole product.

C-monoaryl-*ortho*-carboranes can be obtained from the parent carborane 1,2-$C_2B_{10}H_{12}$ by coupling of the carboranyl copper derivative with aryldiazonium tetrafluoroborates.[10] The copper(I) derivative of the 9-tolyl-1,2-carborane **2** with 4-methylbenzenediazonium tetrafluoroborate gave a mixture of 1,9- and 1,12-ditolyl carboranes, 1,9-(p-$MeC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **12** and 1,12-(p-$MeC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **13**, in equal amounts. A small amount of **13**, identified by NMR spectroscopy, was isolated by fractional crystallization. The mixture, **12** and **13**, was oxidized by the chromium trioxide method to form a mixture of the desired acid monomers, 1,9-(p-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **14** and 1,12-(p-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **15**. Subjecting the mixture of *B*,*C*-diacids **14** and **15** to the model reaction with anisole in TFSA gave a white solid which was identified tentatively as a mixture of carboranyl ether ketones 1,9-(4′-MeO-4-$C_6H_4COC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **16** and 1,12-(4′-MeO-4-$C_6H_4COC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **17**. These reactions are shown graphically in Scheme 5.

All of the derivatives synthesized in this study were characterized by elemental analysis, infrared, solution-state ^{13}C NMR and low resolution mass spectroscopy. Compounds **16** and **17** were insoluble in the common solvents tried, so the solution state NMR spectra were not obtained.

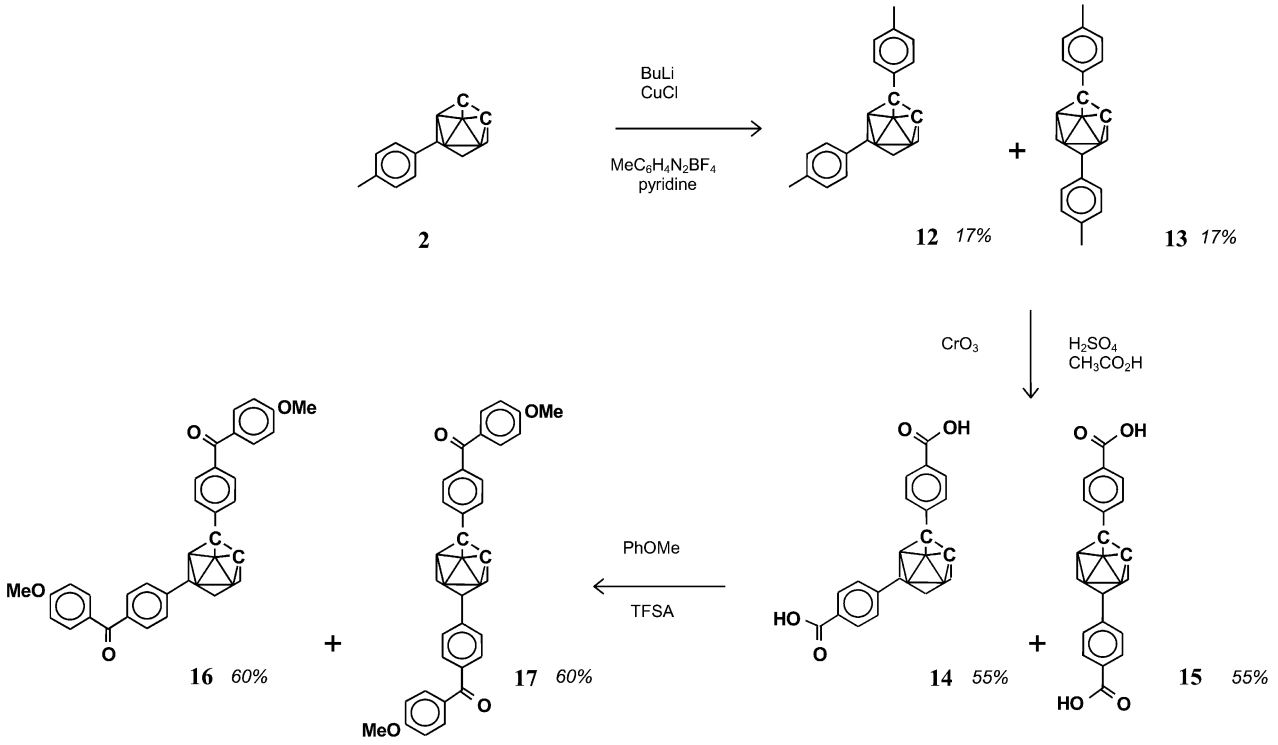
The ^{13}C chemical shift of the carboranyl cage carbon atom is significantly affected when the boron vertex directly opposite is substituted compared to the shift of the related parent carborane. This effect, which has been much studied, is known as the 'antipodal effect'.[21] For example, the iodo carborane 9-I-1,2-$C_2B_{10}H_{11}$ **1** has ^{13}C peaks at 50.7 and 54.9 ppm assigned to C2 and C1 respectively whereas the parent carborane 1,2-$C_2B_{10}H_{12}$ has a peak at 54.5 ppm in $CDCl_3$.[8,15] On the basis of the antipodal effect, the ^{13}C carboranyl peaks in 9- or 12-substituted carboranes **3–7** and **12–15** were assigned. Proton and carbon-13 NMR peaks for the *B*,*C*-diaryl carboranes, **12** and **13**, were assigned by comparison with the NMR data for 1- and 9-(4-methylphenyl)-1,2-carborane.[22]

Conclusions

New derivatives of *ortho* carborane, 1,2-$C_2B_{10}H_{12}$, have been prepared containing the functionalised aryl groups $PhOC_6H_4$ or $HO_2CC_6H_4$ (that permit formation of $C_6H_4OC_6H_4COC_6H_4$ linkages between carborane cages using acylation reactions in TFSA) attached to one or both of the boron atoms (B9 and B12) antipodal to the carbon atoms, in order to test the suitability of such species for use in the preparation of new categories of phenylene ether carboranylene ketone (PECK) polymers. Here we have shown that such systems could undergo model acylation reactions of types that would allow polymer formation from suitable diarylcarborane monomers.

The *B*,*C*-diaryl carboranes, 1,9-(p-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **14** and 1,12-(p-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **15**, containing the functionalised aryl groups $HO_2CC_6H_4$ on one carbon atom (C1) and on the antipodal boron atom (B12) or on the boron atom (B9) antipodal to the unsubstituted carbon atom (C2) also undergo acylation with anisole in TFSA. Of the carboranes synthesized here, the diaryl carboranes 9,12-(p-$HO_2CC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ **10**, **14** and **15** are suitable for the syntheses of PECK polymers by reaction with appropriate phenoxy organic or carborane monomers in TFSA.

Carboranes with one or two p-$PhOC_6H_4$ groups at the boron(s) antipodal to the cage carbon(s) are also suitable for the synthesis of PECK polymers. However these polymers are unlikely to contain only $C_6H_4OC_6H_4COC_6H_4$ repeat units. The model acylation reaction between the monoaryl derivative 9-(p-$PhOC_6H_4$)-1,2-$C_2B_{10}H_{11}$ **5**, and benzoic acid in TFSA



Scheme 5 Syntheses of *B*,*C*-diaryl carboranes.

gave two products, compound **6** (with the expected $C_6H_4OC_6H_4COC_6H_4$ link) and 9-(3-PhCO-4-PhOC_6H_3)-1,2-$C_2B_{10}H_{11}$ **7**.

We consider that *B*-aryl carboranes[23] of the types described here will prove to be suitable precursors from which to prepare carborane-containing polymers with *B*-aryl links. Such polymers may have desirable properties that are not present in polymers generated from *C*-aryl carborane precursors.

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