X-RAY STRUCTURE AND BONDING OF 1-PHENYLETHYNYL-2-PHENYL-1,2-DICARBADODECABORANE(12), [1-(PhC==C)-2-Ph-1,2-C₂B₁₀H₁₀], A MODEL ALKYNE COMPLEX CONTAINING A RICH VARIETY OF CARBON–CARBON BOND TYPES

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Abstract—The crystal and molecular structure of 1-phenylethynyl-2-phenyl-1,2-dicarbadodecaborane(12) (1), prepared by the reaction between 1,4-diphenylbutadi-yne and the decaborane adduct $B_{10}H_{12}(NCMe)_2$ in boiling toluene, have been established by an Xray crystallographic study. Evidence of some delocalization of pi-electronic charge in the phenylethynyl ligand towards the carborane cage is provided by the carbon—carbon bond distances [1.431(2), 1.194(2) and 1.433(2) Å, respectively from benzene ring to carborane isocahedron] and Molecular Orbital Bond Index (MOBI) calculations, which also reveal subtle differences in the bonding of the two skeletal carbon atoms to their boron neighbours in the icosahedron. Consideration of (1) as an adduct in which one alkyne function of PhC=CC=CPh coordinates to an *arachno*-shaped $B_{10}H_{10}$ residue reveals the strong electron-withdrawing capacity of the latter, which is compared with other borane and metal cluster residues.

A recent report¹ of some aryl carboranes, prepared for a study of their second-harmonic generation (SHG) properties, included reference to the new compound 1-phenylethynyl-2-phenyl-1,2dicarbadodecaborane(12), 1-(PhC=C)-1-Ph-1,2- $C_2B_{10}H_{10}$ (1). We prepared this same compound during our own continuing studies of carborane derivatives for polymer synthesis.²⁻⁶ Our work included a single crystal X-ray study of (1) which revealed several features of structural and bonding interest, which we discuss below. They include the rich variety of carbon-carbon bond types; evidence of conjugation between the alkynyl function and the carborane cage; and the presence of an uncoordinated alkynyl unit PhC₂ adjacent to the phenylortho-carborane unit PhC₂B₁₀H₁₀, which itself can be regarded as an alkyne complex in which a PhC₂ unit coordinates to an *arachno*-shaped B₁₀H₁₀ cluster.

RESULTS AND DISCUSSION

Our synthesis of 1, like that of Mingos and coworkers¹ involved the reaction in boiling toluene between 1,4-diphenylbutadi-yne, PhC=CC=CPh, and decaborane. However, instead of carrying out the reaction in the presence of the Lewis base, we used a previously prepared sample of the *arachno* bis(nitrile) adduct $B_{10}H_{12}(NCMe)_2$:

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Fig. 1. Structure of compound 1, 1-PhC=CC-2-Ph-1,2-C₂B₁₀H₁₀, showing atom numbering and highlighting the carbon-carbon links therein.

$$B_{10}H_{14} \xrightarrow{2\text{MeCN}} B_{10}H_{12}(\text{NCMe})_2 \xrightarrow{\text{PhC} \equiv \text{CC} \equiv \text{CPh}}_{-H_2, -2\text{MeCN}} \\
 1-(\text{PhC} \equiv \text{C})-2-\text{Ph}-1,2-\text{C}_2B_{10}H_{10}. (1)$$

Single crystals of compound 1 suitable for X-ray diffraction were grown from hexane. The molecular structure is shown in Fig. 1. Selected bond lengths and angles are given in Table 1.

One feature of the molecular structure worthy of comment is the orientation of the phenyl groups. If they were oriented so as to minimize intramolecular nonbonded repulsions between them, both would lie in planes perpendicular to the plane of the atoms (C2, 1, 13 and 14) that connect them. In fact, although the phenyl group directly attached to the carborane cage does have roughly the expected orientation [shown in projection in Fig. 2(b)—the

C1—C13	1.433(2))	C1B4	1.703(2)
C1—B5	1.704(2))	C1C2	1.710(2)
C1B6	1.724(2))	C1—B3	1.731(2)
C2C21	1.503(2))	C2B11	1.705(2)
C2-B7	1.706(2))	C2—B3	1.741(2)
C2—B6	1.742(2))	B3B8	1.757(3)
B3—B7	1.770(3))	B3—B4	1.775(3)
B4—B9	1.772(3))	B4—B8	1.773(3)
B4—B5	1.780(3))	B5-B10	1.771(3)
B5—B9	1.772(3))	B5—B6	1.779(3)
B6-B10	1.758(3))	B6—B11	1.775(3)
B7B11	1.778(3))	B7B8	1.779(3)
B7B12	1.782(3))	B8—B12	1.782(3)
B 8—B9	1.783(3))	B9B12	1.777(3)
B9—B10	1.783(3))	B10-B11	1.778(3)
B10-B12	1.787(3))	B11—B12	1.774(3)
C13—C14	1.194(2))	C14C15	1.431(2)
C15—C16	1.389(2))	C15C20	1.392(2)
C16—C17	1.388(3))	C17C18	1.378(3)
C18—C19	1.371(3))	C19—C20	1.373(3)
C21—C26	1.391(2))	C21—C22	1.391(2)
C22—C23	1.384(2))	C23—C24	1.378(3)
C24—C25	1.379(3))	C25—C26	1.384(2)
C13—C1—C2	1	15.06(12)	C21-C2-C1		117.63(12)
C14—C13—C1	1'	74.6(2)	C13-C14-C1	5	178.1(2)

Table 1. Bond lengths (Å) and selected bond angles (°) for 1



Fig. 2. The pentagonal pyramidal environments of the carboranyl carbon atoms (a) C1 and (b) C2, viewed down their *exo* bonds (C13 to C1, C21 to C2) and showing in projection the orientations of the phenyl groups.

ring plane almost exactly eclipses the link C2-B3, rather than lying parallel to the B3--B6 axis; torsion angle C22—C21—C2—B3 = -0.6°] the other phenyl group [Fig. 2(a)] lies close to the plane of C2, 1, 13, 14 (torsion angle C16—C15····C1—C2 = 13.8°) and the alkyne function bends slightly [by 5.4(2)° at C13 and by $1.9(2)^\circ$ at C14] towards the first phenyl group, as if attracted to it, placing one ortho hydrogen atom of the second benzene ring near to the pseudo-6-fold axis of the first ring (H16 lies 3.21 Å from the plane of this ring). These orientations of the phenyl groups have implications for their respective capacities to participate in conjugative interactions with the tangentially-orientated p AO's on the cluster carbon atoms 1 and 2, which in turn are the orbitals through which C1 and C2 bond to their neighbours within the caborane icosahedron (Fig. 3), a point to which we return below.

In principle, significant conjugative interactions involving the phenyl or phenylethynyl ligands should be apparent from their carbon–carbon bond distances. Compound 1 contains an unusually rich variety of carbon-carbon bond types. Their bond distances are given in Table 2, classified according to the connectivities (coordination numbers), k, of the atoms they link. The bonds in the benzene rings, linking atoms for which k = 3, are treated as all of one type, and averaged in this Table, which also lists typical interatomic distances in related compounds for purposes of comparison. From these, it is apparent that the formally single bonds to the ligands (and the bond C14-C15) are a little shorter than might have been expected for single bonds of the connectivities concerned, and both phenyl groups show slight lengthening (by ca 0.01 Å) of the bonds to the substituted carbon atoms, i.e. C15-C16/20 and C21-C22/26.

In order to probe the bonding in 1, we have carried out a Molecular Orbital Bond Index calculation to determine the bond indices (B.I.) which correspond to (though they are typically slightly lower than) formal bond orders.¹³ From the bond indices of the carbon–carbon bonds (Table 2) it is

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	d/Å	k	B.I.	Carbon atoms involved	Literature values of d/Å
	1.710(2)	66	0.60	1–2	1.62–1.75 ^{1,9,10a}
	1.503(2)	6–3	1.00	2-21	1.49–1.51 ^{1,9,10}
	1.433(2)	6–2	1.06	1–13	
	1.383(3)	3–3	1.42	aryl	1.37-1.4012
	1.431(2)	3–2	1.10	14-15	1.43–1.44 ^{12b}
	1.194(2)	2–2	2.69	13-14	1.17-1.20 ¹² c

Table 2. Carbon-carbon bond distances (d) and indices (B.I.) in 1

"Higher values have been found in systems in which the *exo* atoms form strong dative π -bonds to the skeletal atoms (see refs 11, 25, 26).

^b For single bonds between sp² and sp¹ carbon atoms.

'For triple bonds in alkynes RC=CR'.



Fig. 3. Frontier orbitals^{7,8} through which atoms C1 and C2 bond to their neighbours in the pentagonal faces of the *nido*-shaped CB_{10} residues.

clear that, within the phenylethynyl ligand, the bonds either side of the alkyne unit (particularly that adjacent to the icosahedron) have acquired some multiple bond character at the expense of the triple bond.

Bond indices for all of the links involving the carbon atoms within the carborane icosahedron are shown in Fig. 4. From these it is apparent that atoms C1 and C2 differ subtly but nevertheless significantly in the way they bond to their neighbouring atoms in the icosahedron (C2 and B3, 4, 5 and 6) than does C(2) (whose skeletal neighbours are C1 and B6, 11, 7 and 3), a difference intelligible in that the exo π -bonding to C1 referred to above slightly reduces its capacity for cluster bonding compared with C2. A particularly revealing feature of the difference between C1 and C2 in the manner in which they bond to their neighbours within the carborane icosahedron is the pattern of stronger bonds in Fig. 4 (indicated by asterisks), when the environments of C1 [Fig. 4(a)] and C2 [Fig. 4(b)] are compared. Atom C2 is seen to bond some 3-4% more strongly to its four boron neighbours than does C1, and moreover there is stronger bonding between B6 and B11, and between B7 and B3, than is the case between the corresponding atoms adjacent to C1 (B3–B4 and B5–B6).

Comparison of Fig. 4 with Figs 2 and 3 shows that these features are fully in line with the conclusion that conjugative interactions exo to the carborane icosahedron involve primarily the p_y orbital on C1 and the p_x orbital on C2, so reducing their contributions to the bonding within the icosahedron, which accordingly is dominated by the p_x orbital on C1 and the p_y orbital on C2.

A further feature of the structure of 1 worthy of comment is prompted by its synthesis from the diyne PhC=C-C=CPh and the *arachno*-borane adduct $B_{10}H_{12}(NCMe)_2$. Compound 1 can be regarded as an adduct in which one of the alkyne functions coordinates to an *arachno*-shaped $B_{10}H_{10}$ residue. The other remains intact as the substituent phenylethynyl unit PhC=C (Fig. 5); this aspect is also emphasised in Fig. 1 by the representation of open bonds within the $B_{10}H_{10}$ residue and filled bonds in the di-yne residue. Coordination to the



Asterisks mark the stronger bonds when the environments of C1 and C2 are compared.

Fig. 4. Bond indices of the cluster bonds near C1 and C2, (a) C1 neighbours, (b) C2 neighbours.



Fig. 5. Formation of 1 represented as the coordination of one alkyne unit of PhC=CC=CPh to an *arachno*-shaped $B_{10}H_{10}$ residue.

boat-shaped $B_{10}H_{10}$ residue causes the carbon atoms originally linked by a triple bond of length 1.20 Å in PhC=CC=CPh to separate to a distance of 1.71 Å (corresponding to a bond of bond index 0.60) while the C--C--C bond angles at the two carbon atoms [C1 and C2 in 1] decrease from 180° to 115-118°.

These dramatic changes resemble in kind (though surpassing in extent) those that occur when alkynes coordinate to transition metal clusters. It is usual, for electron book-keeping purposes, to regard the alkynes as 4-electron ligands, donating both pairs of electrons from their pisystems, when they coordinate to two or more metal atoms, the sigma C-C bond pair being retained by the coordinating alkyne. However, compound 1 provides a reminder that alkynes $RC \equiv CR'$ may alternatively be regarded as sources of two carbyne units, RC and R'C, each a source of three electrons. Indeed, in the formation of 1 from $B_{10}H_{12}(NCMe)_2$ and PhC=CC=CPh, the loss of two 2-electron ligands (2MeCN) and two 1-electron ligands (2H) from the former is compensated by the provision of two 3-electron units (PhC=CC and PhC) from the latter, allowing the *arachno* shape of the $B_{10}H_{10}$ residue to be retained. The dramatic reduction in the carbon-carbon bond order of the alkyne effectively results from conversion to a boron-carbon bonding role of the electrons originally forming the alkyne triple bond, sigma as well as pi, even though a weak carbon-carbon link persists.

The effect on the carbon-carbon bond distance of coordination of an alkyne to assorted metal or boron residues is illustrated by the data in Table 3, from which it is apparent that compound 1, viewed as an η^2 -alkyne complex, like other icosahedral carboranes, falls near the upper end of the range of carbon-carbon distances found in such systems.^{1,14-24} It is also apparent that the effect on the coordinated alkyne increases with the nuclearity of the system to which it is coordinating, whether metallic (when the carbon-carbon distances can range from *ca* 1.30–1.45 Å, depending on the number of metal atoms and the identity of the other ligands) or boron (when the carbon-carbon distances span the higher range of *ca* 1.43–1.73 Å). Even greater C—C distances have been found in certain other icosahedral carborane systems, such as the anions $[1,2-X(Ph)C_2B_{10}H_{10}]^-$ (1.86 Å when X = S, 2.00 Å when X = O) in which special circumstances—strong *exo* π -bonding to the substituent sulphur or oxygen atom—apply.^{25,26}

EXPERIMENTAL

Synthesis of 1

A solution of 1,4-diphenylbutadi-yne (1.01 g, 5 mmol) in dry toluene (25 cm³) was added to a suspension of decaborane bis(acetonitrile) adduct (1.01 g, 5 mmol) in toluene (20 cm³) under nitrogen. After 24 h reflux the red solution was cooled, treated with

Table 3. Carbon-carbon bond lengths in carboranes compared with those in alkyne-metal complexes

Compound	d(CC)/Å	k	References
$1,2-Aryl_2C_2B_{10}H_{10}$	1.70-1.75	6-6	9, 10
$1,2-(BrCH_2)_2C_2B_{10}H_{10}$	1.64	6–6	14
$1,2-H_2C_2B_7H_9$	1.55	4-4	15
$1,2-H_2C_2B_4H_4$	1.54	5–5	16
$2,3-H_2C_2B_4H_6$	1.43	4-4	17
$(Et_2C_2)Co_4(CO)_{10}$	1.44	5–5	18
$(Ph_2C_2)_2Fe_3(CO)_8$	1.44	4-4	19
$(Ph_2C_2)Os_3(CO)_{10}$	1.44	4-4	20
$(Ph_2C_2)Fe_3(CO)_9$	1.41	4–5	21
$(Ph_2C_2)Ni_2Cp_2$	1.35	4-4	22
$(Bu_2^{t}C_2)Ta_2Cl_6$	1.35	4-4	23
Various $R_2C_2ML_n$	1.25-1.35	3–3	24

methanol (20 cm³) then evaporated. The residue was extracted with hexane from which 1 (0.52 g, 33%) crystallized on partial evaporation, m.p. 119– 120°C [Found: C, 60.7; H, 6.3%; M_r (mass spectrum) 316–322. Calc. for C₁₆H₂₀B₁₀: C, 60.0; H, 6.3%; M_r , 312–322] v_{max} (KBr disc/cm⁻¹) 3108w, 3086w, 3077w, 3060w, 3044w, (ArH) 2661w, 2649m, 2605s, 2581s, 2577s, (BH) 2239m (C=C) 756s, 687s (C₆H₅).

NMR spectra of 1 (solvent CDCl₃)

¹H (300 MHz), ¹¹B{¹H} (96.25 MHz) and ¹³C{¹H} (75.5 MHz) spectra were recorded at the frequencies indicated using CDCl₃ as solvent; δ values were identical to, or not significantly different from, those given in ref. 1.

Crystal data for 1

 $C_{16}H_{20}B_{10}, M_r = 320.42$, triclinic, space group $P\bar{1}, a = 7.2825(10), b = 10.4122(14), c = 12.763(2)$ Å, $\alpha = 74.336(11), \beta = 81.418(10), \gamma = 86.172(10)^\circ$, V = 921.0(2) Å³ at 240 K (Cu– K_{α} radiation, $\lambda = 1.54184$ Å), Z = 2, $D_c = 1.155$ g cm⁻³, $\mu = 0.405$ mm⁻¹, F(000) = 332.

Data collection and processing: crystal size $0.68 \times 0.44 \times 0.24$ mm, Stoe-Siemens diffractometer with Cryostream cooler,²⁷ cell parameters from 2θ values (44–57°) of 32 reflections measured at $\pm \omega$, intensities from ω/θ scans with on-line profile fitting,²⁸ 2θ range 7 to 130°, index ranges h 0 to 8, k – 12 to 12, l – 14 to 14 (Friedel opposites were measured instead for some inaccessible reflections); corrections for 5% intensity decay of 3 standard reflections, no absorption corrections.

Structure solution and refinement:²⁹ non-hydrogen atoms by direct methods, H atoms constrained [riding model, with C—H 0.94 Å, B—H 1.11 Å, $U(H) = 1.2 U_{eq}$ (C or B)]; full-matrix least-squares refinement on F^2 for all 3082 measured data, with weighting $W^{-1} = \sigma^2(F_o^2) + (0.0892P)^2 + 0.3378P$, where $P = (F_o^2 + 2F_c^2)/3$; isotropic extinction parameter $\chi = 0.007(1)$, where F_c^2 is multiplied by $(1+0.001\chi F_c^2 \lambda^3 / \sin 2\theta)^{-1/4}$; all shifts < 0.001 times corresponding parameter ESD; final difference map between +0.211 and -0.252 e Å⁻³. For 236 parameters, $wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2} =$ 0.1517 for all data, conventional R = 0.0531 for unweighted F values of 2804 reflections having $F_o^2 > 2\sigma (F_o^2)$, goodness of fit on $F^2 = 1.037$.

Atomic coordinates, complete bond lengths and angles, and displacement parameters have been deposited as supplementary material at the Cambridge Crystallographic Data Centre. Acknowledgement—SERC support of this work is gratefully acknowledged.

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