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Synthesis and crystal structure of an assembly of three *ortho*-carborane cages linked via *para*-phenylene units: effect of aryl orientation on cage C–C bond lengths in *C*-aryl-*ortho*-carboranes†

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The synthesis and crystal and molecular structure are described of $(C_2B_{10}H_{11})C_6H_4(C_2B_{10}H_{10})C_6H_4(C_2B_{10}H_{11})$ (4), an acyclic assembly of three *ortho*-carborane units connected through their carbon atoms by two *para*-phenylene units. For this compound, and published structures of other aryl-*ortho*-carboranes, correlations are noted between the orientations of aryl substituents and cage carbon–carbon distances (C1–C2). *Ab initio* RHF/6-31G* and MP2/6-31G* studies on 1-phenyl-*ortho*-carborane, $PhC_2B_{10}H_{11}$, and other model systems have been used to explore the variations in their energies, C1–C2 bond lengths, and C2–C1–C_{aryl} bond angles with the orientation of their aryl groups, variations believed to reflect weak interactions between the aryl substituents' π systems and the carborane cages. The synthesis of a pentafluorophenyl derivative of 4, $(C_2B_{10}H_{11})C_6H_4(C_2B_{10}H_{10})C_6H_4(C_2B_{10}H_{10})C_6F_5$, is also described. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: carborane; cluster; *ab initio* computations; π-bonding; boron

INTRODUCTION

This paper illustrates the subtle but significant relationships that exist between the cage geometries of *ortho*-carboranes and the orientations of their aryl substituents in mono- and di-aryl derivatives, 1-aryl-1,2-$C_2B_{10}H_{11}$ and 1-aryl′-2-aryl″-1,2-$C_2B_{10}H_{10}$. We focus in our discussion on the compounds shown in Fig. 1. Three compounds, **1**, **2** and **3**, are known species whose structures have previously been determined.[1–4] Here, we report new MP2/6-31G* computational studies on **1**, on 1-(*p*ara-fluorophenyl)-*ortho*-carborane, and on **3**. Compound **4** is new; its synthesis and structure are reported here for the first time.

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†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

Although scores of *C*-monoaryl-*ortho*-carboranes are now known[5–12] well-defined crystal and molecular structures have been reported for only two of them, 1-phenyl-*ortho*-carborane (**1**) and compound **2**, a bis(carboranyl)biphenyl.[1–3] The lack of reliable structural information on other *C*-monoaryl-*ortho*-carboranes is due to disorder problems.[13,14] The unsubstituted CH unit and four B–H units attached to the aryl-substituted cage carbon atom may randomly occupy the five available sites unless 'locked' in particular sites by intermolecular C–H···H–B or related intermolecular interactions;[15–21] the intramolecular energy differences between aryl ring orientations are small, as we shall show. No such disorder problems are found with *C*-aryl-*C*′-substituted-*ortho*-carboranes where both carbon atoms bear substituents other than hydrogen; the sites occupied by the carbon atoms are identified by the substituents, and over 30 such systems have been structurally characterized, e.g. see Refs 22–31.

In our discussion of aryl substituent orientations, we shall use the convention established by Lewis and Welch,[4] who have discussed the aryl group orientation in 1-phenyl-*ortho*-carborane and related carboranes in terms of their θ angle

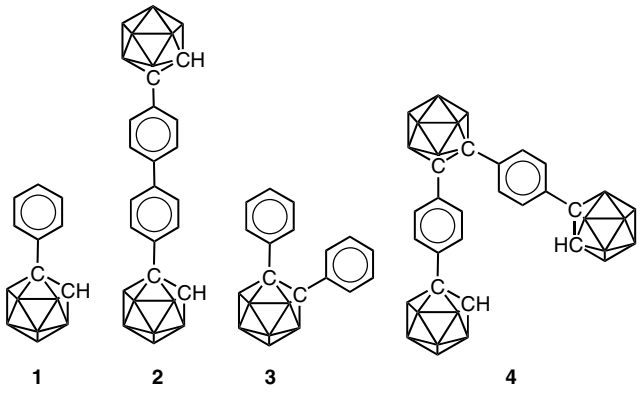


Figure 1. Aryl carboranes **1**–**4** discussed in this study.

values, the differences between 90° and the moduli of the cage C–cage C–C–C torsional angles (Fig. 2). Thus, for 1-phenyl-*ortho*-carborane **1**, $\theta = 90°$ when the cage carbon atoms C1 and C2 lie in the same plane as the aryl ring, but $\theta = 0°$ when they lie in a plane perpendicular to the ring plane.

Welch and co-workers[1,2] have established the molecular structures of two slightly different conformations of compound **1** by crystallographic studies on two distinct crystalline forms, having $\theta = 68.8(2)°$ and 71.7(4)° respectively, and have shown by *ab initio* computational studies at the HF/6-31G* level that there was an energy difference of only 0.3 kcal mol^{-1} between geometries with $\theta = 65°$ (calculated to be the preferred orientation) and $\theta = 0°$. Close intermolecular CH···HB contacts[32] were found in the crystals that apparently anchored the CH units in the preferred sites. In the crystal of compound **2**, arene interactions[15,16] between cage CH units and solvent (benzene) molecules in the crystal apparently helped fix the CH sites.

Further earlier studies have drawn attention to the potential for conjugation between an aryl substituent and the cage carbon–carbon bond in *ortho*-carborane, for strengthening of the exo C_{cage}–C_{aryl} bond as a result of such conjugative effects, and for aryl–aryl repulsive effects in 1,2-diaryl-*ortho*-carboranes $aryl_2C_2B_{10}H_{10}$ that might lead to C_{cage}–C_{cage} bond lengthening in these systems compared with monoaryl carboranes 1-aryl-1,2-$C_2B_{10}H_{11}$.[4] To shed further light on these issues, we decided to carry out a computational study

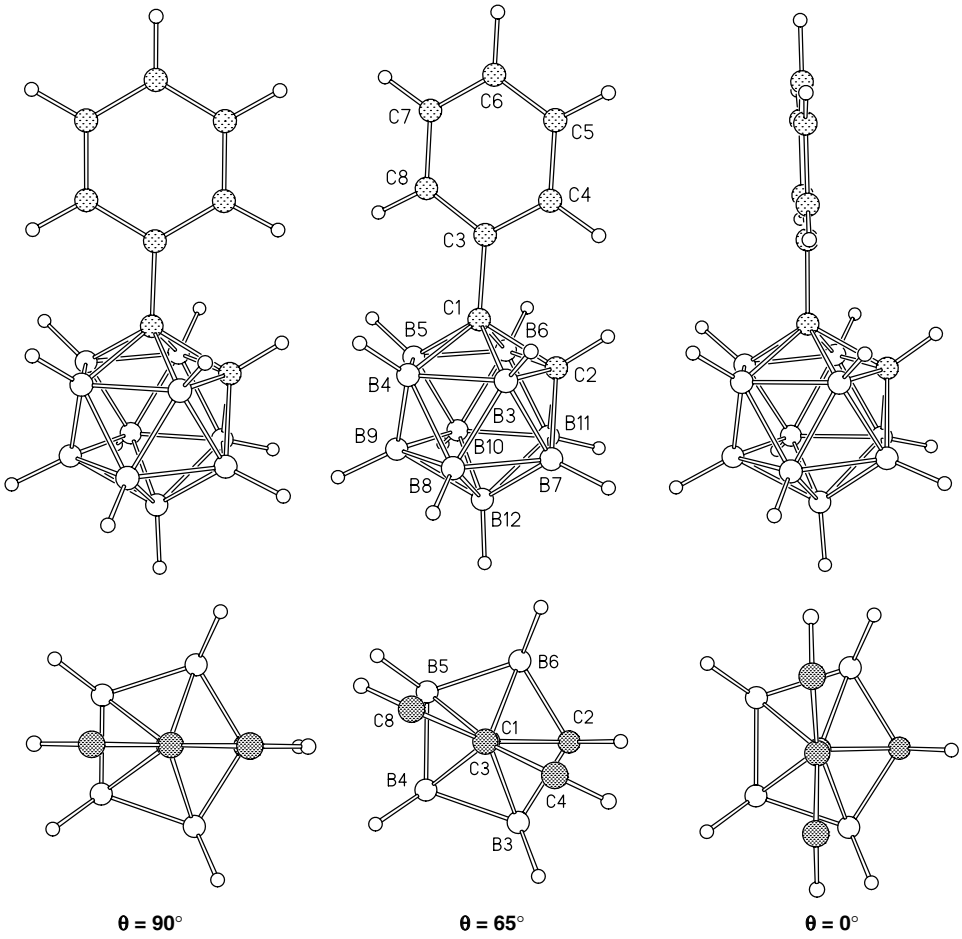


Figure 2. Side and plan views along the C1–C3 bond of different phenyl group orientations in 1-phenyl-*ortho*-carborane **1**.

of compound **1** to explore how the energy and structure (notably the cage C1–C2 bond length) varied with the aryl group orientation angle θ, and to establish the structure of compound **4**, which we had prepared as an intermediate in a programme aimed at the preparation of acyclic and macrocyclic assemblies of carboranes.

RESULTS AND DISCUSSION

Synthesis of 4 and its pentafluorophenyl derivative

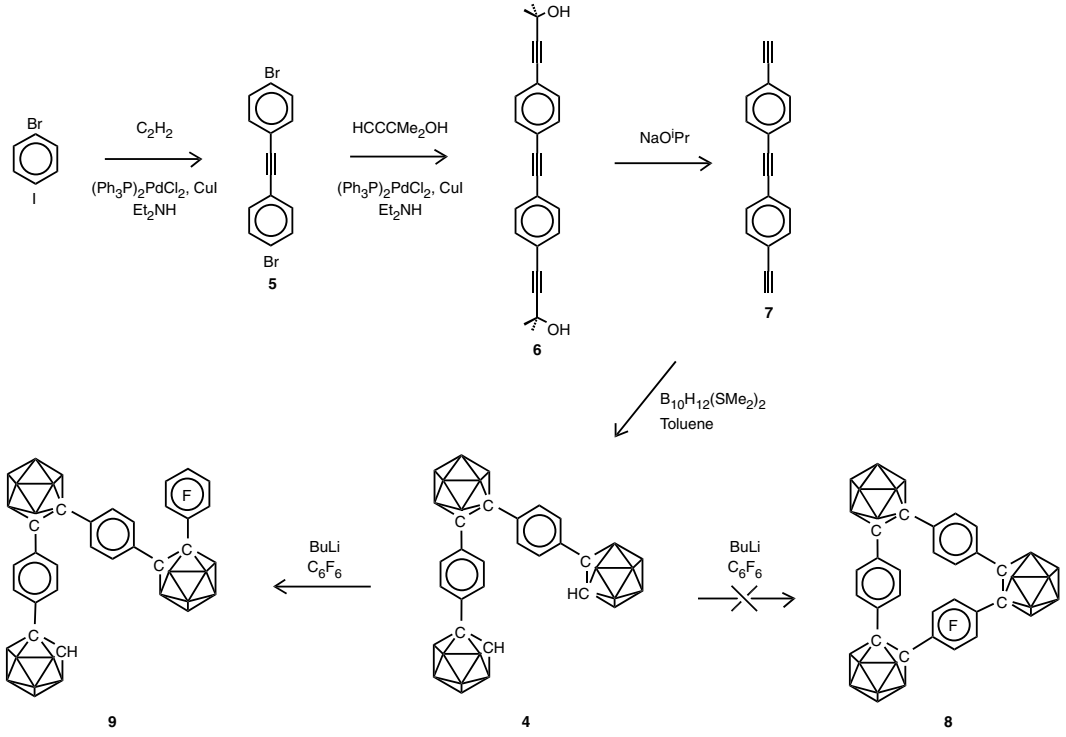
The four-step procedure used to synthesize compound **4**, 1,2-bis(4-*ortho*-carboranylphenyl)-*ortho*-carborane from *p*-bromo,iodobenzene via the alkynes **5**–**7**, is shown in Scheme 1. Reaction of the tri-yne **7**[33] with the decaborane-dimethylsulfide adduct gave compound **4** in 38% yield. The tricarborane **4** was fully characterized by elemental analyses, multinuclear magnetic resonance, infrared (IR) and mass spectroscopy. Solvated crystals of compound **4**, as the adduct **4**·NCMe, were obtained from acetonitrile and structurally characterized by X-ray diffraction.

An attempt was made to convert **4** into the macrocycle **8** (Scheme 1) by successive reaction of **4** with butyllithium and hexafluorobenzene (hexafluorobenzene is known to react with the lithio derivative of phenyl-*ortho*-carborane **1** to form a two-cage product in which two phenyl-*ortho*-carboranyl units are linked by a *para*-tetrafluorophenylene unit).[34,35] The product obtained was the acyclic compound **9**, the first known pentafluorophenyl derivative of *ortho*-carborane.[36] Thus, we were unsuccessful in this attempt to add another macrocyclic assembly of two or three carboranes linked through phenylene units to those derived from *meta*-carborane that we have described elsewhere.[37–39]

Structure of the acetonitrile adduct of compound 4

Suitable crystals of **4** for X-ray crystallographic study were grown from acetonitrile solution, and shown to be the 1 : 1 acetonitrile adduct **4**·NCMe, the molecular structure of which is illustrated in Fig. 3. The acetonitrile molecule participates in N···H–C hydrogen bonding[40–42] (N···C distance 3.31(1) Å) to the C–H unit (C2B–H2B in Fig. 3) of one of the two terminal *ortho*-carboranyl units, but not the other, whose C–H unit (C2A–H2A in Fig. 3) has a nearest (intermolecular) contact (H···H separation 2.35 Å) with a B–H unit of a neighbouring molecule of **4**. The methyl groups of the acetonitrile molecules are also involved in C–H···N hydrogen bonding interactions.

These 'terminal' carboranyl units in **4**·NCMe differ not only in their C–H···X hydrogen bonding interactions, but also in the orientations of the phenylene groups that link them to the central di-substituted carboranyl unit, with θ values of 9.5(7)° (cage A) and 73.1(9)° (cage B), and possibly in their cage C–C distances (1.676(9) Å and 1.646(9) Å respectively). The θ value of 9.5(7)° for cage A is unusual for mono-aryl-*ortho*-carboranes, closer to the value typical of *C*,*C*′-disubstituted-*ortho*-carboranes (where at least one substituent is an aryl group), which also normally have longer



Scheme 1.

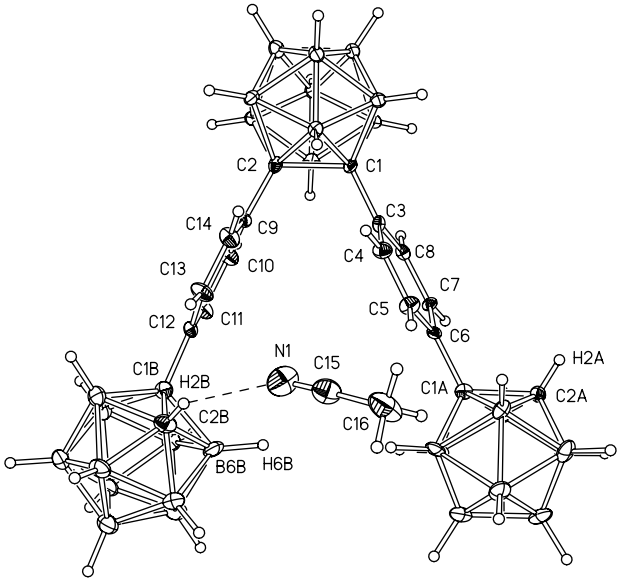


Figure 3. Structure of the acetonitrile adduct of 1,2-bis[4-(1-*ortho*-carboranyl)phenyl]-*ortho*-carborane, **4**·NCMe. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): C1–C3 1.507(8), C6–C1A 1.501(8), C2–C9 1.505(8), C1B–C12 1.511(9).

cage C–C distances. We noted earlier that few mono-aryl-*ortho*-carborane structures have been determined with which to draw comparisons; but, if pyridyl-*ortho*-carboranes 1-R-1,2-$C_2B_{10}H_{11}$ (R = 2′-pyridyl- (**10**), 5-bromo-2′-pyridyl (**11**), 3′-pyridyl- (**12**) and terpyridyl (**13**))[42,43] are included (Fig. 4 and Table 1), then a relationship is evident between the aryl orientation angles θ and the cage C–C distances in these compounds. At low θ values the cage C–C bond length is about 1.66 Å, whereas at high θ values it is *ca* 1.64 Å.

The cage C–C distance for the diaryl carborane unit in **4**·NCMe is 1.732(8) Å, and the θ values are 1.9(7)° and 17.7(7)°, with θ_{av} = 9.8°. The low θ values are to be expected in diarylcarboranes for steric reasons—by facing each other, the aryl groups avoid close contact between their ortho CH units. In reported crystal structures of 1,2-diarylcarboranes, θ_{av} values range between 1.7° and 20.3°, and the cage C1–C2 lengths lie between 1.71 and 1.75 Å.[44–48] The values for the central diaryl-*ortho*-carborane unit in **4** thus lie in the middle of the range characteristic of such compounds.

Computational studies

Welch and co-workers' earlier computations at the RHF/6-31G* level on compound **1**, 1-Ph-1,2-$C_2B_{10}H_{11}$, without symmetry constraints, had revealed one minimum at θ = 65°.[1] We have carried out a comprehensive computational study of **1** at the RHF/6-31G* level to explore whether more than one minimum could be located. The C4–C3–C1–C2 torsion angle was constrained in steps of 10° from 0° to 90° while the rest of the structural parameters were fully optimized. The results are shown in Fig. 5. Apart from the main energy minimum at θ = 65°, we found a second very slight minimum, *ca* 0.2 kcal mol^{-1} higher in energy, at θ = 14.5°. The cage C1–C2 bond length increased by *ca* 0.02 Å as θ decreased from 90° to 0°, and the exo bond angle C3–C1–C2 was at its most acute at *ca* 45°, for reasons attributable to varying intramolecular repulsive interactions involving the ortho C–H units of the phenyl group. These results are in broad agreement with the experimental findings (Table 1).

To assess how well an MP2-optimized geometry for **1** might agree with the structure found by X-ray diffraction, a geometry optimization of **1** was carried out with the torsion angle found in the crystal for C4–C3–C1–C2 constrained at 18.5°. The MP2-optimized geometry obtained, **1a**, was compared with the X-ray structure by geometrical fitting of the cage boron and carbon atoms, giving a misfit value of only 0.0080 Å, one of the lowest misfit values reported for similarly sized carboranes.[49–52] The misfit value reported for the cage atoms between two crystallographically inequivalent molecules in the crystal of diphenyl-*ortho*-carborane **3** was 0.013 Å.[4]

Table 2 shows the excellent correlation found between experimental and computed geometries (**1** and **1a**) for selected bond lengths and angles. The computed bond lengths are consistently *ca* 0.01 Å shorter than the experimental lengths. This consistency, and the low misfit value, illustrates the accuracy of MP2/6-31G* optimized geometries for aryl carboranes.

Table 2 also lists MP2-optimized data for other values of θ that we believe provide a reliable guide to other phenyl group

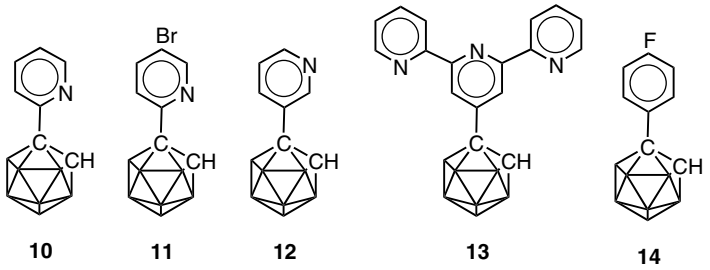


Figure 4. Related carboranes **10**–**14** discussed in this study.

Table 1. Bond lengths and angles in crystal structures of 1-monoaryl-*ortho*-carboranes discussed in this study

Compound		Ref.	θ (°)	cage C–cage C (Å)	cage C–cage C–aryl C (°)	cage C–aryl C (Å)
1-Ph-*ortho*-$C_2B_{10}H_{11}$	**1**	2	71.7(2)	1.649(2)	118.8(1)	1.511(2)
4,4′-(1-*ortho*-$C_2B_{10}H_{11})_2C_{12}H_8$	**2**	5,6	64.2	1.643(7)	117.0(4)	1.516(6)
			80.6	1.634(8)	117.6(4)	1.514(6)
1,2-(4′-(1″-*ortho*-$C_2B_{10}H_{11})C_6H_4)_2$-*ortho*-$C_2B_{10}H_{10}$·NCMe[a]	**4**·NCMe	This work	73.1(9)	1.646(9)	117.6(5)	1.511(9)
			9.5(7)	1.676(9)	118.7(5)	1.501(8)
1-(2′-C_5H_4N)-*ortho*-$C_2B_{10}H_{11}$	**10**	42	71.7	1.632(3)	116.7(2)	1.513(3)
1-(5-Br-2′-C_5H_3N)-*ortho*-$C_2B_{10}H_{11}$	**11**	42	78.6	1.639(5)	117.0(1)	1.514(4)
1-(3′-C_5H_4N)-*ortho*-$C_2B_{10}H_{11}$	**12**	42	0.3	1.663(2)	120.8(1)	1.513(2)
1-Terpyridyl-*ortho*-$C_2B_{10}H_{11}$	**13**	43	48.6	1.649(1)	116.6(1)	1.515(1)

[a] Terminal cages only.

Table 2. Selected parameters from X-ray data of **1** and MP2/6-31G*-optimized geometries **1a–e** and **14a,b**

			Bond length (Å)							
	Fixed angle[a] (°)	θ (°)	C1–C2	C1–C3	C1–B3	C1–B4	C1–B5	C1–B6	C3–C1–C2 (°)	Energy (au)
Expt		71.7(2)	1.649(2)	1.511(2)	1.736(2)	1.716(2)	1.724(2)	1.742(2)	118.8(2)	
1a	18.5	72.5	1.636	1.500	1.728	1.708	1.710	1.735	118.8	−561.13987
1b		66.1	1.637	1.501	1.728	1.708	1.711	1.735	118.2	−561.13989
1d	70	20.3	1.651	1.504	1.732	1.711	1.708	1.732	118.9	−561.13942
1e	80	11.3	1.657	1.503	1.731	1.707	1.705	1.731	120.4	−561.13952
1c		0.5	1.659	1.502	1.731	1.705	1.705	1.731	120.4	−561.13957
14a		63.2	1.637	1.500	1.728	1.709	1.711	1.731	117.9	−660.15761
14b		2.4	1.659	1.501	1.731	1.705	1.705	1.731	120.3	−660.15758

[a] Fixed torsional angle at C4–C3–C1–C2 during geometry optimization.

orientations. Though the minima calculated at the MP2-level have θ values a little different from those calculated at the restricted Hartree–Fock level, the results are in line with those represented graphically in Fig. 5.

Two entries in Table 2 relate to another model compound, 1-*para*-fluorophenyl-*ortho*-carborane,[5] 1-(*p*-FC_6H_4)-1,2-$C_2B_{10}H_{11}$ (**14**), used as a model to probe whether the presence of an electron-withdrawing atom in the *para* position of the aryl substituent (directly opposing the electron-withdrawing effect of the carborane cage) might influence the ease of rotation of the aryl group with respect to the carborane cage. Two energy minima, **14a** and **14b** at $\theta = 63.2°$ and 2.4° respectively, were found for this compound (*cf* 66.1° and 0.5° for **1**), with cage C1–C2 distances identical to those in the unfluorinated compound, but differing far less in energy, suggesting that an electron-withdrawing substituent in the *para* position may well facilitate aryl group rotation. It is worth noting that, in compound **4**, the central carborane cage may itself function as such an electron-withdrawing substituent.

We have also carried out calculations on diphenyl-*ortho*-carborane **3**, to generate an energy/geometry profile. Calculations at the HF/6-31G* level gave a poor fit with experimental data, giving a C1–C2 distance of 1.67 Å, significantly shorter than the experimental value of 1.733(4) Å for $\theta_{av} = 1.7°$.[4] However, at the more accurate MP2/6-31G* level of theory, the fully optimized geometry of diphenyl-*ortho*-carborane **3a** had $\theta_{av} = 17.4°$ and C1–C2 = 1.705 Å (Fig. 6). For a better comparison with the X-ray data, the C4–C3–C1–C2 torsional angle was constrained at 90°, giving $\theta_{av} = 3.4°$ and a C1–C2 distance of 1.718 Å for the optimized geometry **3b** (0.1 kcal mol^{-1} higher in energy than **3a**).

The difference between the computed cage C1–C2 bond lengths in **3a** and **3b** is 0.013 Å. The two crystallographically independent molecules in the crystal of **3** differ by a similar amount, though the experimental structures have closer θ_{av} values (8.3° and 1.7°).[4] A consistent pattern nevertheless emerges: the C1–C2 bond lengthens as θ_{av} decreases. Two other diaryl-*ortho*-carboranes with two distinct geometries in the crystal show the same feature.[47,48]

Comparison of the cage C1–C2 bond lengths in the parent carborane $C_2B_{10}H_{12}$ and in its mono- and di-phenyl derivatives, **1** and **3**, is instructive. The bond lengths are 1.62 Å,[53] 1.66 Å and 1.72 Å respectively if one retains a consistent orientation of the phenyl groups in **1c** ($\theta = 0.5°$)

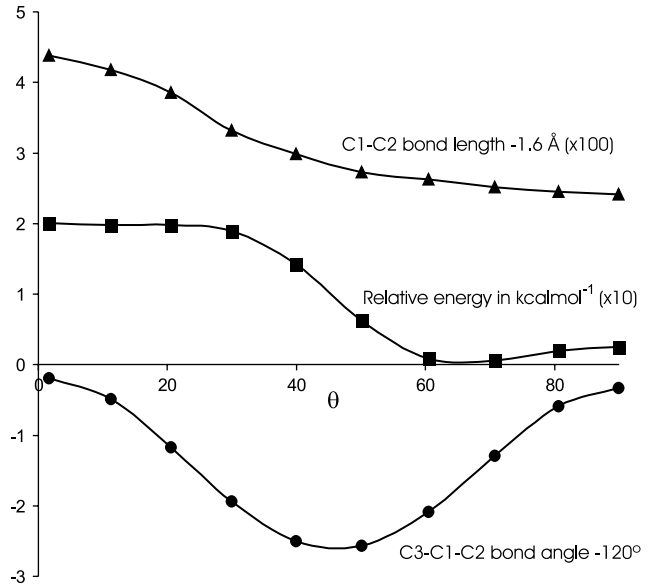


Figure 5. Graph showing relative energy, bond lengths and angles on rotation of the phenyl group in 1-phenyl-*ortho*-carborane **1** at the HF/6-31G* level of theory. The C1–C3 bond length (1.515–1.519 Å) is not significantly affected by θ.

and **3b** ($\theta_{av} = 3.4°$), roughly perpendicular to the C2–C1–C_{aryl} plane. The effect of two phenyl groups on the C1–C2 bond length is little more than twice the effect of one similarly oriented phenyl group, suggesting that the effect is a cumulative electronic one—the presence of one or two phenyl groups oriented perpendicular to the C_{aryl}–C1–C2–C_{aryl}/H plane proportionally reduces the bond order—rather than a steric one due to repulsions between the aryl groups.

Examination of the molecular orbitals computed for 1-Ph-1,2-$C_2B_{10}H_{11}$ in geometries **1a** and **1b** (Fig. 7) shows the

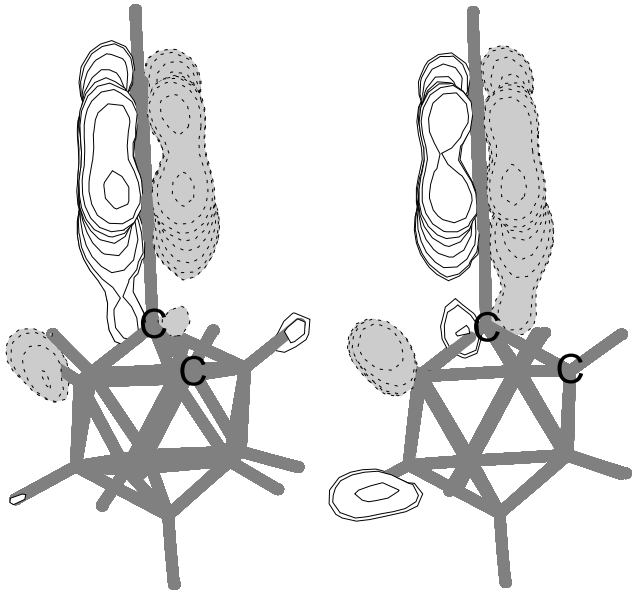


Figure 7. Two low-lying occupied molecular orbitals for fully optimized minima **1b** and **1c**.

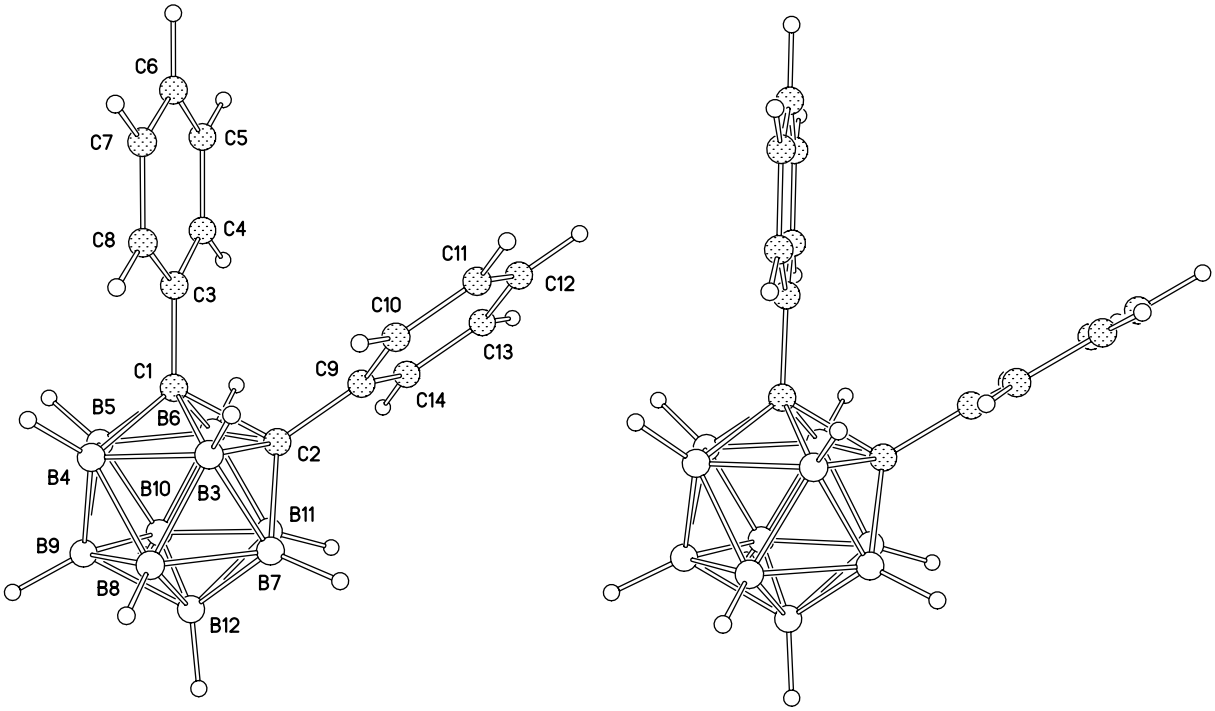


Figure 6. MP2-optimized geometries of 1,2-diphenyl-*ortho*-carborane **3a** and **3b**.

presence of π-bonding in the exo C1–C_{aryl} bond for both ring orientations. Such π-bonding will be at the expense of cage C1–C2 σ bonding when the aryl group is perpendicular to the C_{aryl}–C1–C2 plane. Since the exo π-bonding will be present irrespective of the ring orientation, it does not lead to variations in the exo C1–C_{aryl} bond length. Extreme variations in cage C1–C2 bond lengths attributable to exo π-bonding have been noted previously, e.g. in the dianion $[C_2B_{10}H_{11}]_2^{2-}$, in which a carbon–carbon double bond links two carborane cages,[54,55] in anions $[PhCB_{10}H_{11}CX]^-$ (X = O or S)[56,57] and in species $(RS)_2C_2B_{10}H_{10}$.[58]

CONCLUSIONS

A new V-shaped three-cage assembly of three *ortho*-carborane cages linked by *para*-phenylene units, $(C_2B_{10}H_{11})C_6H_4(C_2B_{10}H_{10})C_6H_4(C_2B_{10}H_{11})$ (**4**) has been synthesized and structurally characterized as its 1 : 1 acetonitrile adduct. In the crystal, the molecules of **4** show two distinct orientations of the terminal carborane cages with respect to the phenylene groups that link them to the central cage, and their cage carbon–carbon distances vary with aryl group orientation in a manner that is also evident in the published structures of related aryl- and pyridyl-*ortho*-carboranes.

Ab initio calculations have been carried out to probe the variation of cage geometry with aryl group orientation for 1-phenyl-*ortho*-carborane **1**, for 1,2-diphenyl-*ortho*-carborane **3** and for *p*ara-fluorophenyl-*ortho*-carborane. These have shed light on the energetics of rotation of aryl groups on carborane cages. The ease of rotation is the cause of disorder problems in many crystalline mono-aryl-*ortho*-carboranes, in which the unsubstituted cage CH unit needs to be anchored in a particular site by C–H···H–B or related hydrogen bonding interactions if it is not to be disordered over the five alternative sites normally available. Our calculations have revealed which orientations of the aryl groups with respect to the carborane cages are (marginally) preferred, and have revealed weak π-bonding interactions between the cage and the ring that are reflected in a lengthening of the cage C1–C2 bond when the aryl group lies in a plane perpendicular to the C_{aryl}–C1–C2 plane. When both cage carbon atoms, C1 and C2, bear aryl substituents oriented thus, a cumulative effect on the C1–C2 bond length is found. From the data at present available, typical cage C1–C2 bond lengths are 1.62 Å, 1.66 Å and 1.72 Å for $C_2B_{10}H_{12}$, 1-aryl-1,2-$C_2B_{10}H_{11}$ and 1,2-$aryl_2$-1,2-$C_2B_{10}H_{10}$ respectively when the aryl groups are perpendicular to the C_{aryl}–C1–C2 plane.

EXPERIMENTAL

Synthesis

IR spectra were recorded as KBr discs on a Perkin Elmer 1600 series FTIR instrument with values reported in wavenumbers. NMR spectra were measured in $CDCl_3$ solutions using Varian Unity-300 (^{1}H, ^{11}B, ^{13}C), Bruker AM250 (^{1}H, ^{13}C, ^{19}F) and/or Varian Inova 500 (^{1}H, ^{11}B) instruments. All chemical shifts are reported in δ (ppm) and coupling constants in hertz. ^{1}H NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm)—care was taken to verify the $CHCl_3$ peak among aromatic protons by running another solution of a lower concentration. ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm). ^{11}B NMR spectra were referenced externally to $Et_2O{\cdot}BF_3$, $\delta = 0.0$ ppm, and ^{19}F to $CFCl_3$, $\delta = 0.0$ ppm. Peak assignments of cage boron, hydrogen and carbon atoms were determined with the aid of selective ^{1}H{^{11}B}, correlated ^{1}H–^{13}C spectra and comparison with literature values of related aryl carboranes.[59,60] Mass spectra were recorded on a VG Micromass 7070E instrument under electron impact conditions at 70 eV.

All reactions (except diazotization) were conducted under dry nitrogen. Butyllithium refers to the solution in hexanes of the stated concentration. Thin layer chromatography (TLC) was conducted on pre-spread silica coated sheet Merck Art. No. 5735. Chromatographic silica refers to Merck Art. No. 9385. Acetylene from a commercial cylinder was bubbled through concentrated sulfuric acid.

*1,2-Bis(4-bromophenyl)ethyne (**5**)*[61]

4-Bromoiodobenzene (36.6 g) in diethylamine (180 cm^3) was stirred and flushed with dinitrogen, and a solution of palladium chloride bis(triphenylphosphine) (127 mg) and copper(I) iodide (54 mg) in warm piperidine (7 cm^3), prepared under dinitrogen, was added by syringe. A slow stream of acetylene was passed over the solution for 20 h. The precipitate was washed with diethylamine and then with water and dried *in vacuo* to give the dibromoalkyne (19.36 g, 89%), m.p. 184–187 °C, suitable for use in the following preparation.

*1,2-Bis(4-[3-hydroxy-3-methylbut-1-ynyl]phenyl)ethyne (**6**)*

1,2-Bis(4-bromophenyl)ethyne (**5**; 10.0 g) and 2-methylbut-3-yne-2-ol in diethylamine (40 cm^3) were stirred and flushed with dinitrogen before addition of palladium(II) chloride bis(triphenylphosphine) (102 mg) and copper(I) iodide (40 mg) and the mixture was heated under reflux for 9 h. The precipitate was separated after cooling, washed with diethylamine and then with water and dried under vacuum to give the triyne-diol **6** (7.00 g), m.p. 204–206 °C, raised to 212–214.5 °C by recrystallization from propan-2-ol. Evaporation of the diethylamine mother liquors furnished a further crop (1.54 g) of recrystallized product (total yield 8.54 g, 85%). Found: C, 84.1; H, 6.6. $C_{24}H_{22}O_2$ requires: C, 84.2; H, 6.5.

*1,2-Bis(4-ethynylphenyl)ethyne (**7**)*[33]

The triyne-diol **6** (5.29 g) was added to a warm solution obtained by dissolving sodium (160 mg) in propan-2-ol

(30 cm^3) and heated under gentle reflux with a stream of nitrogen passing up the condenser (to remove liberated acetone) for 6 h. After cooling overnight, the precipitate (3.33 g) was washed with propan-2-ol and recrystallized from toluene (*ca* 40 cm^3) to give pale orange flakes of the triyne **7** (2.87 g, 82%), m.p. 186.4–190 °C decomp. Found: C, 95.0; H, 4.4. $C_{18}H_{10}$ requires C, 95.6; H, 4.5. ν_{max} 3273 (ethynyl CH); 1926w; 1679w, 1499, 1406 (aryl skel.); 1359; 1267; 1105; 1024w; 838 (aryl CH out of plane); 692; 674; 665; 645; 624; 545; 522; 450. Mass spectrum: 226, M^+.

*1,2-Bis [4-(1-ortho-carboranyl)phenyl]-ortho-carborane (**4**)*

Bis-[4-ethynylphenyl] ethyne (**7**; 2.10 g, 9.13 mmol) and decaborane-dimethylsulfide complex (9.12 g, 37.4 mmol) in toluene (42 cm^3) were heated in an oil bath at 85 °C for 50 h after the initial vigorous evolution of hydrogen had slackened. The solvent was evaporated, methanol (50 cm^3) was added to the cooled residue and the mixture was warmed gently until further vigorous evolution of hydrogen had subsided and then heated under reflux for 6 h. The pale yellow precipitate of the tris-carborane (1.64 g) was separated and, on standing, the filtrate deposited an oily liquid that solidified on scratching to give a further quantity (2.95 g) of the crude product (containing a higher proportion of acetylenic impurity). The combined solids were extracted with toluene (50 cm^3), insoluble matter was separated by filtration and the filtrate was evaporated to *ca* 15 cm^3, diluted with cyclohexane (60 cm^3) and filtered. The filtrate was evaporated and the residue was dissolved in boiling acetonitrile (240 cm^3). A small sample (150 mg) of the tris-carborane, which separated on standing, was used for characterization, after drying in vacuum, m.p. 370–373 °C. For X-ray crystallography the solvated crystals were stored in contact with some mother liquor. Evaporation of the solution and washing the residue with acetonitrile gave the product **4** (1.90 g, 38%), m.p. *ca* 360–370 °C, which was used in the following experiment. Found: C, 37.3; H, 6.9. $C_{18}H_{40}B_{30}$ requires C, 37.2; H, 6.9. ν_{max}: 3067 (carborane CH); 2925w; 2595vs (BH); 1607, 1511, 1407 (aryl skel.); 1283w; 1262; 1078; 1020w; 1002; 847 (aryl out of plane bend); 730 (carborane skel.); 695w; 585; 504. $\delta^1H\{^{11}B\}$: 7.24 (d, 4H, J_{HH} 7, aryl CH *ortho* to end cage), 7.15 (d, 4H, J_{HH} 7, aryl CH *meta* to end cage), 3.71 (2H, cage CH), 3.04 (2H, B3,6H, middle cage), 2.47 (2H, B9,12H, middle cage), 2.39 (4H, B4,5,7,11H middle cage), 2.30 (8H, B8,10H middle cage, B3,6,9H end cage), 2.23 (10H, B4,5,8,10,12H end cage), 2.15 (4H, B7,11H end cage). $\delta^{11}B\{^1H\}$: −1.8 (4B, B9,12 middle cage, B9 end cage), −3.5 (2B, B12 end cage), −8.6 (8B, B4,5,7,11 middle cage, B8,10 end cage), −11.0 (12B, B3,6,8,10 middle cage, B3,6,4,5 end cage), −12.3 (4B, B7,11 end cage). $\delta^{13}C\{^1H\}$: 135.9 (*ipso* aryl C from end cage), 132.0 (*para*), 130.9 (*meta*), 127.4 (*ortho*), 83.3 (cage C of middle cage), 74.5 (cage CC_6H_4 of end), 59.6 (cage CH). Mass spectrum: [RMM of $C_{18}H_{40}B_{30}$ 580.82] 557–586, 581.81 100%, M^+.

*Reaction of tris-carborane **4** with hexafluorobenzene to give the pentafluorophenyl compound **9***

The tris-carborane (1.64 g, 2.80 mmol) in 1,2-dimethoxyethane (30 cm^3) was treated dropwise at room temperature with butyllithium (2.4 cm^3, 2.5 M, 6.0 mmol) and the solution was added dropwise with stirring and ice-cooling to 1,2-dimethoxyethane (100 cm^3) with simultaneous dropwise addition at the same rate of a solution of hexafluorobenzene (570 mg, 3.0 mmol) in the same solvent (32 cm^3) over *ca* 1 h. The mixture immediately turned inky-blue and retained this colour after standing at room temperature for 18 h, but quickly became pale yellow on exposure to air prior to filtration and evaporation. The resinous residue (2.28 g) was extracted with diethyl ether (50 cm^3), leaving an off-white powder (912 mg) whose IR spectrum and TLC (diethyl ether, streak R_f 0–0.4) suggest that it consisted of oligomers of the tris-carborane with tetrafluorophenylene linkages, which was not further characterised. The ethereal solution was passed through chromatographic silica (9.2 g), evaporated, extracted with chloroform (3 cm^3) and the filtered solution was applied to chromatographic silica (8.2 g) and eluted with cyclohexane containing 5% v/v of ethyl acetate. The first fractions (30 cm^3) were evaporated and the residue (264 mg, 13%) was recrystallized from acetonitrile with filtration through Hyflo to give the pentafluorophenyl derivative (130 mg), m.p. 273–275 °C. Found: C, 38.6; H, 5.5. $C_{24}H_{39}B_{30}F_5$ requires: C, 38.6; H, 5.3. ν_{max}: 3074 (carborane CH), 2926w (aryl CH), 2598vs (BH); 1647, 1533, 1509 (aryl skel.); 1479 (CF); 1407; 1083; 1001; 848 (aryl CH out of plane); 727 (carborane skel.), 587; 506. $\delta^1H\{^{11}B\}$: 7.32–7.20 (m, 8H, aryl CH); 3.82 (s, 1H, carborane CH); 3.28 (2H, B3,6H of C_6F_5 cage), 3.08 (2H, B3,6H of middle cage), 2.63, 2.46, 2.40, 2.34, 2.30, 2.23 (26H, BH); $\delta^{11}B\{^1H\}$: −1.8 (6B, B9,12 all cages), −8.6 and −10.9 (24B); $\delta^{19}F$ −130.2 (m, 2F, *ortho* to cage); −146.1 (t, 1F, J_{FF} 23, *para*); −158.9 (dd, 2F, J_{FF} 23, 28, *meta*); $\delta^{13}C\{^1H\}$: 147.2 (d, J_{CF} 252, *ortho*-CF), 142.3 (d, J_{CF} 265, *para*-CF), 135.6 (d, J_{CF}265, *meta*-CF), 135.9 (*ipso* aryl C to cage with CH), 133.1 (*ipso* to cage C_6F_5), 132.6 (*para* to cage C_6F_5), 131.9 (*para* to cage CH), 130.8 (*meta* to cage CH), 130.6 (*meta* to cage C_6F_5), 129.9 (*ortho* to cage C_6F_5), 127.4 (*ortho* to cage CH), 100.9 (*ipso* of C_6F_5 group), 84.0 (cage CC_6H_4 of C_6F_5 cage), 84.0 (cage CC_6H_4 of C_6F_5 cage), 83.2 (middle cage C near CH cage), 82.9 (middle cage C near C_6F_5 cage), 75.9 (cage CC_6H_4 of CH cage), 74.5 (cage CC_6F_5), 59.6 (cage CH). Mass spectrum [RMM of $C_{24}H_{39}B_{30}F_5$ 746.87] 732–753, 747.29 100%, M^+, and 722–731, 727.26 13% $(M - HF)^+$.

Crystallography

A single-crystal structure determination of **4**·NCMe was carried out from data collected at 150(1) K using graphite monochromated Mo *Kα* radiation ($\overline{\lambda} = 0.71073$ Å) on a Bruker SMART 1K CCD diffractometer equipped with a Cryostream N_2 flow-cooling device.[62] Series of narrow ω-scans (0.3°) were performed at several ϕ settings in such a way as to cover a sphere of data to a maximum resolution of 0.70 Å. Cell parameters were determined and refined using

Table 3. Crystal data for **4**·NCMe

Formula	$C_{20}H_{43}B_{30}N$
M	621.85
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	20.6055(3)
b(Å)	12.4998(2)
c(Å)	15.1739(2)
β(°)	109.179(1)
U(Å^3)	3691.34(8)
Z	4
μ(Mo $K\alpha$) (mm^{-1})	0.051
Reflections measured	32 695
Unique reflections	8440
R_{int}	0.179
$R[F^2 \geq 2\sigma(F^2)]$	0.096
$wR(F^2)$, all data	0.318

the SMART software.[63] Raw frame data were integrated using the SAINT program.[64] No absorption correction was applied. The structure was solved using direct methods and refined by full-matrix least squares on F^2 using SHELXTL.[65] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were placed in calculated ideal positions and refined using 'riding mode'. Crystal data and some experimental details are given in Table 3. The relatively high final R value is due to the rather poor quality of the crystal. Selected bond distances and angles for **4**·NCMe are given in the text, Fig. 3 caption and Table 1. The crystal structure for **4**·NCMe has been deposited in the CSD (codename NURLER).

Computations

All *ab initio* computations were carried out with the Gaussian 98 package.[66] The graph was constructed from each optimized geometry of 1-phenyl-*ortho*-carborane **1** with a fixed torsional angle of C2–C1–C3–C4 in steps of 10° between 0° and 90° at the HF/6-31G* level of theory. It should be pointed out here that the θ values are based on both torsional angles, i.e. C4–C3–C1–C2 and C8–C3–C1–C2.

The molecules 1-phenyl-*ortho*-carborane **1**, 1,2-diphenyl-*ortho*-carborane **3** and 1-(*p*ara-fluorophenyl)-*ortho*-carborane **14** were optimized at different starting geometries at the HF/6-31G* level with no symmetry constraints. Frequency calculations were computed on these optimized geometries at the HF/6-31G* level for imaginary frequencies—none as found. For geometries with a fixed torsional angle of C2–C1–C3–C4, the starting geometries were optimized initially at the HF/6-31G* level. Optimization of all these geometries was then carried out at the computationally intensive MP2/6-31G* level of theory to give **1a–e**, **3a,b** and **14a,b**. The root-mean-squared fitting method used for comparison of experimental and theoretical geometries was carried out using the *ofit* command in the *xp* program as part of the SHELXL package.[65]

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REFERENCES

1. Brain PT, Cowie J, Donohue DJ, Hnyk D, Rankin DWH, Reed D, Reid BD, Robertson HE, Welch AJ. *Inorg. Chem.* 1996; **35**: 1701.
2. Thomas RL, Rosair GM, Welch AJ. *Acta Crystallogr. Sect. C* 1996; **52**: 1024.
3. Jiang W, Knobler CB, Hawthorne MF. *Inorg. Chem.* 1996; **35**: 3056.
4. Lewis ZG, Welch AJ. *Acta Crystallogr. Sect. C* 1993; **49**: 705.
5. Hawthorne MF, Berry TE, Wegner PA *J. Am. Chem. Soc.* 1965; **87**: 4746.
6. Brown DA, Colquhoun HM, Daniels JA, MacBride JAH, Stephenson IR, Wade K. *J. Mater. Chem.* 1992; **2**: 793.
7. Heying TL, Ager Jr JW, Clark SL, Mangold DJ, Goldstein HL, Hillman M, Polak RJ, Szymanski JW. *Inorg. Chem.* 1963; **2**: 1089.
8. Hnyk D, Všetečka V, Drož L, Exner O. *Collect. Czech. Chem. Commun*. 2001; **66**: 1375.
9. Coult R, Fox MA, Gill WR, Herbertson PL, MacBride JAH, Wade K. *J. Organometal. Chem.* 1993; **462**: 19.
10. Förster B, Bertran J, Teixidor F, Viñas C. *J. Organometal. Chem.* 1999; **587**: 67.
11. Frixa C, Mahon MF, Thompson AS, Threadgill MD. *Tetrahedron Lett*. 2002; **43**: 1557.
12. Songkram C, Tanatani A, Yamasaki R, Yamaguchi K, Kagechika H, Endo Y. *Tetrahedron Lett.* 2000; **41**: 7065.
13. Lindeman SV, Struchkov YT, Shlover VE, Khotina IA, Teplyakov MM, Korshak VV. *Makromol. Chem.* 1987; **188**: 1511.
14. Murphy DM, Mingos DMP, Forward JM. *J. Mater. Chem.* 1993; **3**: 67.
15. Blanch RJ, Williams M, Fallon GD, Gardiner MG, Kaddour R, Raston CL. *Angew. Chem. Int. Ed. Engl*. 1997; **36**: 504.
16. Lee H, Knobler CB, Hawthorne MF. *Chem. Commun.* 2000; 2485.
17. Davidson MG, Hibbert TG, Howard JAK, Mackinnon A, Wade K. *Chem. Commun.* 1996; 2285.
18. Macías R, Rath NP, Barton L. *J. Organometal Chem.* 1999; **581**: 39.
19. Harakas G, Vu T, Knobler CB, Hawthorne MF *J. Am. Chem. Soc.* 1998; **120**: 6405.
20. Barberà G, Viñas C, Teixidor F, Rosair GM, Welch AJ. *J. Chem. Soc. Dalton Trans.* 2002; 3647.
21. Godfrey PD, Grigsby WJ, Nichols PJ, Raston CL. *J. Am. Chem. Soc.* 1997; **119**: 9283.
22. Clegg W, Coult R, Fox MA, Gill WR, MacBride JAH, Wade K. *Polyhedron* 1993; **12**: 2711.
23. McGrath TD, Welch AJ *Acta Crystallogr. Sect. C* 1995; **51**: 654.
24. Thomas RL, Rosair GM, Welch AJ. *Chem. Commun.* 1996; 1327.
25. Vyakaranam K, Li S, Zheng C, Hosmane NS. *Inorg. Chem. Commun.* 2001; **4**: 180.
26. Balema V, Blaurock S, Hey-Hawkins E. *Z. Naturforsch. Teil B* 1998; **53**: 1273.
27. Lee Y-J, Kim S-J, Kang C-H, Ko J, Kang SO, Carroll PJ. *Organometallics* 1998; **17**: 1109.
28. Brummer H, Apfelbacher A, Zabel M. *Eur. J. Inorg. Chem.* 2001; 917.
29. Sillanpää R, Kivekäs R, Teixidor F, Viñas C, Núñez R. *Acta Crystallogr. Sect. C* 1996; **52**: 2223.
30. Maurer JL, Berchier F, Serino AJ, Knobler CB, Hawthorne MF. *J. Org. Chem*. 1990; **55**: 838.

31. McWhannell MA, Rosair GM, Welch AJ, Teixidor F, Viñas C. *Acta Crystallogr. Sect. C* 1996; **52**: 3135.
32. O'Dowd C, Kennedy JD, Thornton-Pett M. *J. Organometal. Chem.* 2002; **657**: 20.
33. Rusanov AL, Kestov ML, Belomoina NM. *High Perform. Polym.* 2001; **13**: 153.
34. Zakharkin LI, Lebedev VN. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* 1972; 2337.
35. Thomas RL, Welch AJ. *Acta Crystallogr. Sect. C* 1996; **52**: 1689.
36. Batsanov AS, Fox MA, Howard JAK, Wade K. *J. Organometal. Chem.* 2000; **597**: 157.
37. Clegg W, Gill WR, MacBride JAH, Wade K. *Angew. Chem. Int. Ed. Engl.* 1993; **32**: 1328.
38. Gill WR, Herbertson PL, MacBride JAH, Wade K. *J. Organometal. Chem.* 1996; **507**: 249.
39. Colquhoun HM, Lewis DF, Herbertson PL, Wade K, Baxter I, Williams DJ. In *Contemporary Boron Chemistry*, Davidson MG, Hughes AK, Marder TB, Wade K (eds). Special Publication of the Royal Society of Chemistry, No. 253. RSC: Cambridge, UK, 2000; 59.
40. Crăciun L, Custelcean R. *Inorg. Chem.* 1999; **38**: 4916.
41. Davidson MG, Fox MA, Gray FL, Hibbert TG, Wade K. In *Contemporary Boron Chemistry*, Davidson MG, Hughes AK, Marder TB, Wade K (eds). Special Publication of the Royal Society of Chemistry, No. 253. RSC: Cambridge, UK, 2000; 223.
42. Alekseyeva ES, Batsanov AS, Boyd LA, Fox MA, Hibbert TG, Howard JAK, MacBride JAH, Mackinnon A, Wade K. *J. Chem. Soc. Dalton Trans.* 2003; 475.
43. Armspach D, Constable EC, Housecroft CE, Neuburger M, Zehnder M. *J. Organometal. Chem.* 1998; **550**: 193.
44. McGrath TD, Fox MA, Welch AJ. *Acta Crystallogr. Sect. C* 2000; **56**: 487.
45. Thomas RL, Welch AJ *Acta Crystallogr. Sect. C* 1996; **52**: 1689.
46. Lindeman SV, Khotina IA, Teplyakov MM, Struchkov YT, Korshak VV. *Makromol. Chem.* 1988; **189**: 471.
47. Murphy DM, Mingos DMP, Haggitt JL, Powell HR, Westcott SA, Marder TB, Taylor NJ, Kanis DR. *J. Mater. Chem.* 1993; **3**: 139.
48. Thomas RL, Welch AJ. *Polyhedron* 1999; **18**: 1961.
49. Fox MA, Goeta AE, Howard JAK, Hughes AK, Johnson AL, Keen DA, Wade K, Wilson CC. *Inorg. Chem.* 2001; **40**: 173.
50. Fox MA, Goeta AE, Hughes AK, Johnson AL. *J. Chem. Soc. Dalton Trans.* 2002; 2132.
51. Fox MA, Hughes AK, Malget JM. *J. Chem. Soc. Dalton Trans*. 2002; 3505.
52. Batsanov AS, Fox MA, Goeta AE, Howard JAK, Hughes AK, Malget JM. *J. Chem. Soc. Dalton Trans.* 2002; 2624.
53. Schleyer PvR, Najafian K. *Inorg. Chem*. 1998; **37**: 3454.
54. Getman TD, Knobler CB, Hawthorne MF. *J. Am. Chem. Soc*. 1990; **112**: 4593.
55. Getman TD, Knobler CB, Hawthorne MF. *Inorg. Chem*. 1992; **31**: 101.
56. Brown DA, Clegg W, Colquhoun HM, Daniels JA, Stephenson IR, Wade K. *J. Chem. Soc. Chem. Commun.* 1987; 889.
57. Coult R, Fox MA, Gill WR, Wade K. *Polyhedron* 1992; **11**: 2717.
58. Llop J, Viñas C, Oliva JM, Teixidor F, Flores MA, Kivekäs R, Sillanpää R. *J. Organometal. Chem*. 2002; **657**: 232.
59. Fox MA, MacBride JAH, Wade K. *Polyhedron* 1997; **16**: 2499.
60. Fox MA, Wade K. *Polyhedron* 1997; **16**: 2517.
61. Harrison RM, Brotin T, Noll BC, Michl. *J. Organometallics* 1997; **16**: 3401.
62. Cosier J, Glazer AM. *J. Appl. Crystallogr.* 1986; **19**: 105.
63. *SMART-NT. Data Collection Software*, Version 5.0. Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1998.
64. *SAINT-NT. Data Reduction Software*, Version 5.0. Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1998.
65. *SHELXTL*, Version 5.1. Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1998.
66. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery Jr JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98*, Revision A.9. Gaussian, Inc., Pittsburgh, PA, 1998.

