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Journal of Organometallic Chemistry 680 (2003) 155–164
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Big macrocyclic assemblies of carboranes (big MACs): synthesis and crystal structure of a macrocyclic assembly of four carboranes containing alternate *ortho*- and *meta*-carborane icosahedra linked by *para*-phenylene units

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Received 28 February 2003; received in revised form 2 April 2003; accepted 17 April 2003

Dedicated to Prof. Fred Hawthorne, pioneer and world authority on carborane and borane chemistry, on the occasion of his 75th birthday

Abstract

The macrocyclic compound, $[1,2\text{-}C_2B_{10}H_{10}\text{-}1,4\text{-}C_6H_4\text{-}1,7\text{-}C_2B_{10}H_{10}\text{-}1,4\text{-}C_6H_4]_2$ (**5**)—a novel cyclooctaphane, was prepared by condensation of the C,C′-dicopper(I) derivative of *meta*-carborane with 1,2-bis(4-iodophenyl)-*ortho*-carborane. The X-ray crystal structure of $\mathbf{5}\cdot C_6H_6\cdot 6C_6H_{12}$ was determined at 150 K, revealing an extremely loose packing mode. Molecule **5** has a crystallographic C_s and local C_{2v} symmetry; the macrocycle adopts a butterfly (dihedral angle 143°) conformation with the *ortho*-carborane units at the wingtips and the phenylene ring planes roughly perpendicular to the wing planes. Multinuclear NMR spectra suggest that molecule **5** in solution inverts rapidly via the planar D_{2h} geometry, which (from *ab* initio HF/6-31G* calculations) is only 1 kcal mol^{-1} higher in energy than the C_{2v} one. An attempt to prepare an even larger macrocycle, comprising three *para*-carborane and three *ortho*-carborane units linked by six *para*-phenylene units, was unsuccessful.

Keywords: Macrocycle; Carborane icosahedra; Butterfly conformation

1. Introduction

Over the past decade there has been much interest in macrocyclic assemblies of carborane polyhedra linked by organic units or metal atoms [1–9]. Hawthorne has prepared macrocycles in which *ortho*-carborane icosahedra are linked through flexible organic linkers and has shown how the flexibility and multiple Lewis acidity of macrocycles with alternating *ortho*-carborane icosahedra and mercury atoms (mercuracarborands) provides scope for their use in molecular recognition, optical sensors and catalysis [1]. There is also recent interest in macrocyclic assemblies of metallacarborane polyhedra linked by metal or organic units [10].

In Durham, we have focused on macrocycles of more rigidly defined geometry in which carborane icosahedra are linked through aromatic (phenylene or pyridylene) rings [6–8]. Our aim was to generate carborane assemblies which, subjected to deboronation and metallation reactions, would in turn afford metallacarborane assemblies in which the metal atoms were held close enough together to participate in collaborative di- or tri-metallic reactions of potential catalytic interest [8].

To date, our work has primarily concerned systems like compounds **1**–**3** (Fig. 1) formally derived from the known organic macrocycle **4**, hexa-*meta*-phenylene [11], by replacement of selected benzene rings in **4** by *meta*-carborane icosahedra (and by pyridine rings in the case of **2**). That planar hexagonal organic ring systems can formally be replaced by 3-dimensional carborane icosa-

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doi:10.1016/S0022-328X(03)00313-9

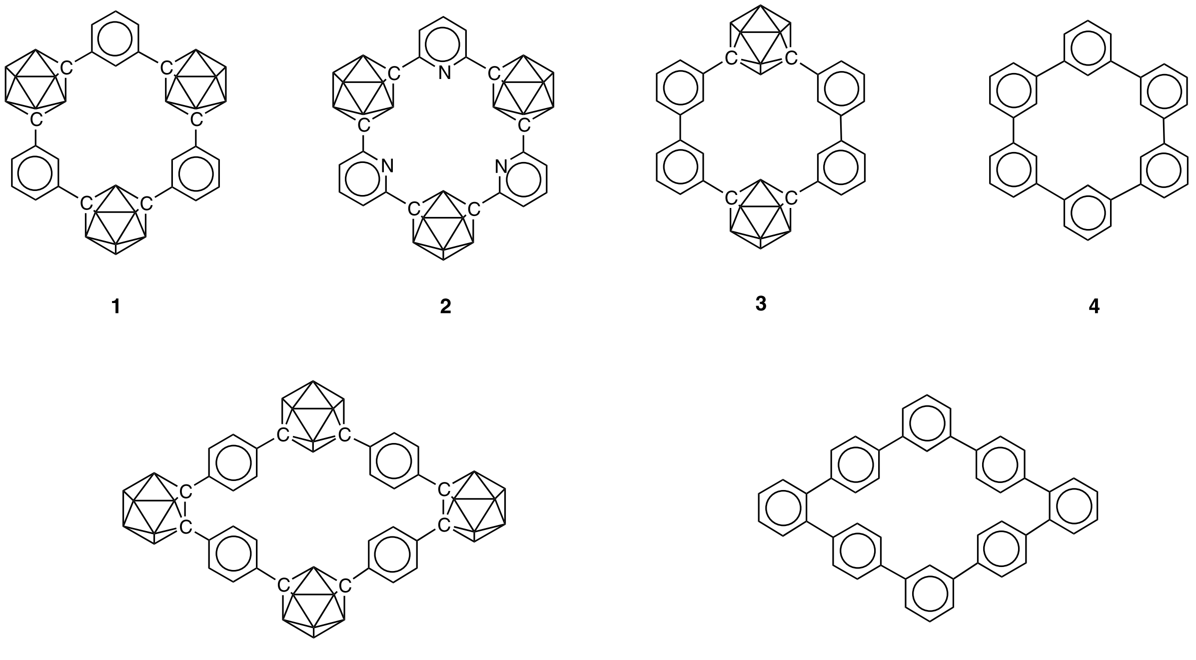


Fig. 1. Macrocycles incorporating carboranes: relationship to cyclo-phenylenes.

hedra without excessive bond angle strain is a valuable consequence of the similarity between the preferred angles between bonds to substituents on a benzene ring (60, 120, 180° for *ortho*-, *meta*- or *para*-substituents, respectively) and those to the carbon atoms of the parent icosahedral carboranes (53, 115 and 180°, respectively) [12].

Here we report the extension of this work to macrocycle **5** (Fig. 1), which we believe to be the first phenylene-linked assembly of carborane icosahedra to contain both *ortho*- and *meta*-carborane units. We have described this compound previously in conference proceedings [13]. The octa(phenylene) analogue of **5**, compound **6**, has not to our knowledge been reported.

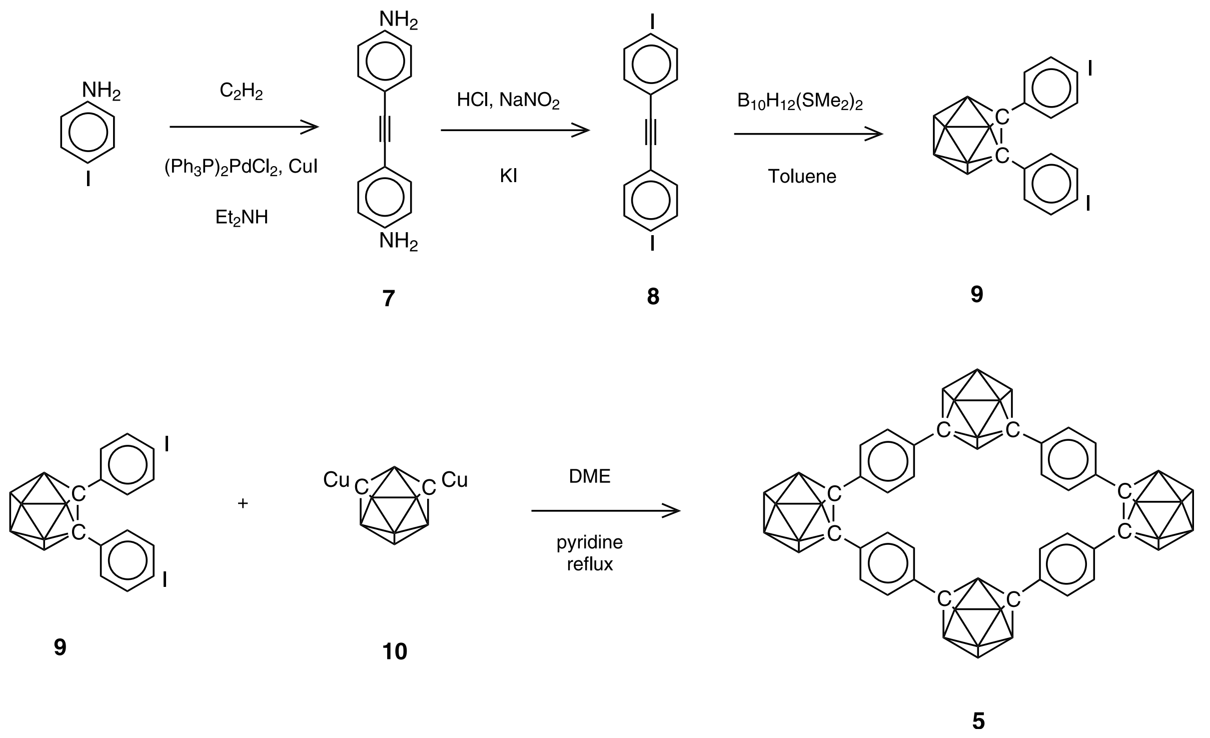
2. Results and discussion

2.1. Synthetic aspects

The steps by which compound **5** was prepared are shown in Scheme 1. Details are given in Section 3. Because *ortho*-carborane, unlike *meta* or *para*, is only mono-arylated when its di-copper(I) derivative reacts with aryl iodides [14,15], it was necessary to attach the aryl substituents to what were to become the carborane skeletal carbon atoms before the carborane cage was prepared from the alkyne and decaborane. 1,2-Bis(4-iodophenyl)-*ortho*-carborane has been prepared previously [16,17]. Our route differs from that used by the earlier workers in that they obtained the di-iodoarylyne **8** directly from acetylene and 1,4-diiodobenzene (we obtained an intractable mixture of oligomers in a similar experiment), and that we used the dimethyl sulfide, rather than the acetonitrile, complex of decaborane, $B_{10}H_{12}L_2$ ($L = Me_2S$).

Ring-closing reactions in attempted syntheses of macrocycles are notoriously prone to acyclic by-product formation, and the final stage in our synthesis of compound **5** (Scheme 1) proved no exception. Reaction of the bis(iodophenyl)carborane **9** with di-copper(I) *meta*-carborane **10**, needing the formation of four new carbon–carbon bonds to complete the macrocycle, gave a mixture of six main components from which some 9% yield of compound **5** was isolated by a combination of chromatography and fractional crystallisation. A by-product compound **11** (Fig. 2) was also isolated and characterized by NMR, IR and mass spectroscopy. The mass spectra of the other fractions showed what we believe were molecular ions appropriate for the masses of compounds **12**–**15**, which were not however fully separated. Their structures are inferred on the assumption that no unexpected reaction, particularly cleavage of phenyl–carborane bonds, has occurred. De-iodination, giving compound **14**, could result from copper/iodine exchange and subsequent protolysis of the aryl–copper links on work-up.

A further reaction explored was that between the bis(iodophenyl) carborane **9** and the di-copper(I) derivative of *para*-carborane **16**, in the hope that the triangular macrocycle **17** (Scheme 2), containing three *ortho*- and three *para*-carborane icosahedra, might



Scheme 1. Synthesis of macrocycle **5**, $[1,2\text{-}C_2B_{10}H_{10}\text{-}1,4\text{-}C_6H_4\text{-}1,7\text{-}C_2B_{10}H_{10}\text{-}1,4\text{-}C_6H_4]_2$.

form. This reaction gave a complex mixture containing at least 10 components in addition to some unchanged starting material **9**, probably all carboranes judged by their similar fluorescent properties on thin layer chromatography (TLC). Mass spectrometry of the more abundant fractions did not reveal any of the desired product, compound **17**. Two products from the reaction were identified from mass and infra-red spectroscopy as

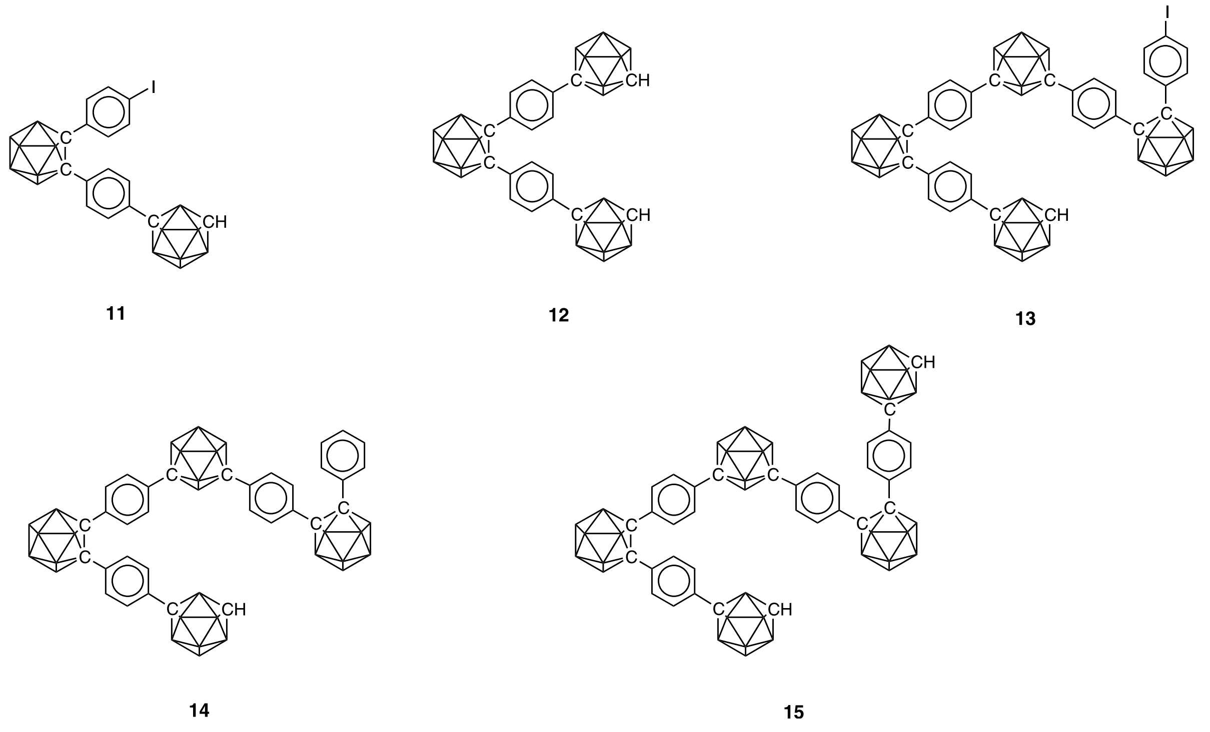
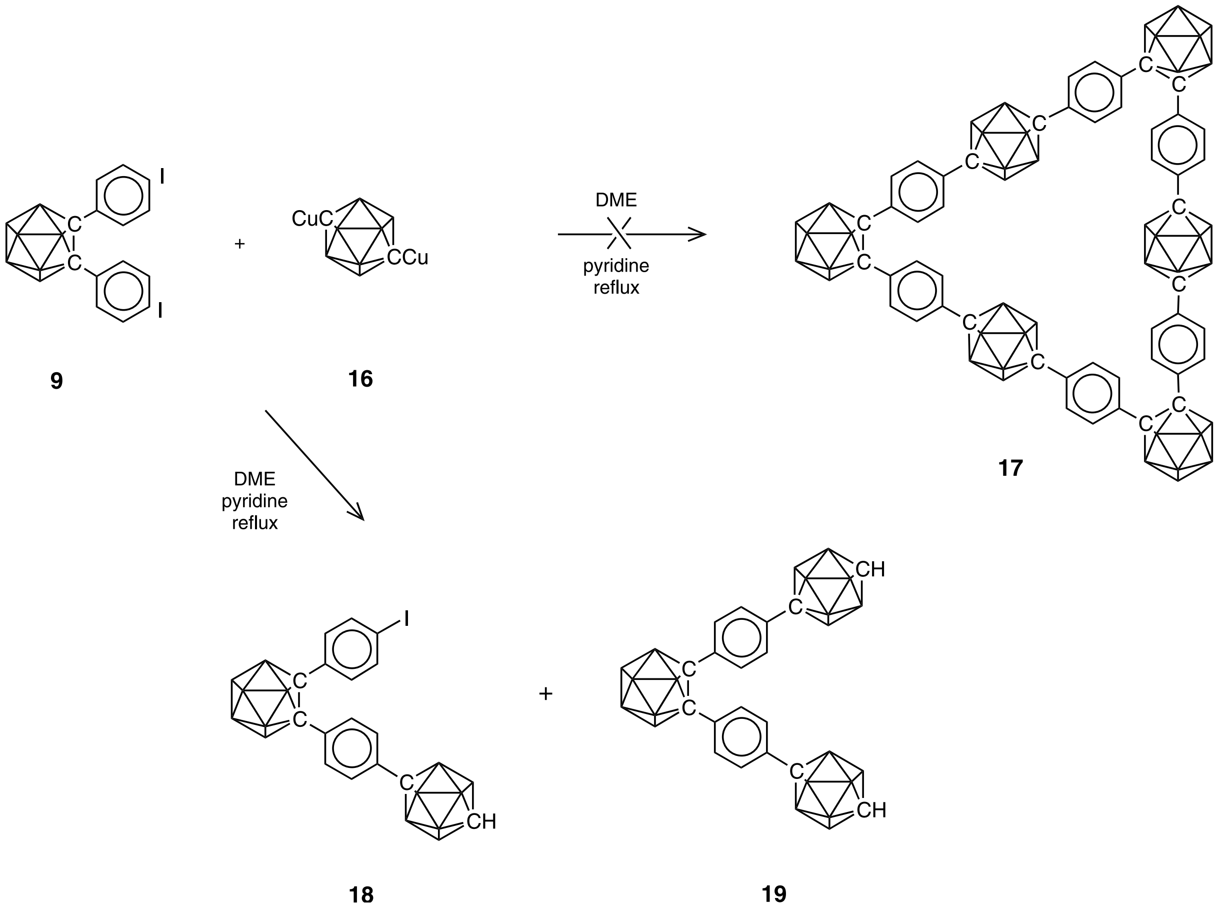


Fig. 2. By-products detected in the synthesis of **5**.



Scheme 2. Attempted synthesis of macrocycle 17, [1,2-$C_2B_{10}H_{10}$-1,4-C_6H_4-1,12-$C_2B_{10}H_{10}$-1,4-C_6H_4]$_3$.

the iodo-compound **18** and the three cage assembly **19** (*para*-carborane analogues of compounds **11** and **12**, respectively).

So far, carborane macrocycles with rigid aromatic links successfully synthesized are limited to those containing *meta*-carborane links (**1**–**3** and **5**) [6–8]. Our unsuccessful attempts in synthesizing macrocycles containing only *ortho*- and/or *para*-carborane and phenylene links here and elsewhere [18,19] suggest that these cycles are unlikely to prove readily accessible.

2.2. Spectroscopic aspects

The proton NMR spectrum of the macrocycle **5** in $CDCl_3$ shows two doublets, with second-order effects, in the aromatic region at 7.26 and 7.17 ppm corresponding to protons adjacent to *ortho*- and *meta*-carborane substituents on the benzene ring. The observed coupling constant of 8.5 Hz is expected for $^3J_{HH}$ couplings in substituted benzenes. The boron-decoupled proton spectrum of **5** shows five lines in the BH region, with intensities of 1:1:6:1:1 while the proton-decoupled boron NMR spectrum of **5** shows three broad peaks of 1:1:8 intensity ratio. Carbon-13-NMR data for **5** reveal six peaks with four in the aromatic region. All these observed NMR data indicate the macrocycle either has planar symmetry (D_{2h}) or apparent D_{2h} symmetry arising from fast equilibrium between two folded conformations via planar symmetry. By comparison with the reported [20] NMR data for 1,2-diphenyl-*ortho*- and 1,7-diphenyl-*meta*-carboranes the peaks corresponding to the cage borons and carbons in the macrocycle are assigned.

However, assignments of the cage proton peaks in the macrocycle here are less straightforward. It has previously been shown for the *meta*-carborane macrocycle **1** that the internal cage protons attached to B2 and B3 resonate at significantly lower field (higher frequency) than those in related diaryl-*meta*-carboranes [6]. This arises from the rigid aryl orientations at the cage carbon atoms in **1** whereas the aryl groups in diaryl-*meta*-carboranes are freely rotating. For the macrocycle **5**, however, the orientations of the aryl groups at the cage carbons of the *meta*-carborane are different from those in **1**. As a result, the internal cage protons attached to B2 and B3 in **5** resonate at significantly higher field (lower frequency) than related diaryl-*meta*-carboranes. Proton NMR shifts calculated from optimized geometries of **1** and **5** at the GIAO-RHF/6-31G*//RHF/6-31G* level are in agreement with the shifts observed for these internal cage protons. Clearly these observations indicate the way cage proton chemical shifts in diaryl-*meta*-carboranes depend on the aryl orientations. Averaged cage proton chemical shifts are observed in aryl carboranes where the aryl groups are freely rotating.

2.3. Structural aspects

The form in which macrocycle **5** crystallised from cyclohexane, as $\mathbf{5}\cdot C_6H_6\cdot 6C_6H_{12}$, proved to have several interesting features, some unexpected. They included the rare space group ($Cmc2_1$, occurrence below 0.2% in the Cambridge Crystallographic Database [21]), the high degree of solvation, the unexpected presence of benzene scavenged as a minor contaminant from the cyclohexane solvent and the spacious packing mode of the cyclohexane molecules.

The butterfly-shaped molecule (Fig. 3) lies on a crystallographic mirror plane, which bisects both *meta*-carborane cages. Thus the asymmetric unit comprises half a molecule of **5**, together with three cyclohexane molecules of crystallisation and, unexpectedly, half a molecule of benzene, which also lies astride the mirror plane. It is noteworthy that benzene was not deliberately introduced at any stage of preparation, but turned out to be present as a trace contaminant of the cyclohexane used for chromatography and recrystallisation. In the crystal, each benzene molecule is 'wedged' into the concave side of the annular cavity of the macrocycle, a cavity too small to accommodate a cyclohexane molecule (Fig. 4).

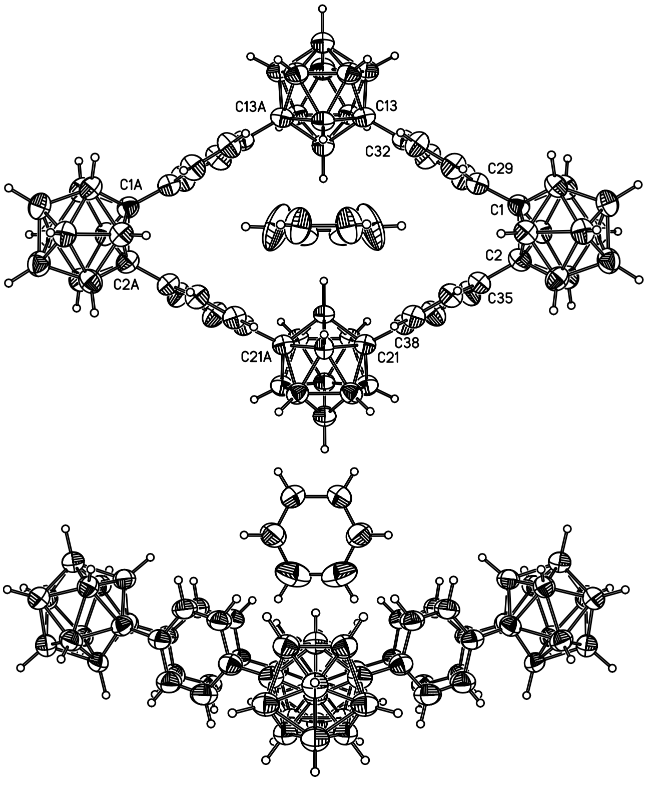


Fig. 3. Molecules of **5** and benzene viewed in the structure of $\mathbf{5}\cdot C_6H_6\cdot 6C_6H_{12}$, showing 30% displacement ellipsoids. Projections on the planes (0 0 1) [top] and (0 1 0) [bottom]. Atoms, symmetrically related via mirror plane, are labelled A. Selected bond distances (Å): C1–C2 1.72(1), C1–C29 1.50(1), C2–C35 1.50(1), C13–C32 1.52(1), C21–C38 1.50(1). Selected bond angles (°): C1–C2-C35 118.9(6), C2–C1–C29 118.4(7).

The $\mathbf{5}\cdot C_6H_6$ units occupy only 39% of the unit cell volume; infinite channels, parallel to the *x*-axis and filled with cyclohexane of crystallisation, account for 51% of the volume. Within these channels, the average volume per cyclohexane molecule (194 $Å^3$) vastly exceeds that in pure crystalline cyclohexane (160 $Å^3$ at 195 K, 140 $Å^3$ at 115 K) [22]. Though spacious, this packing mode leaves no *continuous* residual void, large enough for another solvent molecule, but accounts for the relatively high displacement parameters found, and also explains why the crystals are stable at ambient temperature only under mother liquor, and quickly losing solvent and crystallinity (and some of the observed Bragg's reflections) when exposed to air.

The *para*-phenylene rings lie approximately at right angles to the overall molecular plane, face-to-face as is usual (for steric reasons) for diaryl-*ortho*-carboranes [19,23,24]. Phenyl group orientations in C–aryl-*ortho*-carboranes are usually described by their θ angles, the difference between 90° and the moduli of the cage C–cage C–aryl C–aryl C torsion angles [23]. When θ is 90°, the cage carbons lie in the plane of the phenyl ring but when θ is 0° they lie in a plane perpendicular to the phenyl ring. In macrocycle **5** the θ values are 1.2 and 7.6°, within the values of 0.9–27.6° found for other diaryl-*ortho*-carboranes [23,24], tilting very slightly towards the benzene molecule.

The B–B, B–C and C–C distances in **5** are unexceptional for carborane cage or aryl ring systems [6,8,23–25]. The cage C···C distances in the carborane icosahedra are 1.72 (1) Å in the *ortho*-carborane cages and 2.67 (1) Å in the *meta*-cages.

Although in principle macrocycle **5** might be planar (D_{2h}) without significant bond angle strain, in the

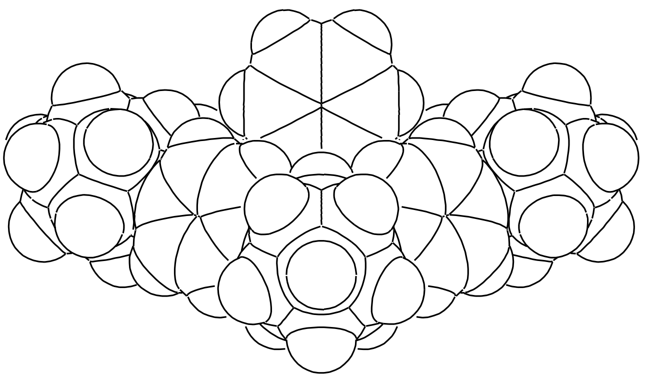


Fig. 4. Space-filling plot of molecules of **5** and benzene. Sphere radii are proportional to the respective van der Waals' radii.

crystal it adopts a butterfly conformation of approximate C_{2v} symmetry, with the *ortho*-carborane moieties at the 'wingtips', and with a dihedral angle between the wing planes of 143° (calculated by the positions of the cage carbons). The phenylene substituents subtend angles (calculated from four cage carbons) of 58.4° at the *ortho*-carborane cages and of 112.4° at the *meta* carborane cages, within the ranges typical for diarylcarboranes [23,25].

To clarify the relation between the butterfly conformation of **5** in the solid state and the apparent D_{2h} symmetry from NMR data, we performed *ab* initio calculations of molecule **5** (Fig. 5). The optimisation of its geometry with an imposed C_{2v} symmetry constraint resulted in a butterfly conformation with the fold (inter-wing) angle of 151.4°, similar to that found in the crystal. The optimisation with a D_{2h} symmetry constraint (i.e. an imposed planarity of the macrocycle) gave the energy only ca. 1 kcal mol^{-1} higher. Thus it is feasible for molecule **5** in solution to undergo rapid inversion between two opposite butterfly conformations over the low potential barrier of the planar structure, in agreement with NMR data.

3. Experimental

Dimethoxyethane was dried by distillation from potassium. Solutions were dried over sodium sulfate and evaporated in vacuum using a rotary evaporator. Copper(I) chloride was purified by the method of Whitesides et al. [26] and stored under nitrogen. Infrared spectra were recorded as KBr discs on a Perkin–Elmer 1600 series FTIR and NMR spectra were measured in $CDCl_3$ solution except where stated using Varian Unity-300 (^1H, ^{11}B, ^{13}C), Bruker AM250 (^1H, ^{13}C) and/or Varian Inova 500 (^1H, ^{11}B) instruments. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^1H-NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm). ^{13}C-NMR spectra were referenced to the solvent resonance ($CDCl_3$ 77.0 ppm). ^{11}B-NMR spectra were referenced externally to $Et_2O.BF_3$, $\delta = 0.0$ ppm. Peak assignments of cage borons, hydrogens and carbons were determined with the aid of selective $^1H\{^{11}B\}$, correlated $^1H-^{13}C$ spectra and comparison with literature values of related aryl carboranes [19,20,27]. Mass spectra were recorded on a VG Micromass 7070E instrument under EI conditions at 70 eV unless otherwise stated.

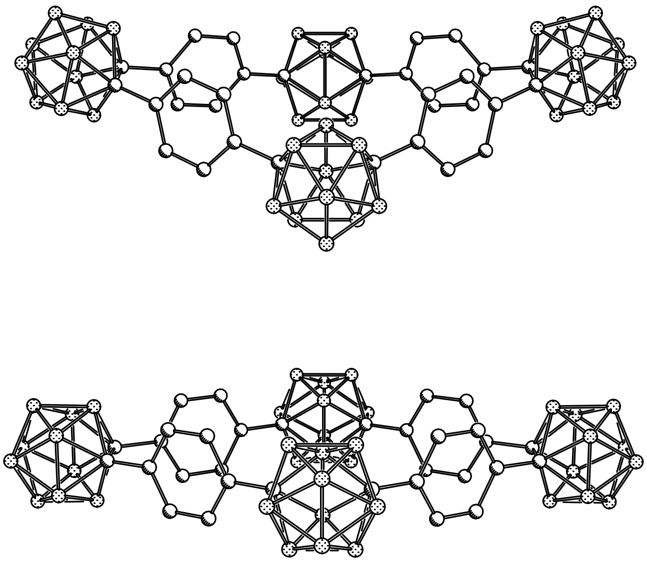


Fig. 5. HF/6-31G* optimized geometries of macrocycle **5**. Top geometry A (C_{2v}) Bottom geometry B (D_{2h}).

All reactions (except diazotisation) were conducted under dry nitrogen. Butyllithium refers to the solution in hexanes of the stated concentration. TLC was conducted on pre-spread silica coated sheet Merck Art. No. 5735. Chromatographic silica refers to Merck Art. No. 9385.

3.1. *Bis-(4-aminophenyl)ethyne 7*

4-Iodoaniline (44.0 g) in diethylamine (100 cm^3) was stirred while a solution, prepared under dinitrogen by warming palladium chloride bis-triphenyl phosphine (153 mg) and copper(I) iodide (54 mg) with piperidine (8 cm^3), was added by syringe. The dinitrogen supply to the flask was replaced by acetylene (admitted above the liquid surface) at ca. 10 cm^3 min^{-1} from a cylinder via a bubbler charged with concentrated sulfuric acid. After 40 h the solid product was filtered off in air, washed with diethylamine (3 × 20 cm^3) and water (2 × 35 cm^3) and dried in vacuum at 78 °C to give a light brown powder (11.5 g, 55%) pure enough for use in the next preparation. A sample recrystallised from ethanol had m.p. 237–240 °C, literature [28] 236 °C.

3.2. *1,2-Bis (4-iodophenyl) ethyne* ***8***

The diamine **7** (11.5 g) was suspended in a warm solution of sulfuric acid (22.0 cm^3) in water (88 cm^3) and cooled in ice to ca. 2 °C. Sodium nitrite (8.2 g) in water (40 cm^3) was added dropwise with stirring, keeping the temperature 4–6 °C, during 45 min. After a further 15 min the turbid solution was added in small portions to a well-stirred solution of potassium iodide (94 g) in water (100 cm^3) contained in a large (e.g. 1.5 l) beaker to accommodate foaming. After 2 h the precipitate was filtered off and washed with water and with dilute sodium bisulfite solution and dried in vacuo at 78 °C to give the slightly impure di-iodo-compound (22.5 g, 95%) as an ochre–yellow powder. Recrystallisation from toluene (380 cm^3) using charcoal gave the pure compound (15.0 g, 63%) m.p. 243–245 °C, literature [29] 238–239 °C.

3.3. 1,2-Bis (4-iodophenyl)-*ortho*-carborane **9**

The di-iodoalkyne 8 (15.0 g) was suspended in toluene (90 cm^3) and decaborane dimethylsulfide complex (12.68 g) was added. The mixture was heated slowly to bath temperature 80–85 °C and after 2 and 4.5 h, nitrogen was streamed through the flask while the upper parts were warmed gently to remove dimethylsulfide released in the reaction. After 22 h, TLC (eluted 2.5% v/v ethyl acetate in cyclohexane) showed that a small proportion of the di-iodoalkyne (R_{f} 0.80) remained; a further quantity (1.22 g) of the decaborane complex was added and heating was continued for a further 26 h. The solvent was removed in vacuum and the cooled residue was treated with methanol (100 cm^3) in portions and heated cautiously to reflux when the initial effervescence had subsided. After 17 h, the solid was separated from the cooled solution and washed with methanol to give the almost pure carborane **9** (11.97 g, 58%) as a pale yellow powder m.p. 215–216.5 °C, literature [16] 214–216 °C. This was unchanged by dissolution in warm benzene (40 cm^3), decantation to remove a little insoluble matter and dilution with warm ethanol (60 cm^3); recovery from the cooled solution was almost quantitative. δ $^{1}\mathrm{H}\{^{11}\mathrm{B}\}$: 7.51 (2H, d, 8.5, C*H* next to I in C_6H_4I), 7.14 (2H, d, 8.5, C*H* next to cage in C_6H_4I), 3.15 (2H, B3,6H), 2.55 (2H, B3,6H), 2.48 (4H, B4,5,7,11H), 2.36 (2H, B8,10H). δ $^{11}\mathrm{B}\{^{1}\mathrm{H}\}$; −2.5 (2B, B9,12), −9.2 (4B, B4,5,7,11), −10.5 (2B, B8,10), −11.5 (2B, B3,6). δ $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$: 137.7 (*C*H next to I), 132.0 (*C*H next to cage), 130.2 (aryl C next to cage), 97.5 (*C*I), 84.2 (cage C).

3.4. The macrocycle **5**

A solution of *meta*-carborane (1.44 g; 10 mmol) in 1,2-dimethoxyethane (80 cm^3) was stirred at room temperature (r.t.) and butyllithium (9.0 cm^3, 2.71 M in hexanes; 24.4 mmol) was added. After 5 min pyridine (6.0 cm^3) was added to the warm turbid solution, which became yellow. This was followed after a further 5 min by copper(I) chloride (3.12 g; 31.5 mmol). The mixture, which soon turned black, was stirred at r.t. for 1 h, heated to 60 °C for 15 min and 1,2-bis(4-iodophenyl)-*ortho*-carborane **9** (5.45 g; 9.9 mmol) was added. The solution, which turned dark red, was heated under reflux for 12 days, cooled, and diluted with ether (400 cm^3). After standing for 24 h the precipitate was separated and the solution was washed with dilute hydrochloric acid (200 cm^3, 2 M) and water (4 × 500 cm^3), dried and evaporated. The residue was warmed with cyclohexane containing 1% v/v of ethyl acetate (30 cm^3), insoluble material (376 mg) was separated and the solution was applied to a column of chromatographic silica (120 g) and eluted with the same solvent in fractions of 25 cm^3. Fractions were examined by TLC on silica using 2.5% v/v ethyl acetate in cyclohexane; nos 12 and 13 contained mainly the starting di-iodocompound (R_{f} 0.75). Fractions 15 and 16 (R_{f} 0.55) were set aside and fractions 19–29 (R_{f} 0.6 with an impurity R_{f} 0.45) were combined and evaporated and the residue (530 mg containing ca. 70% of the macrocycle by comparison (IR, TLC) with the purified compound, corresponding with ca. 9% yield) was twice recrystallised from cyclohexane to give small well-formed colourless solvated crystals of macrocycle **5** (17 mg) which tend to lose cyclohexane at r.t. A further recrystallisation from cyclohexane with slow cooling in a Dewar of hot water gave crystals suitable for X-ray crystallography. Found: C, 59.30; H, 9.46; $C_{32}H_{56}B_{40}\cdot C_6H_6\cdot 6C_6H_{12}$ requires: C, 61.03; H, 9.27 ($C_{32}H_{56}B_{40}\cdot C_6H_6\cdot 5C_6H_{12}$ requires: C, 59.53; H, 8.96%). ν_{max}: 2925 s, 2849 (cyclohexane CH); 2601 vs (BH); 1654 w, 1620 w, 1512 (Ar skel.); 1458, 1449 (cyclohexane CH bend); 1260; 1090; 848 (*p*-phenylene o.o.p. bend); 730 (carborane skel.); 588; 501. δ $^{1}\mathrm{H}\{^{11}\mathrm{B}\}$ 7.26 (d, 8.6 Hz, aryl CH), 7.17 (d, 8.6 Hz, aryl CH), 3.11 (2H, s, B3,6H *ortho* cage), 2.75 (2H, BH), 2.50 (12H, BH), 2.35 (2H, BH), 2.29 (2H, B5,12H *meta* cage). δ $^{11}\mathrm{B}\{^{1}\mathrm{H}\}$ −1.6 (2B, B9,12 *ortho* cage), −5.0 (2B, B5,12 *meta* cage), −9.7 (16B). δ $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$: 137.0 (aryl C next to *meta*-cage); 131.0 (aryl C next to *ortho*-cage), 130.6 (aryl *C*H next to *ortho*-cage), 127.6 (aryl *C*H next to *meta*-carborane), 83.7 (*ortho*-cage C), 77.0 (*meta*-cage C resolved within the solvent triplet; in $C_2D_2Cl_4$ this resonance is unobscured at 76.9 ppm) MS (EI, DCI): 850–875, 872.55 and 873.57 12.8%: [M^{+}]; 564–586, 580.39 100%, $C_{18}H_{40}B_{30}^{+}$; 426–441, 435.23 38.8% $C_{10}H_{29}B_{20}^{+}$ and 433.14–435.23 (5 peaks) $C_{32}H_{56}B_{40}^{2+}$ (M^{2+}); 278.10–291.67 (28 peaks) $C_{18}H_{40}B_{30}^{2+}$. No m.p. was observed in a glass capillary up to 360 °C and DSC of a solvated sample sealed in air showed multiple endothermic peaks between 60 and 95° (desolvation) but no melting endotherm before onset of an exothermic reaction at 450 °C.

Fractions 15 and 16 were combined and extracted, after evaporation, with hot propan-2-ol (ca. 10 cm^3) with separation of insoluble matter. The solution was re-filtered after cooling to r.t. and allowed to evaporate spontaneously to ca. 3 cm^3 with formation of a gelatinous white precipitate which was washed with the same solvent and dried in vacuum at r.t. to give the iodo-compound 11 (250 mg, 4.4%). Found: C, 33.8; H, 5.24; $C_{16}H_{29}B_{20}I$ requires: C, 34.0; H, 5.18%. ν_{max}: 3060 (carborane CH); 2599 vs (BH); 1579, 1511, 1486 (Ar skel.); 1406; 1391; 1084; 1008; 880; 865; 852 and 830 (*p*-phenylene o.o.p. bend); 728 (carborane skel.) 585; 494. δ $^{1}\mathrm{H}\{^{11}\mathrm{B}\}$: 7.49 (2H, d, 8.5, C*H* next to I in C_6H_4I), 7.29 (2H, d, 8.6, C*H* next to *meta* cage in cage-C_6H_4-cage), 7.21 (2H, d, 8.6, C*H* next to *ortho* cage in cage-C_6H_4-

cage), 7.09 (2H, d, 8.5, C*H* next to cage in C_6H_4I), 3.12 (2H, B3,6H *ortho* cage), 3.05 (1H, CH *meta* cage), 2.86 (2H, B2,3H *meta* cage), 2.52 (3H, BH), 2.47 (5H, BH), 2.34 (4H, BH), 2.26 (2H, B8,11H, *meta* cage), 2.19 (2H, B4,6H, *meta* cage). δ $^{11}B\{^{1}H\}$; −2.1 (2B, B9,12 *ortho* cage), −4.0 (1B, B5 *meta* cage), −10.3 (13B), −13.2 (2B, B8,11 *meta* cage), −15.2 (2B, B2,3 *meta* cage). δ $^{13}C\{^{1}H\}$ 137.6 (CH next to I in C_6H_4I), 137.3 (aryl C next to *meta* cage), 132.0 (CH next to cage in C_6H_4I), 131.0 (aryl C next to *ortho* cage in cage-C_6H_4-cage), 130.5 (*C*H next to *ortho* cage in cage-C_6H_4-cage), 130.2 (aryl C next to cage in C_6H_4I), 127.8 (aryl *C*H next to *meta* cage), 97.3 (CI), 84.2 (*ortho* cage C next to C_6H_4I), 83.8 (*ortho* cage C), 77.0 (*meta* cage C), 55.2 (*meta* cage *C*H). MS: [RMM of $C_{16}H_{29}B_{20}I$ 564.51] 559–558, 565.10. 47.9%, [M^{+}].

Mass spectra of the latter (some incompletely separated) fractions showed ions of masses: 552–586, strongest 580.60, $C_{18}H_{40}B_{30}^{+}$ (compound **12** [RMM of $C_{18}H_{40}B_{30}$ 580.83]), 986–1013, strongest 1000.80, $C_{32}H_{57}B_{40}I^{+}$ (compound **13** [RMM of $C_{32}H_{57}B_{40}I$ 1001.11]), 859–880 strongest 875.59, $C_{32}H_{58}B_{40}^{+}$ (compound **14** [RMM of $C_{18}H_{40}B_{30}$ 875.21]) and 996–1023, strongest 1016.31, $C_{34}H_{68}B_{50}^{+}$ (compound **15** [RMM of $C_{34}H_{68}B_{50}$ 1017.41]).

3.5. *Attempted synthesis of macrocycle* ***17***

A solution of *para*-carborane (1.52 g; 10.5 mmol) in 1,2-dimethoxyethane (80 cm^3) was stirred at r.t. and butyllithium (9.0 cm^3, 2.71 M in hexanes; 24.4 mmol) was added. After 5 min pyridine (6.0 cm^3) was added to the warm turbid solution, which became yellow. This was followed after a further 5 min by copper(I) chloride (2.50 g; 25 mmol). The mixture, which soon turned black, was stirred at r.t. for 1 h, heated to 60 °C for 15 min and 1,2-bis(4-iodophenyl)-*ortho*-carborane **9** (6.06 g; 11 mmol) was added. The solution, which turned pink with a white precipitate, was heated under reflux for 3 days, cooled, and diluted with ether (200 cm^3). After standing for 20 h the precipitate was filtered and the solution was washed with dilute hydrochloric acid (200 cm^3, 2 M) and water (3×250 cm^3), dried and evaporated. The glassy residue was warmed with cyclohexane containing 2% v/v of ethyl acetate (30 cm^3) and the solution was applied to a column of chromatographic silica (90 g) and eluted with the same solvent in fractions of 38 cm^3. Fractions were examined by TLC on silica using 2% v/v ethyl acetate in cyclohexane; fraction 8 contained crude iodo-compound 18 (R_f 0.60, 116 mg, 2%). ν_{max}: 3054 (carborane CH); 2609 vs (BH); 1582, 1511, 1487 (Ar skel.); 1405; 1392; 1091; 1008; 889; 854 and 830 (*p*-phenylene o.o.p. bend); 729 (carborane skel.); 668; 587; 493. MS: [RMM of $C_{16}H_{29}B_{20}I$ 564.51] 559–568, 563.77 (100%, [M^{+}]).

Fractions nos 5, 6 and 7 contained mainly the three-cage compound **19** (R_f 0.70, 97 mg, 1.5%) ν_{max}: 3067 (carborane CH); 2610 vs (BH); 1511 (Ar skel.); 1405; 1091; 1009; 887; 855 (*p*-phenylene o.o.p. bend); 738 (carborane skel.); 589; 505. MS: [RMM of $C_{18}H_{40}B_{30}$ 580.83] 573–586, 580.28 (100%, [M^{+}]).

3.6. *X-ray structure determination*

Single crystals of the $\mathbf{5}\cdot C_6H_6\cdot 6C_6H_{12}$ composition were grown from cyclohexane, which contained 6 mg l^{-1} of benzene (from UV). The X-ray diffraction experiment $T = 150$ K was carried out at on a Bruker SMART 3-circle diffractometer with a 1 K CCD area detector, using graphite monochromated Mo–K_{α} radiation ($\bar{\lambda} = 0.71073$ Å) and a Cryostream open-flow N_2 cryostat [30]. Crystal data: $C_{32}H_{66}B_{40}\cdot C_6H_6\cdot 6C_6H_{12}$, M = 1456.21, orthorhombic, space group $Cmc2_1$ (no. 36), $a = 33.018(10)$, $b = 22.574(6)$, $c = 12.266(3)$ Å, $U = 9142(4)$ Å^3, $Z = 4$, $D_{calc} = 1.058$ g cm^{-3}, $\mu = 0.05$ mm^{-1}. Over a hemisphere of the reciprocal space was scanned by 4 series of narrow ω-scans (0.3°), each series at different φ and/or 2θ angle settings. Intensities of 32 922 reflections (including 5572 symmetrically independent ones and 4651 of their Friedel equivalents, $R_{int} = 0.158$) were integrated using SAINT program [31]. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL software [32]. The refinement of 526 parameters (non-H atoms in anisotropic approximation, all H atoms in 'riding' model) converged at $R = 0.081$ [on 1762 unique reflections with $F^2 > 2\sigma(F^2)$], $wR(F^2) = 0.289$ (all data). Crystal packing was analysed using PLATON programs [33].

3.7. *Computations*

All *ab* initio computations were carried out with the GAUSSIAN 94 or 98 packages [34,35]. The two geometries of macrocycle **5** were optimized at the HF/3-21G level then at the HF/6-31G* level with the relevant symmetry constraints, C_{2v} for A and D_{2h} for B. Absolute energies (au) at HF/6-31G* are −2232.02768 and −2232.02604 for A and B, respectively. The geometry of macrocycle **1** was fully optimized without symmetry constraints at the HF/6-31G* level (absolute energy of −1674.06199 au). Theoretical ^{11}H chemical shifts were referenced to TMS with the conversion δ (^{11}H) = $32.78 - \sigma(^{11}H)$ at the RHF/6-31G*//RHF/6-31G* level.

Calculated proton NMR data (GIAO-RHF/6-31G*//RHF/6-31G*) for geometry A (C_{2v}) of macrocycle **5**: 7.49 (aryl CH next to *ortho* cage), 7.20 (aryl CH), 3.37 (B3,6H, *ortho* cage), 2.97 (B9,12H, *ortho* cage), 2.84 (B5,12H, *meta* cage), 2.77 (B2,3H, *meta* cage), 2.76 (B4,6,8,11H, *meta* cage), 2.61 (B4,5,7,11H, *ortho* cage), 2.59 (B8,10H, *ortho* cage), 2.50 (B9,10H, *meta* cage). Similar shifts were obtained for geometry B, D_{2h}.

Calculated proton NMR data (GIAO-RHF/6-31G*//RHF/6-31G*) for optimized geometry of macrocycle **1**: 8.29 (aryl CH inward pointing), 7.44 (2H, aryl CH), 7.28 (1H, aryl CH), 3.80 (B2,3H), 3.28 (B5,12H), 2.78 (B4,6,8,11H), 2.59 (B9,10H). Observed for **1** in $CDCl_3$: 8.14 (aryl CH inward pointing), 7.34 (2H, aryl CH), 7.21 (1H, aryl CH), 3.59 (B2,3H), 2.87 (2H, BH), 2.54 (4H, B4,6,8,11H), 2.37 (2H, BH).

4. Supplementary material

Crystallographic data for $\mathbf{5}\cdot C_6H_6\cdot 6C_6H_{12}$ have been deposited with the Cambridge Crystallographic Data Centre, Dep. no. CCDC 204970. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank EPSRC for an Advanced Research Fellowship (M.A.F., AF/98/2454) and Dr A.S. Batsanov for helpful discussions on X-ray crystallography.

References

[1] (a) X. Yang, C.B. Knobler, M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 30 (1991) 1507;
(b) X. Yang, S.E. Johnson, S.I. Khan, M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 31 (1992) 893;
(c) X. Yang, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 114 (1992) 380;
(d) X. Yang, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 115 (1993) 4904;
(e) Z. Zheng, X. Yang, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 115 (1993) 5320;
(f) X. Yang, C.B. Knobler, Z. Zheng, M.F. Hawthorne, J. Am. Chem. Soc. 116 (1994) 7142;
(g) M.F. Hawthorne, X. Yang, Z. Zheng, Pure Appl. Chem. 66 (1994) 245;
(h) M.F. Hawthorne, in: G. Kabalka (Ed.), Current Topics in the Chemistry of Boron, The Royal Society of Chemistry, 1994, p. 207;
(i) A.A. Zinn, Z. Zheng, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 118 (1996) 70;
(j) Z. Zheng, C.B. Knobler, M.D. Mortimer, G. Kong, M.F. Hawthorne, Inorg. Chem. 35 (1996) 1235;
(k) M.F. Hawthorne, Z. Zheng, Accounds Chem. Res. 30 (1997) 267;
(l) H. Lee, M. Diaz, M.F. Hawthorne, Tetrahedron Lett. 40 (1999) 7651;
(m) H. Lee, M. Diaz, C.B. Knobler, M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 39 (2000) 776;
(n) I.H.A. Badr, R.D. Johnson, M. Diaz, M.F. Hawthorne, L.G. Bachas, Anal. Chem. 72 (2000) 4249;
(o) I.H.A. Badr, M. Diaz, M.F. Hawthorne, L.G. Bachas, Anal. Chem. 71 (1999) 1371;
(p) H. Lee, C.B. Knobler, M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 40 (2001) 2124;
(q) H. Lee, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 123 (2001) 8543.

[2] Z. Zheng, C.B. Knobler, C.E. Curtis, M.F. Hawthorne, Inorg. Chem. 34 (1995) 432.

[3] C. Songkram, R. Yamasaki, A. Tanatani, K. Takaishi, K. Yamaguchi, H. Kagechika, Y. Endo, Tetrahedron Lett. 42 (2001) 5913.

[4] R.N. Grimes, Angew. Chem. Int. Ed. Engl. 32 (1993) 1289.

[5] (a) M.F. Hawthorne, in: W. Siebert (Ed.), Advances in Boron Chemistry, The Royal Society of Chemistry, 1997, p. 261;
(b) M.F. Hawthorne, in: M.G. Davidson, A.K. Hughes, T.B. Marder, K. Wade (Eds.), Contemporary Boron Chemistry, The Royal Society of Chemistry, 2000, p. 197.

[6] W. Clegg, W.R. Gill, J.A.H. MacBride, K. Wade, Angew. Chem. Int. Ed. Engl. 32 (1993) 1328.

[7] W.R. Gill, P.L. Herbertson, J.A.H. MacBride, K. Wade, J. Organomet. Chem. 507 (1996) 249.

[8] H.M. Colquhoun, D.F. Lewis, P.L. Herbertson, K. Wade, I. Baxter, D.J. Williams, in: M.G. Davidson, A.K. Hughes, T.B. Marder, K. Wade (Eds.), Contemporary Boron Chemistry, The Royal Society of Chemistry, 2000, p. 59.

[9] (a) I.T. Chizhevsky, S.E. Johnson, C.B. Knobler, F.A. Gomez, M.F. Hawthorne, J. Am. Chem. Soc. 115 (1993) 6981;
(b) W. Jiang, I.T. Chizhevsky, M.D. Mortimer, W. Chen, C.B. Knobler, S.E. Johnson, F.A. Gomez, M.F. Hawthorne, Inorg. Chem. 35 (1996) 5417.

[10] (a) H. Yao, M. Sabat, R.N. Grimes, F. Fabrizi de Biani, P. Zanello, Angew. Chem. Int. Ed. Engl. 42 (2003) 1002;
(b) X. Meng, M. Sabat, R.N. Grimes, J. Am. Chem. Soc. 115 (1993) 6143;
(c) K.G. Parker, J.M. Russell, M. Sabat, R.N. Grimes, Collect. Czech. Chem. Commun. 64 (1999) 819.

[11] H. Irngartinger, L. Leiserowitz, G.M.J. Schmidt, Chem. Ber. 103 (1970) 1132.

[12] P.v.R. Schleyer, K. Najafian, Inorg. Chem. 37 (1998) 3454.

[13] (a) K. Wade, M.G. Davidson, M.A. Fox, W.R. Gill, T.G. Hibbert, J.A.H. MacBride, Phosphorus Sulfur Silicon 125 (1997) 73;
(b) L.A. Boyd, H.M. Colquhoun, M.G. Davidson, M.A. Fox, W.R. Gill, P.L. Herbertson, T.G. Hibbert, J.A.H. MacBride, R.J. Peace, G.P. Rivers, K. Wade, in: W. Siebert (Ed.), Advances in Boron Chemistry, The Royal Society of Chemistry, 1997, p. 289.

[14] R. Coult, M.A. Fox, W.R. Gill, P.L. Herbertson, J.A.H. MacBride, K. Wade, J. Organomet. Chem. 462 (1993) 19.

[15] M.A. Fox, J.A.H. MacBride, R.J. Peace, K. Wade, J. Chem. Soc., Dalton Trans. (1998) 401.

[16] A.I. Kovredov, Z.S. Shaugumbekova, A.V. Kazantsev, L.I. Zakharkin, J. Gen. Chem. USSR (Engl. Transl.) (1979) 1364.

[17] A.N. Novikov, M.G. Grigor'ev, V.N. Kalinin, N.I. Kobel'kova, E.S. Krongauz, A.P. Travnikova, J. Gen. Chem. USSR (Engl. Transl.) (1979) 1861.

[18] E.S. Alekseyeva, A.S. Batsanov, L.A. Boyd, M.A. Fox, T.G. Hibbert, J.A.K. Howard, J.A.H. MacBride, A. Mackinnon, K. Wade, Dalton Trans. (2003) 475.

[19] E.S. Alekseyeva, M.A. Fox, J.A.K. Howard, J.A.H. MacBride, K. Wade, Appl. Organometal. Chem. 17 (2003) 499.

[20] M.A. Fox, K. Wade, Polyhedron 16 (1997) 2517.

[21] Version 5.24, November 2002. See: F.H. Allen, Acta Crystallogr. Sect. A 54 (1998) 758.

[22] R. Kahn, R. Fourme, D. Andre, M. Renaud, Acta Crystallogr. Sect. B 29 (1973) 131.

[23] Z.G. Lewis, A.J. Welch, Acta Crystallogr. Sect. C 49 (1993) 705.

[24] (a) D.M. Murphy, D.M.P. Mingos, J.L. Haggitt, H.R. Powell, S.A. Westcott, T.B. Marder, N.J. Taylor, D.R. Kanis, J. Mater. Chem. 3 (1993) 139;
(b) T.D. McGrath, M.A. Fox, A.J. Welch, Acta Crystallogr. Sect. C 56 (2000) 487;
(c) R.L. Thomas, A.J. Welch, Acta Crystallogr. Sect. C 52 (1996) 1689;
(d) R.L. Thomas, A.J. Welch, Polyhedron 18 (1999) 1961;
(e) S.V. Lindemann, I.A. Khotina, M.M. Teplyakov, Y.T. Struchkov, V.V. Korshak, Makromol. Chem. 189 (1988) 471.

[25] G.M. Rosair, A.J. Welch, A.S. Weller, Acta. Crystallogr. Sect. C 52 (1996) 2221.

[26] G.M. Whitesides, J.S. Sadowski, J. Lilburn, J. Am. Chem. Soc. 96 (1974) 2829.

[27] M.A. Fox, J.A.H. MacBride, K. Wade, Polyhedron 16 (1997) 2499.

[28] (a) P. Ruggli, F. Lang, Helvetica Chim. Acta 21 (1938) 38;
(b) A.J. Deeming, G. Hogarth, M. Lee, M. Saha, S.P. Redmond, H. Phetmung, A.G. Orpen, Inorg. Chim. Acta 309 (2000) 109.

[29] A.L. Rusanov, M.L. Keshtov, N.M. Belomoina, High Perform. Polym. 13 (2001) S153.

[30] J. Cosier, A.M. Glazer, J. Appl. Crystallogr. 19 (1986) 105.

[31] SMART and SAINT, Version 4.050, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1995.

[32] SHELXTL, Version 5.10. Bruker AXS, Madison, Wisconsin, USA.

[33] A.L. Speck, PLATON for WINDOWS, University of Utrecht, The Netherlands, 1999.

[34] GAUSSIAN 94, Revision E.2, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

[35] GAUSSIAN 98, Revision A.9, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.