Exo-π-bonding to an *ortho*-carborane hypercarbon atom: systematic icosahedral cage distortions reflected in the structures of the fluoro-, hydroxy- and amino-carboranes, 1-X-2-Ph-1,2-$C_2B_{10}H_{10}$ (X = F, OH or NH_2) and related anions[†]

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Abstract

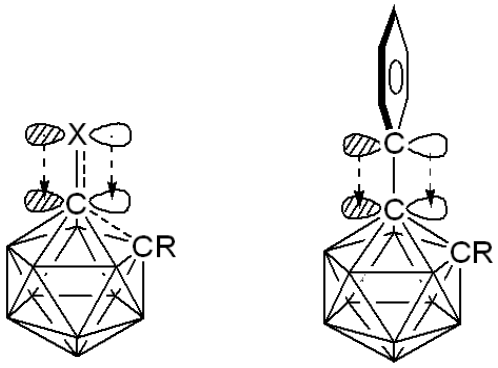
The structures of derivatives of phenyl-*ortho*-carborane bearing on the second cage hypercarbon atom a π-donor substituent (F, OH, O^-, NH_2, NH^- and CH_2^-) were investigated by NMR, X-ray crystallography and computational studies. The molecular structures of these compounds, notably their cage C1-C2 distances and the orientations of their π-donor substituents (OH, NH_2, NH^- and CH_2^-) show remarkable and systematic variations with the degree of *exo* π-bonding, which varies as expected with the π-donor characteristics of the substituent.

[†] Electronic supplementary information (ESI) available: CIF file for five *ortho*-carborane derivatives. Rotatable 3-D molecular structure diagrams of MP2/6-31G* optimised geometries in CHIME format. Tables of energies for MP2/6-31G* optimised geometries, selected structural data for the aminocarborane $PhCb^oNH_2$ and for biscarborane derivatives. See http://www.rsc.org/suppdata/dt/??/?????????/

Introduction

This paper reports synthetic, spectroscopic, X-ray crystallographic and computational studies on an isoelectronic series of *ortho*-carborane derivatives 1-X-2-Ph-1,2-$C_2B_{10}H_{10}$ (R = Ph, X = F, OH, O^-, NH_2 or NH^-, Fig. 1(a)). Throughout this paper we shall refer to them as PhCb^{o}X, where Cb^o represents the *ortho*-carboranylene residue –$CB_{10}H_{10}C$– and the phenyl group is always at the C2 cage atom. These substances were chosen as models to explore the capacity of the carbon atoms of *ortho*-carborane to participate in *exo* C-X π-bonding, and the effects of that π-bonding on the cage geometry. Derivatives of phenyl-*ortho*-carborane were used in order to label the second carbon atom with a group whose influence was already understood; without such a label, CH/BH disorder problems can make X-ray structure determination difficult. Here, our work on PhCb^{o}X systems (some aspects of which have appeared in preliminary accounts[1-5]) is intended to provide a definitive account of the systematically more pronounced cage distortions that occur near the cage carbon atom C1 as *exo* C1-X π-bonding builds up.

Figure 1. (a) Carborane derivatives of type RCb^{o}X, showing *exo*-dative π-bonding (b) Aryl carboranes RCb^{o}Ph show weak *exo*-dative π-bonding



(a) (b)

In 2-phenyl-*ortho*-carborane itself, PhCb^{o}H (Fig 1(a), R = Ph, X = H), the hypercoordinated carbon ('hypercarbon'[6]) atom C1 forms a single bond to the *exo*-hydrogen atom and bonds of lower order to the five neighbouring cage atoms (one carbon, four borons). As the order of the *exo*-C-X bond increases from one to two, we

shall show how the bond to the neighbouring cage carbon atom is particularly affected, increasing in length from *ca* 1.65 Å to *ca* 2.35 Å in $[PhCb^{o}H_2]^-$.

Interest in the capacity of cluster systems (particularly clusters that can be regarded as 3-dimensional aromatic systems) to communicate electronically with substituents is developing in connection with the potential use of clusters connected through unsaturated molecular 'wires' in opto-electronic or other device technology. We ourselves have probed the capacity of carborane units to transmit electronic effects from one aryl substituent to another via the cage, and obtained NMR evidence that aryl substituents on opposite vertices of a *para*-carborane cage (in compounds $aryl^1Cb^paryl^2$; Cb^p = *para*-$CB_{10}H_{10}C$ residue) appear to be able to communicate.[7] Also, in separate studies of the *ortho*-carborane derivatives $PhCb^{o}C{\equiv}CPh$, $aryl^1Cb^{o}aryl^2$ and $arylCb^{o}H$, we have shown how their cage C1-C2 distances are subtly influenced by the orientations of the aryl substituents.[4,8] When the aryl planes are roughly perpendicular to the *ipso*C-C1-C2 plane (as preferred sterically in diaryl derivatives) the skeletal C1-C2 distance is longer than for other ring orientations. Involvement in *exo* C1-C*ipso* dative π-bonding from the aryl π-system reduces the capacity of the appropriate tangential p AO on C1 for C1-C2 skeletal σ-bonding (Fig. 1(b)).

Such effects in aryl-carboranes are, however, small, leading to C1-C2 bond distance changes of <0.04 Å. Far more dramatic effects of C-X *exo*-dative π-bonding on cage geometries, particularly on cage C1-C2 distances in derivatives of *ortho*-carborane, have been found in other systems $RCb^{o}X$ (Fig 1(a)), e.g. in Hawthorne's studies[9,10] on the bis(*ortho*-carboranyl) dianion, $(HCb^{o})_2^{2-}$ (Fig 1(a); R = H^-, X = $Cb^{o}H^-$), in which two *ortho*-carboranyl residues are linked (and opened up towards a *nido* structure) by an *exo*-C=C double bond, and in studies by Xie *et al.*[11] on the anion $[PhCHCb^{o}CH_2Ph^-]$, formed from $PhCH_2Cb^{o}CH_2Ph$ on deprotonation. In this last anion, the benzylidene substituent PhCH is linked to C1 by an *exo* C=C double bond (Fig 1(a), R = $PhCH_2$, X = $PhCH^-$). In addition to the work of Hawthorne and Xie, we should note the X-ray crystallographic and computational work by Welch *et al.* and by Teixidor and Viñas *et al.*.[12-17] Welch carried out systematic studies of aryl-*ortho*-carboranes bearing substituents of varied bulk

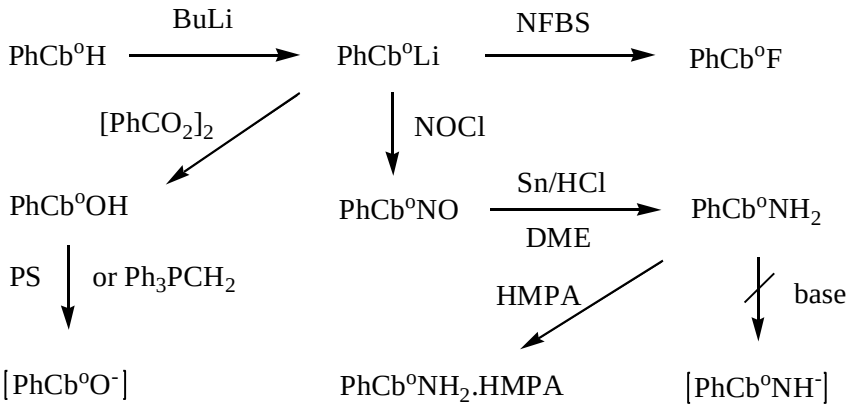
on the second carbon atom, enabling him to document both the steric and subtle electronic effects on the cage C1-C2 distance.[12,13,14,15] Teixidor and Viñas, in extensive studies[16] on thiolato ($RSCb^oR'$) and phosphino (R_2PCb^oR') derivatives of *ortho*-carborane, found the cage C1-C2 distances varied in a manner they attributed to steric and electronic factors and, more recently,[17] to *exo* C-X π-bonding effects such as we advocate below.

Results and Discussion

Synthetic Aspects

The synthetic routes used to functionalize the unsubstituted carbon atom of 1-phenyl-*ortho*-carborane, $PhCb^oH$, are outlined in the Scheme, which shows how the C-lithio-carborane $PhCb^oLi$ proved to be a versatile intermediate through which to attach fluoro, hydroxy or amino groups to the carborane carbon atom. Some of our synthetic procedures were adaptations of literature methods.[18]

Scheme



Previous studies of *ortho*-carborane fluorination reactions have been concerned almost exclusively with fluorination at the boron atoms.[19,20] A rare attempt to fluorinate *ortho*-carborane at the carbon atoms using the powerful fluorinating agent perchloryl fluoride, ClO_3F, reportedly led to an explosion, though 1,7-difluoro-*meta*-carborane FCb^mF was

successfully prepared from ClO_3F and HCb^mH.[20] We ourselves opted for the action of a milder reagent, N-fluorobenzenesulfonamide (NFBS), on the lithio carborane $PhCb^oLi$ in ether as a route to $PhCb^oF$, which was recovered in 24% yield. Although we were unable to grow crystals suitable for X-ray crystallographic study, we have carried out a computational study of its structure as reported below.

In our original studies of the deprotonation of hydroxycarboranes, we studied the effectiveness of a range of amines, and found 'proton sponge', 1,8-bis(dimethylamino)naphthalene, to be the most effective, forming a salt of the anion $[PhCb^oO]^-$ with less residual O…H-N hydrogen bonding than in the salts formed by other amines.[2,5] In the present work, we have used the Wittig reagent, $Ph_3P{=}CH_2$, in order to deprotonate $PhCb^oOH$, which was thereby converted into the triphenyl(methyl)phosphonium salt $[Ph_3PMe]^+[PhCb^oO]^-$.

Attachment of an amino group, NH_2, to a carborane carbon atom is conveniently achieved via the C-nitroso-carborane $PhCb^oNO$, itself preparable from the lithio-carborane and nitrosyl chloride.[21] We found Sn/HCl in dimethoxyethane (DME, monoglyme) to be suitable for the reduction of the nitroso compound in the synthesis of $PhCb^oNH_2$. Crystals of the aminocarborane, and of its 1:1 adduct with HMPA, were grown from hexane solution for X-ray study. However, attempts to deprotonate the amino-carborane to form the amide anion $[PhCb^oNH^-]$ were unsuccessful, the strongly basic conditions inducing cage deboronation and extensive decomposition instead. We therefore carried out a computational study on the anion $[PhCb^oNH^-]$, the results of which are presented in our discussion of structural and bonding aspects below.

The mercapto-carborane $PhCb^oSH$ and the trisulfide $PhCb^oS_3Cb^oPh$ were prepared from the reaction between $PhCb^oNa$ and sulfur in dimethoxyethane followed by hydrolytic work-up, as described in the Experimental Section.[22] The new trisulfide was structurally characterised by X-ray crystallography and is used here as a model for $PhCb^oSH$. The section also lists procedures for the isolation and spectroscopic characterisation of compounds studied in the present work, including the previously unreported proton

sponge and triethylammonium salts, (PSH^+)[$PhCb^oS^-$] and (Et_3NH^+)[$PhCb^oS^-$], and the new *meta* carboranes, the hydroxy-*meta*-carborane $PhCb^mOH$ and the mercapto-*meta*-carborane $PhCb^mSH$. Attempts to prepare the proton sponge salts of these *meta* carboranes were unsuccessful.

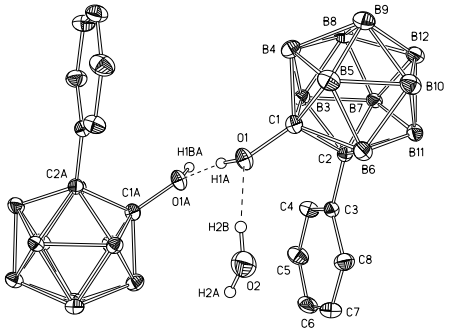
Structural Aspects

In this section, we report new structural studies on the compounds $PhCb^oOH$, $[Ph_3PMe]^+[PhCb^oO]^-$, $PhCb^oNH_2$, $PhCb^oNH_2.OP(NMe_2)_3$ and $PhCb^oS_3Cb^oPh$, discussing each in turn. In the following sections, we discuss the systematic icosahedral cage distortions shown by these and related compounds associated with *exo*-π-bonding, and the bonding implications for the hypercarbon atom C1.

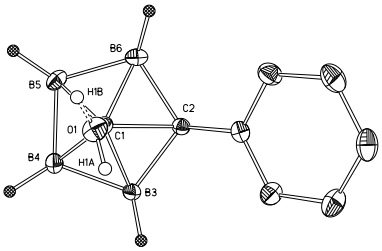
1-Hydroxy-2-phenyl-*ortho*-carborane, $PhCb^oOH$, isolated as the hemi-hydrate $PhCb^oOH.0.5\ H_2O$.

In the crystalline hemi-hydrate, the water molecules are linked to pairs of hydroxy-carborane molecules (themselves related through an inversion centre) by O-H…O hydrogen bonding interactions, as shown in Fig 2(a), which also shows the presence of direct O-H…O hydrogen bonding between the hydroxy groups. Each OH group is disordered equally over two orientations as a result of the inversion symmetry. The planes in which the hydrogen-bonding interactions and phenyl substituents lie are best seen from Figs 2(b) and 2(c), the former viewed down the *exo*-C1-O bond, the latter down the *exo* C2-phenyl bond. Both the hydrogen-bonding and phenyl ring planes are roughly perpendicular to the O-C1-C2-C(phenyl) plane.

Figure 2. Structure of the hemihydrate $PhCb^{o}OH.0.5H_2O$. (a) hydrogen bonding interactions (only one disorder component is shown); distances(Å) and angles(º), O1···H2B 2.11, O1A···H1A 1.98, O1···O1A 2.78, O1···O2 2.72, O1···H2B-O2 133, O1A···H1A-O1 174; (b) view down the *exo* OC bond; (c) view down the *exo* PhC bond



(a)



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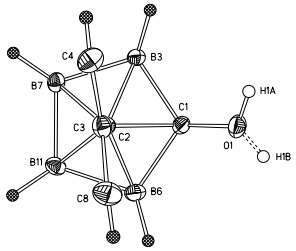


(c)

The carboranyl C1-OH distance in $PhCb^{o}OH.0.5H_2O$, 1.366(2) Å, is significantly shorter than might have been expected had it been a single bond connecting a 2-coordinate oxygen atom to a 6-coordinate carbon atom (a standard C-O single bond in an ether molecule, between 2-coordinate oxygen and 4-coordinate carbon, has a length *ca* 1.43 Å; a standard C=O double bond, as in ketones, has a length *ca* 1.23 Å). We infer that the C1-O bond in $PhCb^{o}OH$ is shortened by dative C-O π-bonding. The cage C1-C2 distance, 1.723(2) Å, on the other hand, is significantly longer than its counterpart in $PhCb^{o}H$, 1-phenyl-*ortho*-carborane (1.649(2) Å,[15] or 1.66 Å when the phenyl group is orientated perpendicular to the C-C1-C2 plane,[8] as in $PhCb^{o}OH$), showing that *exo*-C1-O π-bonding

is at the expense of some skeletal C1-C2 bonding. One can rationalise this most simply by noting that involvement of the tangentially-oriented p AO on C1 in *exo* C1-O π-bonding, (Fig 1(a)), reduces its availability for cage C1-C2 σ-bonding. This rationalization is neatly consistent with the orientation of the O…H and O-H bonds of the hydroxy group's oxygen atom, which clearly involve an oxygen p AO roughly perpendicular to the O-C1-C2 plane, leaving the oxygen p AO in that plane available for dative C1-O π-bonding.

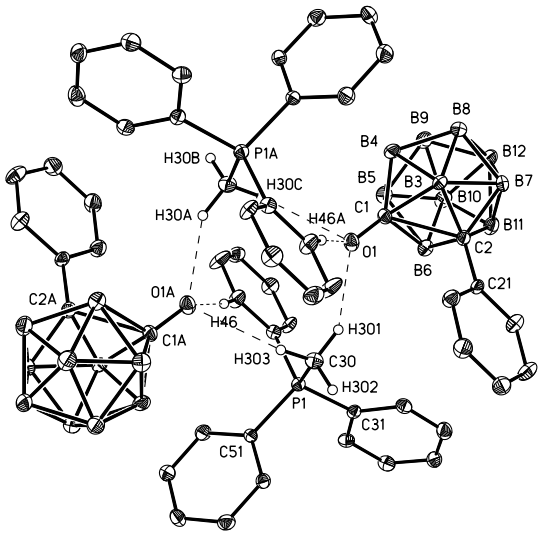
The anion [PhCb^{o}O^{-}], [1-O-2-Ph-1,2-$C_2B_{10}H_{10}$]$^{-}$

We reported the deprotonation of PhCb^{o}OH by 1,8-bis(dimethylamino)naphthalene ('proton sponge', PS) to form the salt [PSH]$^{+}$[PhCb^{o}O]$^{-}$ in 1987,[2] and drew attention to the way the anion could be regarded as an unprecedented example of a pentuply-bridging carbonyl group located (off-centre) over the face of a *nido*-shaped (icosahedral fragment) [$PhCB_{10}H_{10}$]$^{-}$ anionic residue. To probe this anion further, we prepared its triphenyl(methyl)phosphonium salt Ph_3PMe^{+}[PhCb^{o}O]$^{-}$ from Ph_3PCH_2 and PhCb^{o}OH in the present work and determined its structure, which is shown in Fig 5 viewed from a perspective that reveals the hydrogen bonding interactions between the oxygen atom of the anion and carbon-attached hydrogen atoms of the adjacent phosphonium cations in the crystal structure. Each oxygen atom participates in three O…H-C hydrogen bonds, two with methyl groups of two separate phosphonium cations, the third with an *ortho* hydrogen atom of a phenyl group on one of the neighbouring cations. Bond distances and angles within the anion overall (Fig 5) do not differ significantly from those in the proton sponge salt though the C1-C2 bond length is *ca* 0.06 Å longer in the phosphonium salt than in the proton sponge salt. This subtle difference may be due to the different phenyl orientations in these anions.

As expected, the anion [PhCb^{o}O]$^{-}$ shows evidence of far stronger C1-O dative π-bonding, and concomitantly weaker C1-C2 skeletal bonding, than in the parent hydroxy-carborane PhCb^{o}OH. The *exo* C1-O distance in [PhCb^{o}O]$^{-}$ 1.228(7) Å, lies in the normal range for double bonds between 3-coordinate carbon and 1-coordinate oxygen atoms, and the

skeletal carbon-carbon bond, C1-C2, has extended, in the anion $[PhCb^{o}O]^{-}$, to a length (2.065(7) Å) some 0.4 Å greater than that in the parent phenyl-*closo*-carborane, $PhCb^{o}H$.[15] The carborane icosahedron has opened up in response to the greater electron density available at C1. The detailed manner in which it has done so merits closer consideration, which we offer in the next section.

Figure 3. Structure of $[Ph_3PMe]^{+}[PhCb^{o}O]^{-}$. Intermolecular hydrogen bonds(Å) and angles(°) O1···H301 2.26, O1···H46A 2.36, O1···H30C 2.58, O1···C30A 3.53, O1···C46 3.58, O1···C30 3.15, O1···H301-C30A 173, O1···H46A-C46 151, O1···H30C-C30 165.

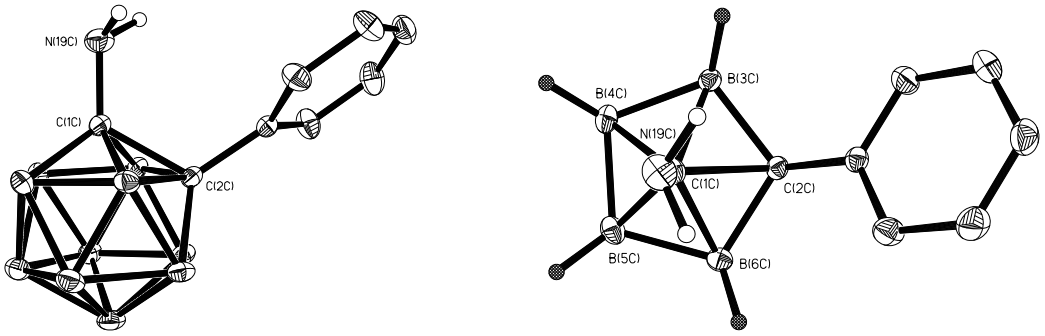


1-Amino-2-phenyl-*ortho*-carborane $PhCb^{o}NH_2$

The aminocarborane $PhCb^{o}NH_2$ proved unusual in crystallising in a form that contained four crystallographically independent molecules A, B, C and D in the asymmetric unit (Fig 4 shows molecule C only). These differed slightly in their interatomic distances. We have used average values of interatomic distances in our discussion below. The amino hydrogen atoms were located and refined in molecules A, C and D with the aid of similarity restraints, but molecule B showed too much thermal motion and/or disorder for

these hydrogen atoms to be located. The structure contains no significant hydrogen-bonding interactions between the amino groups.

Figure 4. Structure of PhCb^{o}NH$_2$ (Molecule C) (a) general view and (b) view down the C-N bond.



(a) (b)

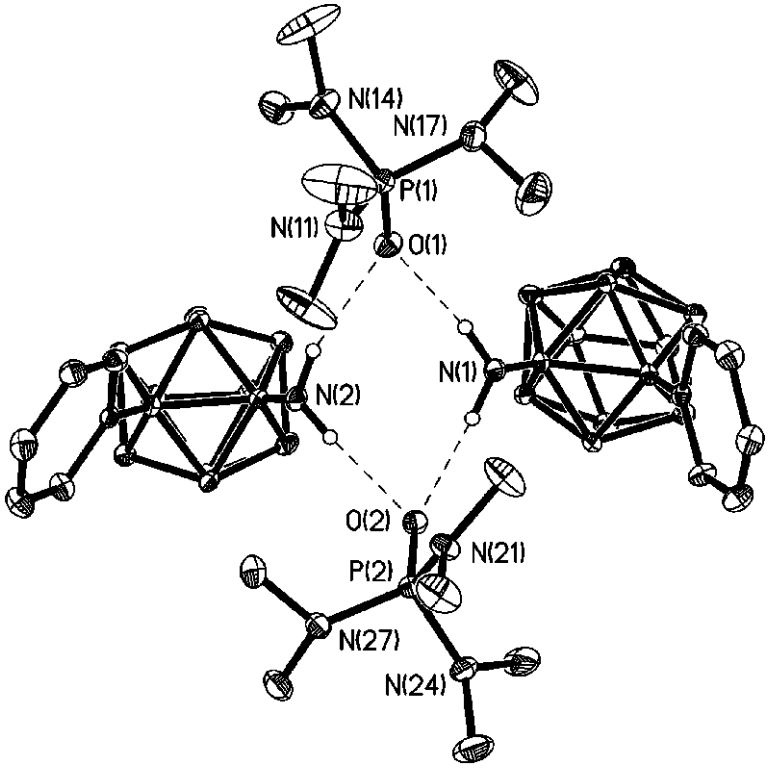
The *exo*-C1-N distances in A to D ranged from 1.391(3) to 1.404(3) Å (mean 1.392(3) Å), a distance implying some multiple bond character, being significantly shorter than the single C-N bonds in primary, secondary or tertiary amines (typically *ca* 1.47 Å). The C1-C2 distances in A to D range from 1.745(3) Å to 1.785(3) Å, mean 1.767 (3), longer than those in PhCb^{o}H (1.66 Å when the phenyl group has a similar orientation[8]) and PhCb^{o}OH (1.715(3) Å). Selected structural data for the four independent molecules of PhCb^{o}NH$_2$ are listed in the ESI.

Despite the large uncertainties in the refined hydrogen atom positions, the coordination at nitrogen appears, from the X-ray data, to be pyramidal, with the amino group hydrogen atoms leaning slightly towards the phenyl group, and the nitrogen lone-pair electrons in the plane N-C1-C2. It is also worth noting that there are close N-H…B (N-H…H-B) interactions between molecules A(NH$_2$) and B(BH) and between molecules C(NH$_2$) and D(BH) in the crystal.

1-Amino-2-phenyl-*ortho*-carborane – HMPA adduct, $PhCb^{o}NH_2.OP(NMe_2)_3$

1-Amino-2-phenyl-*ortho*-carborane (like *ortho*-carborane $HCb^{o}H$ itself[23]) forms a 1:1 hydrogen bond adduct with HMPA, the crystal structure of which was determined. Strong N-H…O hydrogen bonding interactions hold the constituent molecules together in the crystal (Fig 5) in dimeric units $[PhCb^{o}NH_2.OP(NMe_2)_3]_2$ containing non-equivalent carborane residues with C1-N distances of 1.363(8) Å and 1.360(9) Å and C1-C2 distances of 1.853(8) Å and 1.818(8) Å. Despite the larger uncertainties in these distances, it appears that in this adduct the C1-C2 distance is significantly longer than in $PhCb^{o}NH_2$, a difference intelligible in that the involvement of the amino N-H bonds in N-H…O hydrogen bonding will weaken them, and so allow the amino nitrogen atom in the HMPA adduct to be a stronger π-donor to the carborane cage carbon atom C1.

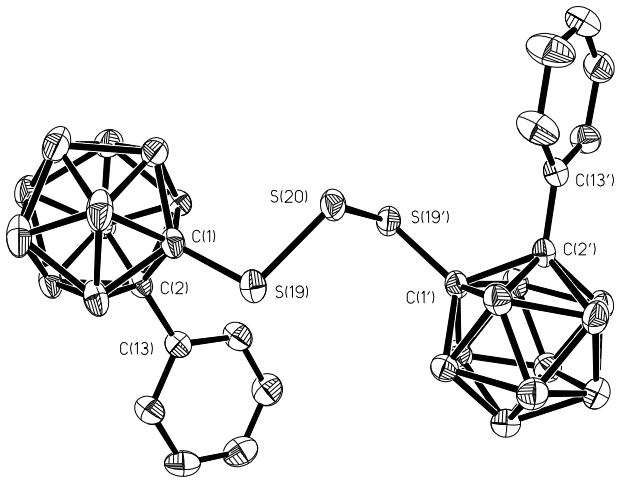
Figure 5. Structure of $PhCb^{o}NH_2.OP(NMe_2)_3$ adduct. Hydrogen bonds (Å) and angles (°): O1…H1B 2.07, O1…H2A 2.20, O2…H1A 2.17, O2…H2B 2.01, O1…N1 2.96, O1…N2 3.07, O2…N1 2.99, O2…N2 2.90, O1…H1B-N1 167, O1…H2A-N2 164, O2…H1A-N1 154, O2…H2B-N2 172.



The trisulfide PhCb^{o}S$_3$Cb^{o}Ph

As we were unable to grow crystals of the 1-mercapto-2-phenyl-*ortho*-carborane suitable for X-ray crystallography, the structure of the new trisulfide is included here as a closely related model. The trisulfide molecule contains non-equivalent carborane residues since it has no centre of symmetry in the crystal studied. The C1-C2 bond lengths of 1.731 and 1.734 Å are insignificantly longer than 1.723 Å for the C1-C2 bond in 1-hydroxy-2-phenyl-*ortho*-carborane. The orientation of the S-S bond with respect to the C1-C2 bond in each carborane residue is similar to the orientation of the OH bond found for the hydroxy carborane PhCb^{o}OH. It is assumed here that the effect of the sulphur atom is similar to that of the oxygen atom on the cage geometry for C-hydroxy and C-mercaptocarboranes. The S_3 bridge is unremarkable with S-S bonds of 2.037 Å and S-S-S angle of 108.5º – similar parameters have been found in structurally characterized diaryl trisulfides.[24]

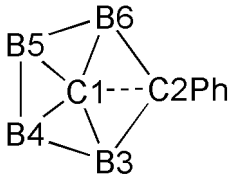
Figure 6. Structure of PhCb^{o}S$_3$Cb^{o}Ph.



The systematic icosahedral cage distortions associated with *exo*-π-bonding

The systems described in the previous section show how π-bonding from a substituent X to a carbon atom of an *ortho*-carborane cage is reflected not only in the relative shortness of the C1-X bond but also in the length of the cage C1-C2 bond, and that the extent of π-bonding from a substituent atom bearing a hydrogen atom (e.g. as in OH) changes very significantly when that atom is deprotonated (e.g. to O^-). Other lesser distortions of the carborane cage become evident if one examines the lengths of all of the cage bonds, C-B and B-B as well as C-C, near C1, the carbon atom bearing the π-donor substituent. Relevant data for the systems $PhCb^oX$ studied in our work are collected in Tables 1 and 2 (experimental and computed data respectively), presented in the sequence of increasing C1-C2 distances from left to right. Structural data of the parent phenyl-*ortho*-carborane $PhCb^oH$ determined in 1996 by Welch *et al.*[15] and of the fully *nido* anion $[PhCHB_{10}H_{10}CPh]^-$ determined in 1973 by Tolpin and Lipscomb[25] are also listed in Table 1. Focussing initially on bond length changes in the neighbourhood of C1 one can see that, irrespective of the identity of the *exo*-atom, dative C1-X π bonding from that atom leads not only to a substantial lengthening of the cage bond C1-C2, but also to a smaller but nevertheless significant increase in the lengths of the bonds between C1 and B3 and B6 (the boron atoms linked to both of the cage carbon atoms), though the bonds to B4 and B5 shorten slightly. The bonds between B3/6 and C2 also shorten. The boron-boron bonds between atoms B3 and B4, also B5 and B6 are not significantly affected, though that between B4 and B5 lengthens slightly on deprotonation.

Table 1. Crystallographically determined geometrical data for PhCb^{o}X. Standard uncertainties for individual results in our present work are available in the supplementary material (CIF).



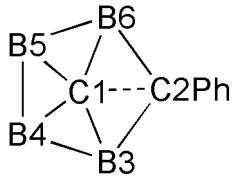
X	H[a]	OH	$S_3Cb^{o}Ph$	NH_2	NH_2. HMPA	S^{-b}	O^- PSH^{+c}	O^- $YlidH^+$	HPh^{-d}
			Av(2)[e]	Av(4)[e]	Av(2)[e]				
C1-C2	**1.649**	**1.723**	**1.735**	**1.767**	**1.835**	**1.835**	**2.001**	**2.065**	**2.857**
C1-X	0.97	1.366	1.787	1.396	1.362	1.729	1.245	1.227	
C1-B3/6	1.720	1.716	1.718	1.715	1.728	1.745	1.818	1.838	2.380
C1-B4/5	1.700	1.700	1.703	1.698	1.687	1.699	1.684	1.675	1.668
C2-B3/6	1.739	1.736	1.738	1.722	1.708	1.724	1.692	1.699	1.662
B3/6-B4/5	1.782	1.777	1.786	1.780	1.761	1.760	1.771	1.782	1.879

[a] Ref. 15.
[b] Ref. 3.
[c] Ref. 2.
[d] Ref. 25.
[e] Av(n) = average from n unique molecules, C1-B3/6, B3/6-B4/5 bonds etc are averaged

B4-B5	1.786	1.779	1.775	1.775	1.788	1.772	1.801	1.814	1.864
Tors1(CX)[f]	-	70.1/116.1	96.1/123.3	71.1	107.8	-	-	-	-
Tors2(CPh)[g]	18.5	83.6	74.5	75.4	59.3/81.8	88.1	87.7	39.2	33.3
δ1	0.041	0.066	0.095	0.101	0.126	0.093	0.188	0.235	0.776
δ2	0.066	0.066	0.088	0.089	0.123	0.109	0.131	0.156	0.158

[f] Torsional angle of C2-C1-Y/Z-H where applicable
[g] Torsional angle of C1-C2-C(Ph)-C(Ph)

Table 2. MP2/6-31G* optimized geometry data for PhCb^{o}X



X	H[h]	H[i]	F	OH	SH	NH_2[j]	NH_2[k]	OLi	ONa	S^-	O^-	NH^-[l]	NH^-[m]	CH_2^-	HH^-
C1-C2	**1.636**	**1.659**	**1.674**	**1.715**	**1.729**	**1.743**	**1.766**	**1.837**	**1.913**	**1.999**	**2.151**	**2.298**	**2.287**	**2.362**	**2.756**
C1-X	1.088	1.088	1.352	1.373	1.782	1.411	1.405	1.296	1.278	1.690	1.227	1.302	1.299	1.363	-
C1-B3/6	1.709	1.701	1.703	1.707	1.705	1.704	1.709	1.764	1.782	1.772	1.885	1.898	1.888	1.871	2.294
C1-B4/5	1.693	1.695	1.689	1.696	1.700	1.701	1.698	1.705	1.696	1.685	1.671	1.637	1.642	1.628	1.641
C2-B3/6	1.731	1.731	1.734	1.724	1.725	1.718	1.718	1.714	1.705	1.701	1.685	1.668	1.672	1.667	1.647
B3/6-B4/5	1.772	1.769	1.771	1.774	1.776	1.773	1.773	1.757	1.762	1.769	1.775	1.795	1.792	1.811	1.846
B4-B5	1.780	1.773	1.783	1.776	1.771	1.767	1.771	1.786	1.795	1.784	1.830	1.840	1.833	1.826	1.847
Tors1(CX)	-	-	-	95.5	96.8	118.5	63.1	0.0	0.1	-	-	90.5	90.2	86.2	
Tors2(CPh)	18.5	90.5	91.7	73.7	91.3	92.3	91.8	85.3	88.1	91.4	91.4	13.4	87.1	90.6	91.1

[h] More stable minimum with phenyl group along the C1-C2 plane, see Ref.8
[i] Less stable minimum with phenyl group perpendicular to the C1-C2 plane, see Ref. 8.
[j] With hydrogens at N orientated away from the phenyl group.
[k] With hydrogens at N orientated towards the phenyl group.
[l] More stable minimum with phenyl group along the C1-C2 plane – see figure 7(a).
[m] Less stable minimum with phenyl group perpendicular to the C1-C2 plane.

Table 3. Crystal data and refinement information

Compound	$PhCb^{o}OH$ $\cdot 0.5H_2O$	$PhCb^{o}O^{-}$ Ph_3PMe^{+}	$PhCb^{o}NH_2$	$PhCb^{o}NH_2$ $\cdot OP(NMe_2)_3$	$PhCb^{o}S_3Cb^{o}Ph$
Formula	$C_8H_{16}B_{10}O \cdot 0.5H_2O$	$C_{19}H_{18}P^{+}C_8H_{15}B_{10}O^{-}$	$C_8H_{17}B_{10}N$	$C_8H_{17}B_{10}N \cdot C_6H_{18}N_3OP$	$C_{16}H_{30}B_{20}S_3$
M	245.3	512.6	235.3	414.5	534.8
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1$	$P2_12_12_1$
a /Å	12.628(3)	10.845(1)	10.6738(7)	10.526(3)	8.0923(3)
b /Å	6.8043(16)	11.260(1)	22.3100(16)	21.680(3)	14.8660(7)
c /Å	16.020(4)	11.511(1)	23.3165(16)	12.111(2)	24.1238(8)
α /°		84.97(1)			
β /°	96.97(3)	86.27(1)	102.677(2)	115.48(2)	
γ /°		86.21(1)			
U /Å^3	1366.3(6)	1394.7(2)	5417.1(6)	2495.0(9)	2902.1(2)
T /K	160	150	160	293	295
Z	4	2	16	4	4
μ /mm^{-1}	0.06	0.12	0.06	1.05	2.37
Reflections measured	3045	5922	33320	5324	6796

Unique reflections	2395	4393	12397	4179	4793
R_{int}	0.046	0.046	0.043	0.033	0.017
Reflections with $I > 2\sigma(I)$	1910	3415	7978	3104	4351
R ($I > 2\sigma$), R_w (on F^2, all data)	0.054, 0.146	0.098, 0.230	0.069, 0.219	0.050, 0.129	0.032, 0.093
Absolute structure parameter				0.02(3)	–0.012(16)
Max., min. el. Density /e Å^{-3}	0.26, –0.22	0.38, –0.36	0.83, –0.33	0.16, –0.16	0.16, –0.19

Very similar bond length changes are also shown by calculations at the MP2/6-31G* level, which reproduce, with remarkable precision, the X-ray data (Table 2). Encouraged by the agreement between calculated and experimentally determined structures, we also carried out a calculational (MP2/6-31G*) study of the isoelectronic 1-fluoro-2-phenyl-*ortho*-carborane, $PhCb^oF$. Compared with its oxygen analogues, $PhCb^oOH$ and $[PhCb^oO]^-$, the fluoro-carborane $PhCb^oF$ has a (calculated) structure less affected by dative π-bonding from the substituent fluorine, as expected because the greater electronegativity of fluorine makes it a weaker π-donor than oxygen (whether as OH or particularly O^-). Though we have been unable to grow suitable crystals of $PhCb^oF$ to confirm the structural details by X-ray crystallography, we are encouraged to believe that these calculated distances are realistic, as the solution NMR chemical shifts found for $PhCb^oF$ agree well with those predicted from the calculated structure (a criterion increasingly valuable in boron cluster chemistry). In the reported X-ray determined geometry of the related compound $PhCb^oBr$ the C1-C2 distance is 1.692(8) Å.[14] This value is less than 0.02 Å longer than that calculated for $PhCb^oF$.

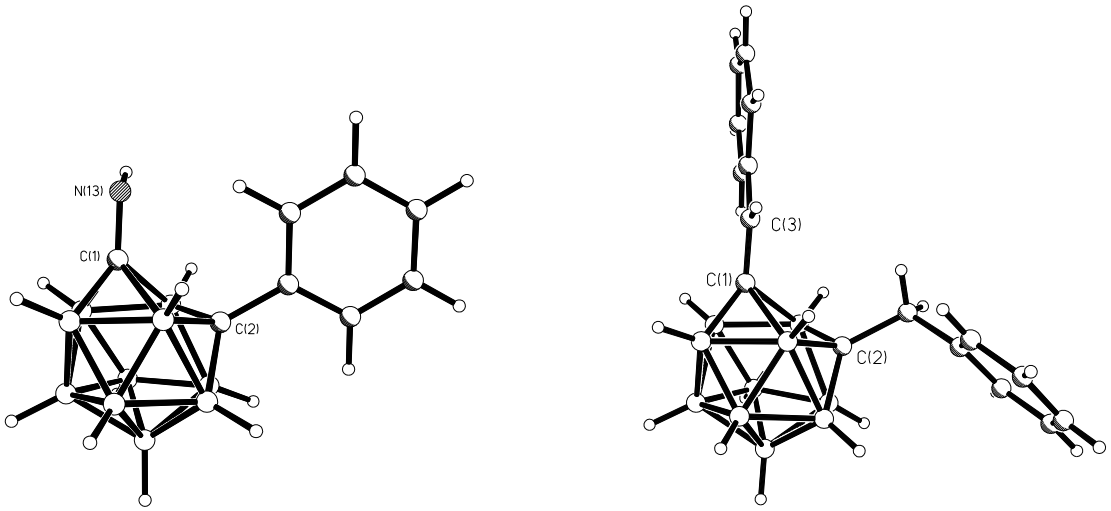
To shed more light on the amino group orientation of $PhCb^oNH_2$, we carried out calculations at the MP2/6-31G* level, which revealed two minima, each with the lone pair in the plane N-C1-C2, but differing in whether the amino hydrogen atoms leaned away from or toward the phenyl group. These minima, of which the former was found to be the more stable, differed in energy by only *ca* 2 kJ/mol. It is likely these orientations depend on the weak intermolecular hydrogen bonds present in the crystal as shown for the two crystal structures of $PhCb^oNH_2$ reported here.

Table 2 also includes interatomic distances calculated, at the MP2/6-31G* level, for two minima of the anion $[PhCb^oNH]^-$ which we were unable to prepare because the amine $PhCb^oNH_2$, when treated with bases powerful enough to deprotonate it, suffered general decomposition, apparently after the initial deboronation to *nido*-C_2B_9 species that characteristically occurs when a *closo*-C_2B_{10} species reacts with suitable nucleophiles. The preferred orientation for the *exo* NH unit is like that of the isoelectronic hydroxy species (X = OH), but the greater π-donor character of $[NH]^-$ than [OH] is reflected in the

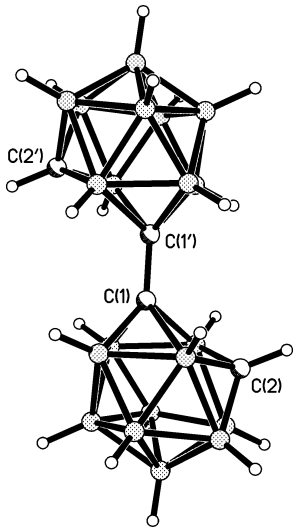
longer C1-C2 distance (*ca* 2.29 Å) found for $[PhCb^{o}NH]^{-}$. The minimum with the phenyl group alongside the two cage carbons (C1 and C2) shown in figure 7(a) is estimated to be 0.6 $kJmol^{-1}$ more stable than the minimum with the phenyl group perpendicular to the C1-C2 plane. The effect of the two phenyl group orientations on the C1-C2 distances in $[PhCb^{o}NH]^{-}$ is only 0.01 Å.

Looking at the X-ray data for the two salts of $[PhCb^{o}O]^{-}$,[2] the two phenyl group orientations are similar to those found for $[PhCb^{o}NH]^{-}$. The slightly shorter C1-C2 distances found when the phenyl group is perpendicular to the plane of the cage carbons C1 and C2 in these anions suggest an opposite effect to that found in neutral aryl-*ortho*-carboranes. The potentially electron-withdrawing character of the phenyl group and the potentially electron-donating character of the cage in these anions may result in some electron density being transferred from the C2 atom to the π-bond orbital of the phenyl group. This would account for shortening of the C1…C2 distance when the phenyl group is perpendicular to the plane of C1 and C2.

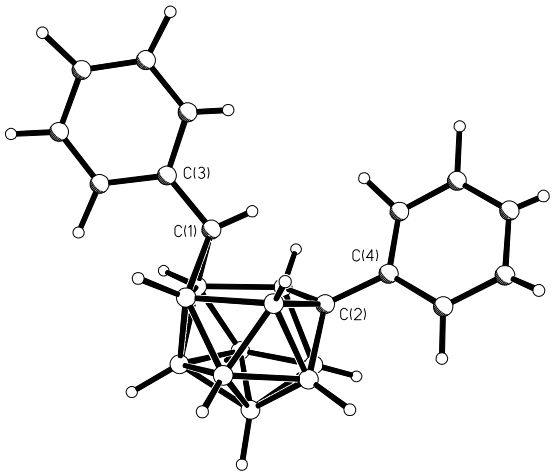
Figure 7. (a) Calculated structure of $[PhCb^{o}NH]^{-}$, (b) Experimental structure of $[PhCH_2Cb^{o}CHPh]^{-}$ (Ref. 11), (c) Experimental structure of $[HCb^{o}]_2^{2-}$ (Ref. 9) and (d) Experimental structure of $[PhCb^{o}HPh]^{-}$ (Ref. 25)



(a) (b)



(c)



(d)

A further structural feature of carboranes bearing π-donor substituents is the deviation from planarity of the CB_4 pentagon (that containing atoms C2 B3 B4 B5 B6) over which the carbon atom that bears the π-donor substituent, C1, is located. In a homogeneous icosahedral cluster such as $[B_{12}H_{12}]^{2-}$, such a 'tropical' set of atoms is necessarily planar.[26] However, in *ortho*-carborane, HCb^oH, the CB_4 pentagons beneath the carbon atoms are non-planar. This is a consequence of the differing covalent bonding radii of boron and carbon atoms, which in turn reflects their different nuclear charges and electronegativities. The shorter C1-C2 (1.62 Å) and C-B (1.72 Å) bonds than B-B bonds (1.77 Å) in HCb^oH make its pseudo-spherical shape slightly flattened in the vicinity of the carbon atoms, which are depressed slightly towards the cluster centre. Thus, in HCb^oH, atom C2 lies 0.065 Å beneath the plane in which boron atoms B3 to B6 lie, folded down towards the cluster centre. This displacement from planarity, listed as 'δ' in Table 1, increases as the interatomic distance C1-C2 increases.

Also included in Table 1 are interatomic distances for some other systems bearing π-donor substituents on a cage carbon atom (C1). They include the thiocarborane anion $[PhCb^oS]^-$ and the trisulfide $PhCb^oS_3Cb^oPh$, the structures of which (but not that of $PhCb^oSH$) have been determined here and elsewhere.[3] Similar distortions from the shape of the parent carborane, HCb^oH, are evident, though compared with the analogous

oxygen systems, the sulfur systems show lesser distortions when negatively charged, reflecting the lesser π-donor capacity of the sulfur ligand than the oxygen analogue. Other thio-carborane systems have been found by other research groups to show similar distortions.[17,27]

By contrast, the benzylidene anion $[PhCH_2Cb^oCHPh]^-$ (Fig. 7(b)) characterised by Chui, Li and Xie[11] shows the dramatically increased cage carbon-carbon bond length of 2.416(3) Å to be expected when the benzylidene substituent is involved in a full *exo*-double bond (1.365(3) Å), C1=CHPh. The electron-withdrawing capacity of the *ortho*-carborane cage ensures that the anionic charge (formally on the methylene carbon atom deprotonated on forming this anion from 1,2-dibenzyl-*ortho*-carborane, $PhCH_2Cb^oCH_2Ph$,) is delocalized into the cage. The cage as a result opens up (even more than the systems already discussed) towards the *nido*-type fragment of a 13-vertex system expected of a carborane containing 12 skeletal atoms held together by 14 skeletal electron pairs. Significantly, the benzylidene unit PhCH in $[PhCH_2Cb^oCHPh]^-$ lies in a plane perpendicular to the C-C1-C2 plane (Fig. 7(b)), indicating that the *exo* C1=C π-bonding involves a tangential p AO on C1 that lies in that plane.

Remarkably similar distortions of the carborane cage to those in $[PhCH_2Cb^oCHPh]^-$ are found in Hawthorne's dicarboranyl dianion $[HCb^o]_2^{2-}$, (Fig. 7(c)) which also contains an *exo* C1=C double bond (C1-C2 2.41 Å, C=C 1.37 Å).[9,10] That these cages should nevertheless not be regarded as fully opened up to *nido* structures can be seen by comparison with the fully *nido* skeletal structures of anions $[RCHB_{10}H_{10}CR]^-$ (Fig. 7(d)) (R = Ph or Me, C1-C2 2.86 and 2.82 Å respectively)[25,28,29] or with the dianion $[RCHB_{10}H_{10}C]_2^{2-}$ (R = H, C1-C2 2.79 Å)[10] derived from *closo* parents $RCB_{10}H_{10}CR$ and $HCb^o{}_2$ respectively by hydride reduction. In these last systems, the C1 carbon atom has moved to a distance of *ca* 2.8 Å away from C2, the carbon atom to which it was attached in the parent neutral *ortho*-system. This is appropriate for 12-atom *nido* systems in which the carbon atoms occupy opposite sites on a (folded) six-atom open face as shown in Figure 7(d) for $[PhCHB_{10}H_{10}CPh]^-$.[25] Note that the RCH system, incorporating C1, has an orientation with respect to the CB_{10} residue appropriately twisted through 90° from the

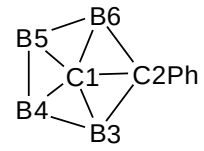
orientation of the benzylidene residue PhCH in the anion $[PhCH_2Cb^oCHPh]^-$. Experimental and calculated (MP2/6-31G*) geometric data for the dicarborane $HCb^o{}_2$ and related derivatives are listed in the ESI.[9,10,30]

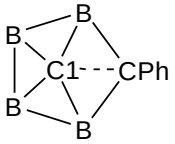
Interestingly, calculations on the related dianions $[RCB_{10}H_{10}CR]^{2-}$ (R=Ph or Me), which can in principle be formed from the known monoanions[25,28,29] $[RCHB_{10}H_{10}CR]^-$ by removal of the *endo*-proton on C1, show C1…C2 distances of *ca* 2.50 Å (R = Ph), closer to those in $[PhCH_2Cb^oCHPh]^-$ and $[HCb^o]_2{}^{2-}$ (Figs 7(b) and 7(c) respectively). Cartesian coordinates of the MP2/6-31G* optimized geometry for $[PhCB_{10}H_{10}CPh]^{2-}$ are in the ESI. The full sequence of structures is illustrated schematically in Fig 8, which shows how the cage C1…C2 bond lengthening induced by a π-donor ligand on C1, with which we are concerned here, can be regarded as only partial cage opening towards a *nido*-structure, which is not even reached for the systems containing *exo* C1=C double bonds.

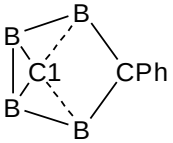
Figure 8

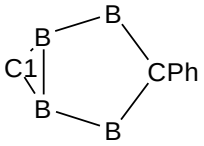
Progressive cage opening of compounds PhCb^{o}X as X varies

X	C1….C2	C-X	Ref.
H(calc)	1.66		8
F(calc)	1.67	1.35	
OH	1.72	1.37	
$S_3Cb^{o}Ph$	1.74	1.79	
NH_2	1.77	1.39	
NH_2.HMPA	1.84	1.36	
S^-	1.84	1.75	3
O^-	2.01	1.24	2
O^-	2.07	1.23	
NH^-(calc)	2.30	1.30	
CH_2^-(calc)	2.36	1.36	
HPh^-	2.86		25









The bonding environment around C1, the atom bearing the π-donor substituent

Figure 8 and Table 1 show how the compounds PhCb^{o}X studied here and elsewhere[15,25] now chart relatively fully the progression from a 12-atom *closo* to a 12-atom near-*nido* structure that occurs as the degree of π-bonding from a substituent X to the hypercarbon atom C1 builds up. The build-up occurs in the sequences X = F<OH<NH_2 or O^-<NH^- <$CHPh^-$ as the electronegativity of the donor atom decreases (and so its π-donor capacity increases), and as the C1X unit effectively progresses from a unit with three atomic orbitals available for skeletal bonding to one with two atomic orbitals available for skeletal bonding. This is because one of the tangentially-orientated p AO's on C1 (that in the X-C1-C2 plane) becomes progressively less available for skeletal bonding as its

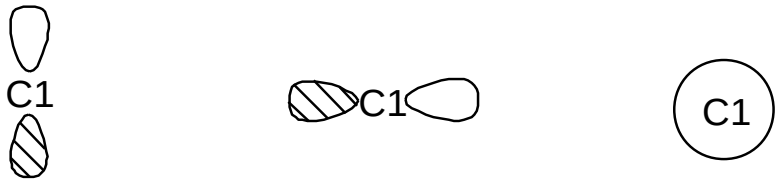
involvement in *exo*-π-bonding increases. The movement of the C1X unit over the CB_4 pentagon (which it caps when X=H), progressively further away from C2, is reminiscent of the lateral displacement shown by cationic ligated metal units ML_x^{n+} over the open face of a *nido*-shaped $[CB_{10}H_{11}]^{3-}$ residue in metalla-monocarba-borane complexes $CB_{10}H_{11}ML_x$, as the number of frontier orbitals the metal unit can offer decreases from three to two.[31] Indeed, it is helpful to regard the C1X units in the present series of compounds as dicationic, $[C1X]^{2+}$, in considering the sites they occupy and the orientations they adopt over the open pentagonal (C2B3B4B5B6) face of the *nido*-shaped $[RCB_{10}H_{10}]^{3-}$ residue.

The frontier orbitals of the $[RCB_{10}H_{10}]^{3-}$ residue (Fig 9) resemble those of a pyrrole ring π-system, i.e. like those of a cyclopentadienide anion but with one heteroatom in the ring of higher electronegativity than the other atoms, so breaking the degeneracy of the HOMO. The HOMO of $[PhCB_{10}H_{10}]^{3-}$ (Fig 9, orbital *nido* (i)) is an orbital that donates electronic charge to the $[C1X]^{2+}$ unit into the vacant 'tangentially' orientated p AO on C1, the one not involved in π-bonding between C1 and X (orbital CX(i), Fig 9). Frontier orbital *nido*-(ii) will be a less suitable orbital to donate charge to the $[C1X]^{2+}$ cation because involvement of carbon makes this orbital lower in energy. The orbital *nido*-(iii), suitable to interact with a radially-orientated orbital on C1, is of yet lower energy.

Orbitals *nido*-(i) and *nido*-(ii) are thus orientationally discriminating with respect to X. If X has cylindrical symmetry, as in the case of X = F, O^- or S^- this has no structural consequences. However, where X = OH, NH_2, CH_2^-, etc., the plane in or near which the hydrogen atoms lie will preferably be perpendicular to the X-C1-C2 plane so that the 'lone pair' on X responsible for π-donation to C1 (orbital C1X(ii)) lies in that plane, leaving orbital C1X(i) free for bonding to B3, B4, B5 and B6. Similar orientational effects on π-donor ligands are familiar features of transition metal coordination chemistry.[32]

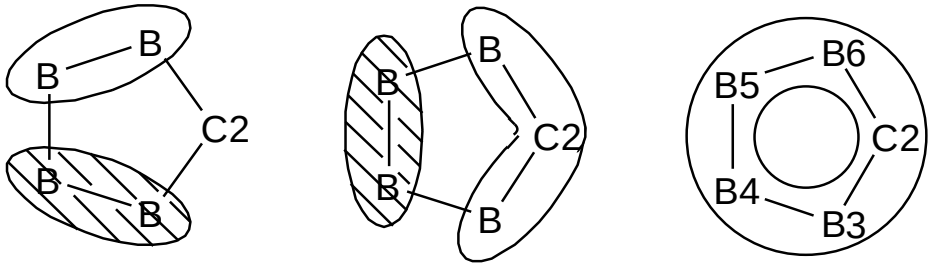
Figure 9. The frontier orbitals involved in bonding a $[C1X]^{2+}$ unit to a *nido*-shaped $[PhCB_{10}H_{10}]^{3-}$ residue

(a) $[C1X]^{2+}$ unit viewed down the X-C1 axis



C1X(i) C1X(ii) C1X(iii)

(b) $[PhCB_{10}H_{10}]^{3-}$ unit viewed down the X-C1 axis



nido-(i) *nido*-(ii) *nido*-(iii)

In the cases of the anions $[PhCb^{o}O]^{-}$ and $[PhCb^{o}S]^{-}$ which we previously described[2,3] as novel examples of a carbonyl or thiocarbonyl ligand occupying a pentuply-bridging site over the *nido*-shaped $[PhCB_{10}H_{10}]$ residue, the LUMO of CO^{2+} will be the orbital C1X(iii) that in neutral CO accommodates the lone pair on carbon, which will receive electronic charge from orbital *nido*(iii), whilst *nido*(ii) and particularly *nido*(i) will transfer electronic charge into the π^* orbitals of the CO or CS ligand unit, i.e. into C1X(ii) and C1X(i) respectively, reducing the C1X bond order from three in free CO or CS to *ca* two in the oxy- or thio-carborane anion $[PhCb^{o}X]^{-}$. Alternatively, treating these

anions as derived from the parent hydroxy derivative or thiol $PhCb^{o}X$ (where X = OH or SH), in which the bond order of the *exo* C1X bond is essentially a single bond strengthened only slightly by C1-X dative π bonding from an oxygen or sulfur 'lone pair' in an orbital matching C1X(ii), then deprotonation at oxygen or sulfur allows the electron-withdrawing effect of the carborane cage, no longer competing for electron density with the proton that has been removed, to lead to a dramatic increase in the C1-X bond order to about 1.3 to 1.5.[2,3]

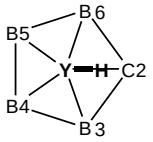
When the *exo*-bonds to the hypercarbon C1 are fully double bonds, between two carbon atoms, as is the case in the anions $[PhCH_2Cb^{o}CHPh]^-$ and $[HCb^{o}]_2^{2-}$ (Figs 7(b) and 7(c) respectively),[9-11] the unit $[C1X]^{2+}$ occupies a site over the four boron atoms B3, B4, B5 and B6, to bond to which it uses primarily orbitals C1X(i) and C1X(iii), C1X(ii) being involved in the π-component of the C=C double bond. However, there is still very weak C1-C2 bonding, which is only fully broken in the case of the limiting anionic systems $[RCHB_{10}H_{10}CR]^-$ (R= Ph or Me)[25,25,29] (Fig 7(d)) in which atom C1, instead of bearing one *exo* substituent atom to which it is linked by a bond of partial or fully double bond character, now bears two σ–bonded substituents, R and H, leaving merely two AOs (conveniently thought of as tetrahedrally disposed with respect to those σ–bonded substituents) with which to bond to the *nido* CB_{10} cage. These anionic systems are thereby converted into 12-atom 14 skeletal electron pair *nido*-systems.

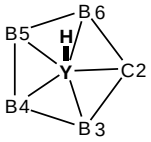
The orientational effect of the π-donor substituent: energies and bond distances

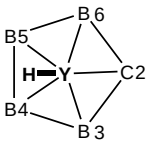
In the *ortho*-carboranes discussed here, we have noted that, for derivatives such as $PhCb^{o}NH_2$ or $PhCb^{o}OH$, where the π-donor atom bears one or two substituent hydrogen atoms, the location of these hydrogen atoms indicates a consistent pattern of orientational preferences about the C1-X bond. To probe such effects further, we have carried out *ab initio* calculations using hydrides $HCb^{o}X$ as model compounds, exploring how the orientation of the group X affects the C1-C2 distance and overall energy. The model geometries were optimised at the MP2/6-31G* level of theory with a fixed C2-C1-Y/Z-H torsion angle of 0°, 90° and 180°.

Figure 10 shows that, although the *exo*-C1-Y or C1-Z distances do not change much with the orientation of their substituent hydrogen atoms, the cage C1-C2 distances in these systems show truly remarkable orientational effects. When the substituent X is orientated with a torsion angle of 0º and/or 180º, i.e. when the hydrogen atom on Y or Z lies in the C2-C1-Y/Z plane, the distance C1-C2 is significantly shorter than when the torsion angle is 90º. The differences are particularly pronounced for the anions (X = CH_2^- and NH^-). The orientational effect on the overall energy depends on the substituent, e.g. large for X = CH_2^- (orientational energy difference 7.7 kJ/mol) but negligible for X = OH. These results overwhelmingly confirm the description of the bonding environment at the hypercarbon C1 first suggested here in 1987 for the [$PhCb^oO^-$] anion.[2]

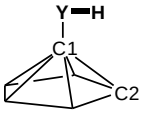
Figure 10. Bond length (Å) and relative energy ($kJmol^{-1}$) data for MP2/6-31G* optimised geometries for model compounds $HCb^{o}X$. The torsion angles C2-C1-Y/Z-H in these model compounds were fixed at 0º, 90º or 180º.

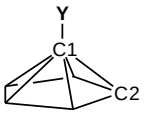


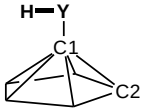




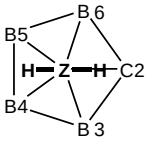
0º 90º 180º

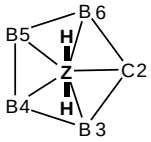




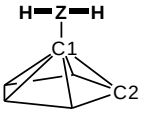


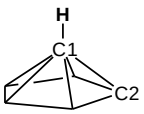
X = NH^-, Y = N^-	C1-C2	1.829	2.305	1.672
	C1-N	1.310	1.295	1.328
	Relative Energies	+4.1	0	+4.0
X = OH, Y = O	C1-C2	1.631	1.659	1.611
	C1-O	1.383	1.378	1.384
	Relative Energies	+0.1	0	+0.1
X = SH, Y = S	C1-C2	1.627	1.651	1.620
	C1-S	1.801	1.790	1.802
	Relative Energies	+0.6	0	+0.7





0º 90º

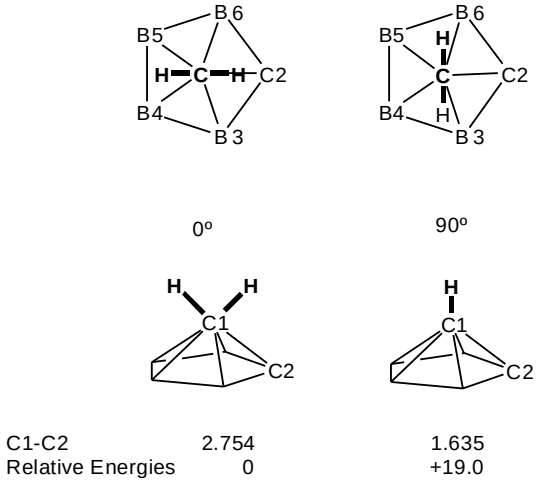




X = CH_2^-, Z = C^-	C1-C2	1.637	2.402
	C1-C	1.391	1.356
	Relative Energies	+7.7	0
X = NH_2, Z = N	C1-C2	1.612	1.713
	C1-N	1.396	1.383
	Relative Energies	+1.3	0

By contrast the orientational preference for the anionic systems $[RCHB_{10}H_{10}CR]^-$ (R= Ph or Me) [25,29] (Fig. 7(d)) where the two σ–bonded substituents, R and H, at C1 lie in the C-C1-C2 plane is confirmed by comparison of the energies for the two optimized geometries of the model compound $HCb^oH_2^-$ shown in figure 11. This is expected as merely two AOs - tetrahedrally disposed with respect to those σ–bonded substituents - are available to bond to the *nido* CB_{10} cage. The optimized geometry of *nido*-$HCb^oH_2^-$ where the hydrogens at C1 are at 90º to the C1-C2 bond shows a C1-C2 bond length of 1.635 Å (which is curiously similar to 1.62 Å found in *ortho*-carborane, HCb^oH).[8] The bond distances of 2.099 Å for C1-B3/B6 and of 1.922 Å for C1-B4/5 in this geometry are consistent with tetrahedral hybridisation at C1, with one sp^3 hybrid AO on C1 used for the bond to C2, the other forming a 3c2e bond to boron atoms 4 and 5.

Figure 11. Bond length (Å) and relative energy ($kJmol^{-1}$) of MP2/6-31G* optimised geometries for model compound $HCb^oH_2^-$. These geometries were C_s symmetry constrained.



Before leaving the question of the orientational preferences of *exo* π-bonding groups X in compounds $PhCb^oX$ (X is orientated so that the C-X *exo* π-bond uses a pAO on the cage

carbon atom, C1, that lies in the C2-C1-X plane, orbital C1X(ii) in Fig 9), it is worth noting that this contrasts with the situation in derivatives of the aromatic ring systems with which carborane clusters ("3-dimensional aromatic clusters") are often compared.[33] In aromatic ring systems, *exo* π-bonding (or conjugative interaction with unsaturated substituents) necessarily involves the pAO on carbon orientated perpendicular to the C_n ring plane, as in cyclopentadienone, quinones etc.

NMR Spectroscopic Aspects

Comprehensive multinuclear NMR data for compounds made here are reported in the experimental section. Salient features deserve brief mention here in view of the structural and bonding issues discussed.

Earlier boron NMR studies on hydroxy and thio carboranes revealed that the substituent at C1 affected the antipodal B12 boron shift.[3,5] It is apparent from these and our present studies that the stronger the *exo*-π-bond is at C1, the more shielded the antipodal B12 shift becomes. Here we find the antipodal effect also occurs for the proton attached to the antipodal B12 atom (i.e. B12H). In acetone, the proton shift of B12H moves from 2.35 to 1.92 and 1.17 ppm for $PhCb^oH$, $PhCb^oOH$ and $[PhCb^oO^-]$, respectively.

Solvent effects on the acidic *exo*-hydrogens at the cage carbon atoms of carboranes in NMR spectroscopy are well documented.[34,35] Here solvent effects on the acidic hydrogens of OH and NH_2 groups for $PhCb^oOH$ and $PhCb^oNH_2$ are significant. From chloroform to acetone the ^{11}B shift corresponding to the antipodal B12 moves from -8.8 to -11.2 for $PhCb^oOH$ and from -8.3 to -9.6 for $PhCb^oNH_2$. The hydrogens of the OH and NH_2 groups interact with the weakly basic acetone molecules, resulting in increased electron densities at the O and N atoms. The O and N atoms are therefore able to form stronger π-bond overlap with the C1 atom, which in turn influences the boron shift at B12. The C1 shifts for both compounds are about 7 ppm to higher frequency on changing from chloroform to acetone.

A previous study on C-hydroxy carboranes and their anions made use of *ab initio* computations to examine their likely structures by optimising their geometries and calculating the NMR shifts derived from these geometries at the HF/6-31G* level of theory.[36] We assigned the observed ^{11}B NMR shifts of these compounds by 2D ^{11}B-^{11}B{^{1}H} COSY spectra and used higher levels of theory for calculated NMR shifts. The agreement between observed and computed NMR data for the anion [HCb^{o}O^{-}] is much better at the GIAO-B3LYP/6-311G*//MP2/6-31G* levels of theory. Computed GIAO-B3LYP/6-311G* NMR data generated from the MP2/6-31G* optimised geometries of other compounds discussed here (Table 2) are included in the experimental section, as these molecular geometries are likely to be found in solution.

The reported boron NMR data for Xie's anion [PhCH$_2$Cb^{o}CHPh]$^{-}$ clearly indicate a lack of symmetry in solution.[11] Calculated GIAO-NMR shifts generated from the X-ray molecular geometry of the benzylidene anion [-2.0 (B9), -3.0 (B6), -5.1 (B7), -7.5 (B3), -11.8 (B12), -12.0 (B4), -14.2 (B11), -18.1 (B5), -21.7 (B10), -28.1 (B8) ppm] are in good agreement with the observed (but unassigned) shifts [-1.6 (2B), -5.3 (2B), -11.0(1B), -11.9 (1), -13.5(1), -16.0 (1), -23.0 (1), -26.2 (1) ppm]. The barrier to rotation about the short C1-C*exo* bond must therefore be substantial. This is supported by the calculated data of the model geometry HCb^{o}CH$_2^{-}$, which gives a rotational barrier of 7.7 kJ/mol (Figure 10).

Concluding comments

This paper has documented the structural changes, and explored the bonding implications thereof, over a series of derivatives of *ortho*-carborane, RCb^{o}X, bearing substituents R and X on the two hypercoordinated cage carbon atoms, X being able to act as a π-donor and so form an *exo* X-C bond of bond order between 1 and 2. Our own work has involved systems with R = Ph,[1-5] though we have included in our discussions literature data present on other systems.[9-11,15,25]

Herein, we have reported new X-ray structural studies on systems $PhCb^{o}X$ with X = OH (as a hemihydrate), O^- (as the methyltriphosphonium salt), NH_2 (as the parent system and HMPA adduct) and $S_3Cb^{o}Ph$, and extended our earlier reports of systems with X = O^- or S^- (as proton sponge salts).[2,3] We have also reported new synthetic and multinuclear NMR spectroscopic studies on such systems and carried out MP2/6-31G* calculations to determine the optimised geometries for systems $PhCb^{o}X$ with X=H (as a reference compound in which X is not a π-donor), F, OH, SH, NH_2, OLi, ONa, S^-, O^-, NH^-, CH_2^- and H_2^- (another reference compound, a *nido*-carborane anion on which the potentially π-bonding atom of group X is replaced by two terminal hydrogen atoms one *exo*, one *endo*). Our data on $PhCb^{o}X$ systems reveal the following

1. As expected, the degree of π-bonding in the *exo* C1-X bond increases with the π-donor capacity of X, i.e. as the electronegativity of X decreases, as in the sequences CF < COH < CNH_2, CO^- < CNH^- < CCH_2^-, COH < CO^- or CNH_2 < CNH^-.
2. The length of the cage C1-C2 bond increases (and its bond order decreases) as the C1-X bond order increases, i.e. in the sequences just noted, e.g. from 1.67 Å when X = F to 1.77 Å (X = NH_2), 2.07 Å (X = O^-) and 2.36 Å (X = CH_2^-).
3. The lengthening of the cage C1-C2 bond may be regarded as the standard[37] opening up, from *closo* towards *nido*, expected as electron density is transferred from X to the cage, though comparison with the *nido* anion $[PhCB_{10}H_{10}CHPh]^-$,[25] i.e. $[PhCb^{o}HPh]^-$ for which C1-C2 is 2.86 Å, shows that opening up to be incomplete.
4. The preferred orientation of the group X with respect to the cage bond C1-C2, whether revealed by X-ray studies or by MP2/6-31G* calculations (which rival, even surpass, X-ray studies in reliability and precision for carboranes) shows that the *exo* π-bonding uses a tangential AO on C1 that lies in the C2-C1-X plane, thereby reducing its availability for C1-C2 sigma bonding.
5. The migration of the unit C2-Ph away from C1-X over the pentagon C1B2B3B4B5, as C1-X π-bonding increases in the systems, can alternatively be

rationalised by frontier orbital considerations of the type long familiar to coordination chemists discussing the sites of cationic metal units $[ML_x]^{n+}$ over *nido*-mono-carba-borane anionic residues $[RCB_{10}H_{10}]^{3-}$.[31]

A final comment about implications for future work is appropriate. Throughout the series of systems RCb^oX discussed here, it has been evident that the extra electronic charge made available to the cage as C-X π-bonding builds up causes the cage to open up, towards the *nido* structure expected if an extra skeletal pair of electrons were added. This raises the question as to whether reclosure of the cage can be effected by oxidation of such systems, leaving a unit X *exo* π-bonded to a (hyper)*closo* cage. We suggest it would be profitable to explore the issue, a timely pointer to which has been provided by an interesting pair of papers by Balakrishnarajan and Hoffmann[38] that have appeared since the work reported here was completed. They have carried out calculational studies to explore what happens structurally to B_6, B_7, B_{10}, B_{12} *closo* borane cages bearing *exo* O- or NH- units when they are oxidised, and drawn perceptive analogies with aromatic ring redox chemistry, 3-dimensional 'quinonoid' structures etc. This area looks ripe for future experimental study.

Experimental Section

General

NMR spectra were measured using Varian Unity-300 (^{1}H, ^{11}B, ^{13}C), Bruker AM250 (^{1}H, ^{13}C), Bruker Avance 400 (^{1}H, ^{11}B, ^{13}C) and/or Varian Inova 500 (^{1}H, ^{11}B) instruments. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^{1}H NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm; C_6D_6, 7.15; $(CD_3)_2CO$, 2.05; $(CD_3)_2SO$, 3.31). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm; $(CD_3)_2CO$, 30.0; $(CD_3)_2SO$, 39.5). ^{11}B NMR spectra were referenced externally to $Et_2O.BF_3$, δ = 0.0 ppm. Peak assignments of cage borons and hydrogens were determined where possible with the aid of 2D $^{11}B\{^{1}H\}$-$^{11}B\{^{1}H\}$ COSY, selective $^{1}H\{^{11}B\}$ and ^{1}H-^{11}B correlation spectra. Infrared spectra were recorded from KBr discs on Perkin Elmer 1600 series FTIR or Perkin Elmer 1720X FTIR spectrometers. Mass spectra (MS) were recorded on a VG Micromass 7070E instrument under E.I conditions (EI) at 70 eV or or on a Micromass LCT instrument using Electrospray (ES) Ionisation with a cone voltage of 30 volts. Values of M show the isotope range $^{10}B_n$ to $^{11}B_n$ including a ^{13}C contribution if observed. Elemental carbon, hydrogen and nitrogen analyses were performed using Exeter Analytical CE-440 or Carlo Erba Strumentazione EA Model 1106 instruments. Boron was determined by oxygen flask combustion followed by atomic absorption on a Perkin Elmer 5000 Atomic Absorption Spectrophotometer. Sulfur was converted to sulfate and analysed by ion chromatography.

All manipulations were carried out under dry, oxygen-free N_2. Dry diethyl ether (Et_2O) was obtained by reflux and distillation over Na wire. Hexanes and toluene were distilled over Na and K respectively. Dimethoxyethane was dried by distillation from potassium. The phenyl-carboranes, 1-phenyl-*ortho*-carborane and 1-phenyl-*meta*-carborane, were made by our copper coupling method[39] with iodobenzene and the related parent carborane. The ylid $Ph_3P{=}CH_2$ was made by a literature method.[40] Other reagents were used as supplied. Preparative thin layer chromatography (tlc) was conducted on pre-spread silica coated sheet Merck Art. No. 5735.

NMR data for 2-phenyl-*ortho*-carborane PhCb^{o}H (i.e. 1-phenyl-*ortho*-carborane[13,35] but numbered here for direct comparison with other 1-X-2-phenyl-*ortho*-carborane derivatives discussed in this study)

Observed NMR ($CDCl_3$): $^{1}H\{^{11}B\}$: 7.50 (2H, *ortho* CH), 7.38 (1H, *para* CH), 7.34 (2H, *meta* CH), 3.97 (1H, CH), 2.62 (2H, B3,6H), 2.53 (2H, B7,11H), 2.46 (B12H), 2.35 (3H, B8,10,9H), 2.30 (2H, B4,5H). $^{13}C\{^{1}H\}$: 133.4 (*ipso* aryl C), 129.9 (*para* aryl C), 128.8 (*meta* aryl C), 127.5 (*ortho* aryl C), 76.5 (C2), 60.1 (C1). ^{11}B: -1.2 (1B, d, B12), -3.5 (1B, d, B9), -8.1 (2B, d, B8,10), -9.9 (2B, d, B7,11), -10.3 (2B, d, B3,6), -11.9 (2B, d, B4,5). NMR ($(CD_3)_2CO$): $^{1}H\{^{11}B\}$: 7.70 (2H, *ortho* CH), 7.55 (1H, *para* CH), 7.50 (2H, *meta* CH), 5.16 (1H, CH), 2.55 (2H, B3,6H), 2.50 (2H, B7,11H), 2.35 (B12H), 2.24 (5H, B7,8,9,10,11H). $^{13}C\{^{1}H\}$: 134.6 (*ipso* aryl C), 130.9 (*para* aryl C), 130.1 (*ortho* aryl C), 128.8 (*meta* aryl C), 78.1 (C2), 61.7 (C1). ^{11}B: -2.8 (1B, d, B12), -4.8 (1B, d, B9), -9.1 (2B, d, B8,10), -10.9 (2B, d, B3,6,7,11), -12.8 (2B, d, B4,5).

Calculated NMR/ppm of 2-phenyl-*ortho*-carborane with tors2 at 18.5°: ^{1}H: 7.53 (2H, *ortho* CH), 7.51 (1H, *para* CH), 7.46 (2H, *meta* CH), 3.85 (1H, CH), 3.05 (2H, B7,11H), 3.04 (B12H), 2.96 (B9H), 2.93 (2H, B8,10H), 2.89 (2H, B3,6H), 2.77 (2H, B4,5H). ^{13}C: 144.5 (*ipso* aryl C), 135.4 (*para* aryl C), 134.7 (*meta* aryl C), 132.8 (*ortho* aryl C), 81.9 (C2), 63.6 (C1). ^{11}B: -2.4 (1B, B12), -3.6 (1B, B9), -8.5 (2B, B8,10), -11.8 (2B, B3,6), -12.0 (2B, B7,11), -14.0 (2B, B4,5).

Calculated NMR/ppm of 2-phenyl-*ortho*-carborane with tors2 at 90°: ^{1}H: 7.88 (2H, *ortho* CH), 7.58 (1H, *para* CH), 7.48 (2H, *meta* CH), 3.39 (1H, CH), 3.35 (2H, B3,6H), 3.13 (B12H), 2.95 (B9H), 2.88 (2H, B8,10H), 2.84 (2H, B7,11H), 2.79 (2H, B4,5H). ^{13}C: 142.2 (*ipso* aryl C), 138.3 (*ortho* aryl C), 136.5 (*para* aryl C), 134.4 (*meta* aryl C), 84.9 (C2), 69.9 (C1). ^{11}B: 0.0 (1B, B12), -3.7 (1B, B9), -9.6 (2B, B8,10), -10.5 (2B, B7,11), -13.3 (2B, B4,5), -15.2 (2B, B3,6).

NMR data for 1-hydroxy-*ortho*-carborane HCb^{o}OH

NMR[36,41] ($CDCl_3$)/ppm: $^{1}H\{^{11}B\}$: 4.95 (br, OH), 3.96 (1H, CH), 2.52 (2H, BH), 2.43 (2H, BH), 2.25 (1H, B9H), 2.13 (2H, BH), 2.04 (2H, B7,11H), 1.90 (1H, B12H); $^{13}C\{^{1}H\}$: 98.7 (COH), 62.9 (CH). ^{11}B: -3.8 (1B, d, B9), -12.1 (7B, d, B3,4,5, 6,8,10,12), -14.5 (2B, d, B7,11).

NMR ($(CD_3)_2CO$)/ppm: $^{1}H\{^{11}B\}$: 4.84 (1H, CH), 2.53 (2H, B3,6H), 2.39 (2H, B4,5H), 2.14 (1H, B9H), 2.05 (2H, B7,11H), 1.93 (2H, B8,10H), 1.78 (1H, B12H); $^{13}C\{^{1}H\}$: 102.0 (COH), 65.6 (CH). ^{11}B: -4.7 (1B, d, B9), -12.0 (4B, d), -12.7 (2B, d), -13.2 (1B, d, B12), -17.9 (2B, d, B7,11).

Calculated NMR/ppm: ^{1}H: 3.79 (1H, CH), 3.08 (OH), 2.94 (4H, B3,4,5,6H), 2.89 (1H, B9H), 2.69 (2H, B7,11H), 2.67 (2H, B8,10H), 2.57 (1H, B12H); ^{13}C: 104.7 (COH), 69.7 (CH). ^{11}B: -3.1 (B9), -11.7 (B12), -11.8 (B8,10), -12.6 (B4,5), -14.5 (B3,6), -15.3 (B7,11).

NMR data for 1-hydroxy-*meta*-carborane $HCb^{m}OH$

NMR[36,41] ($CDCl_3$)/ppm: $^{1}H\{^{11}B\}$: 3.27 (br, OH), 2.96 (2H, B2,3H), 2.84 (1H, CH), 2.62 (1H, B5H), 2.47 (2H, B4,6H), 2.07 (2H, B9,10H), 1.98 (2H, B8,11H), 1.94 (1H, B12H); $^{13}C\{^{1}H\}$: 101.4 (COH), 51.6 (CH). ^{11}B: -4.5 (1B, d, B5), -11.2 (2B, d, B4,6), -13.0 (2B, d, B9,10), -15.8 (5B, d, B2,3,8,11,12). Calculated NMR/ppm: ^{1}H: 3.50 (2H, B2,3H), 3.05 (2H, B4,6H), 2.88 (1H, B5H), 2.51 (1H, CH), 2.65 (2H, B8,11H), 2.54 (2H, B9,10H), 2.47 (1H, B12H), 2.17 (COH); ^{13}C: 110.0 (COH), 56.6 (CH). ^{11}B: -6.3 (B5), -11.6 (B4,6), -13.6 (B9,10), -16.2 (B8,11), -16.9 (B12), -17.4 (B2,3).

NMR data for 1-hydroxy-*para*-carborane $HCb^{p}OH$

NMR[36,41] ($CDCl_3$)/ppm: $^{1}H\{^{11}B\}$: 3.32 (br, OH), 2.46 (5H, BH), 2.44 (1H, CH), 2.06 (5H, BH); $^{13}C\{^{1}H\}$: 106.4 (COH), 46.8 (CH). ^{11}B: -12.8 (5B, d), -17.0 (5B, d). Calculated NMR/ppm: ^{1}H: 3.00 (B2-5H), 2.59 (B6-11H), 2.21 (CH), 2.03 (OH); ^{13}C: 117.3 (COH), 55.1 (CH). ^{11}B: -13.7 (B2-5), -18.0 (B6-11).

1-hydroxy-2-phenyl-*ortho*-carborane $PhCb^{o}OH$

The compound 1-phenyl-*ortho*-carborane (2.20g, 10 mmole) was dissolved in dry toluene (20mL) and lithiated with a solution of n-BuLi (4mL, 2.5M in hexanes, 10 mmol). After stirring under reflux for two hours, the solution was cooled in an ice bath before dry ether (20mL) was added. Over a period of twenty minutes, benzoyl peroxide solution was added dropwise to the yellow solution whilst still in the ice bath. This resulted in a cloudy orange solution which reverted back to yellow at the end of the addition. The solution was left to reflux for a further two hours. After cooling to room temperature, distilled water (30mL) was added dropwise, followed by 10% sodium

hydroxide solution (50mL), giving two layers which were transferred to a separating funnel. The organic layer was isolated and washed with the sodium hydroxide solution a further twice. The combined aqueous layers were acidified with HCl, giving a white precipitate. This solution was washed with three portions of ether and the organic layers washed with potassium hydrogen carbonate solution (3 x 50mL). The organic layers were dried over $MgSO_4$, filtered, and the solvent removed, giving a viscous yellow oil which solidified after two hours drying on a vacuum line. The resulting yellow solid was recrystallised from wet hexane to give clear colourless needles of the 1-hydroxy-2-phenyl-*ortho*-carborane hemihydrate in 21% yield (based on 50% conversion). M.p.: 71ºC. Analysis ($C_8H_{16}B_{10}O{\cdot}0.5H_2O$): C 38.8 (39.2), H 7.0 (7.0). MS (EI): M, 232-239 ($C_8H_{16}B_{10}O$ = 236). IR: cm^{-1} 3644 s, 3484 s (O-H stretch); 2594 s (carboranyl B-H); 1616 m; 1489 m; 1439 m; 1226 s (C-O); 1067 m; 1030 m; 939 w; 883 w; 800 w; 726 m; 687 m; 572 m; 410 m. NMR ($CDCl_3$)/ppm: $^1H\{^{11}B\}$: 7.72 (2H, d, *ortho*-aryl CH), 7.45 (1H, t, *para*-aryl C-H), 7.40 (2H, t, *meta*-aryl CH), 2.82 (2H, BH), 2.57 (2H, BH), 2.42 (2H, BH), 2.33 (1H, B9H), 2.13 (1H, B12H), 2.07 (2H, B8,10H), 1.25 (1H, s, OH); $^{13}C\{^1H\}$: 131.1 (*ortho* aryl C), 130.5 (*para* aryl C), 129.9 (*ipso* C), 128.7 (*meta* aryl C), 102.7 (cage COH), 83.7 (cage CPh). $^{11}B\{^1H\}$: -4.3 (1B, d, J_{BH}=149 Hz, B9), -8.8 (1B, d, J_{BH}=160, B12), -10.6 (6B, d, B4,5,7,11,3,6), -14.5 (2B, d, J_{BH}=151, B8,10). NMR ($(CD_3)_2CO$)/ppm: $^1H\{^{11}B\}$: 7.74 (2H, d, *ortho*-aryl CH), 7.44 (1H, t, *para*-aryl C-H), 7.40 (2H, t, *meta*-aryl CH), 5.05 (1H, br, OH), 2.81 (2H, B3,6H), 2.47 (2H, B4,5H), 2.30 (2H, B7,11H), 2.19 (1H, B9H), 1.92 (3H, B8,10,12H); $^{13}C\{^1H\}$: 132.1 (*ipso* aryl C), 131.8 (*ortho* aryl C), 131.0 (*para* aryl C), 129.4 (*meta* C), 110.3 (cage COH), 86.1 (cage CPh). $^{11}B\{^1H\}$: -5.6 (1B, d, J_{BH}=148 Hz, B9), -10.6 (2B, d, B3,6), -11.2 (3B, d, B4,5,12), -11.6 (2B, d, B7,11), -14.3 (2B, d, J_{BH}=152, B8,10). Calculated NMR (B3LYP/6-311G*//MP2/6-31G*) ^1H: 8.00 (2H, *ortho*-aryl CH), 7.61 (1H, *para*-aryl C-H), 7.51 (2H, *meta*-aryl CH), 3.21 (2H, B3,6H), 3.10 (2H, B4,5H), 2.97 (2H, B9,7,11H), 2.85 (1H, OH), 2.77 (1H, B12H), 2.63 (2H, B8,10H); ^{13}C: 139.5 (*ipso* C), 139.3 (*ortho* aryl C), 136.5 (*para* aryl C), 134.2 (*meta* aryl C), 109.2 (cage COH), 91.6 (cage CPh). ^{11}B: -3.5 (1B, B9), -9.4 (1B, B12), -11.3 (2B, B7,11), -11.6 (2B, B4,5), -12.9 (B3,6), -13.6 (2B, B8,10).

Protonated proton sponge salt of the 1-oxo-2-phenyl-1,2-carborane anion (PSH^+)($PhCb^oO^-$)

A solution of proton sponge (0.104g, 0.48 mmol) in hexane (10 ml) was added dropwise to a solution of 1-hydroxy-2-phenyl-*ortho*-carborane (0.114g, 0.48 mmol) in hexane, affording a white precipitate. This was filtered off, washed with fresh hexane and recrystallized from hot toluene, affording off-white crystals identified as the (PSH^+)($PhCb^oO^-$) salt, yield 0.14g (0.31 mmol, 65%). M.p.: 146-148ºC. Analysis ($C_{22}H_{34}B_{10}N_2O$): C 59.0 (58.6), H 7.4 (7.6), N 6.5 (6.2). MS (ES): M^+, 231-237 ($C_8H_{15}B_{10}O^-$ = 235), M^-, 215 ($C_{14}H_{19}N_2$ = 215). IR: 3436m,br (NH), 3058w, 3022w (phenyl CH), 2923m (methyl CH), 2566vs, 2554vs, 2526s (BH), 1491m (CO), 1468m, 1430m, 1112 m, 1075m, 1034m, 1031m, 831m, 773m, 764s, 695m, 541m. NMR ($(CD_3)_2CO$)/ppm: $^1H\{^{11}B\}$: 7.59 (2H, d, *ortho*-aryl CH), 7.08 (1H, t, *para*-aryl C-H), 7.06 (2H, t, *meta*-aryl CH), 2.42 (2H, B3,6H), 2.03 (2H, B7,11H), 1.96 (3H, B4,5,9H), 1.47 (2H, B8,10H), 1.17 (1H, B12H); $^{13}C\{^1H\}$: 149.5 (cage CO), 141.2 (ipso C), 129.0, 127.3, 126.9 (aryl CH), 88.0 (cage CPh). $^{11}B\{^1H\}$: -6.1 (2B, d, J_{BH}=157 Hz, B3,6), -7.4 (1B, d, J_{BH}=144, B9), -12.0 (2B, d, J_{BH}=154, B7,11), -15.1 (2B, d, J_{BH}=155, B4,5), -18.0 (2B, d, J_{BH}=145, B8,10), -22.2 (1B, d, J_{BH}=144, B12). Proton and carbon NMR data corresponding to the cation are identical to those reported elsewhere.[42] NMR ($(CD_3)_2SO$)/ppm: $^1H\{^{11}B\}$: 7.59 (2H, d, *ortho*-aryl CH), 7.27 (1H, t, *para*-aryl C-H), 7.25 (2H, t, *meta*-aryl CH), 2.44 (2H, B3,6H), 2.05 (2H, B7,11H), 1.98 (1H, B9H), 1.95 (2H, B4,5H), 1.47 (2H, B8,10H), 1.16 (1H, B12H); $^{13}C\{^1H\}$: 150.3 (cage CO), 140.1 (*ipso* C), 128.8, 128.3, 126.9 (aryl CH), 88.1 (cage CPh). $^{11}B\{^1H\}$: -6.3 (2B, d, B3,6), -7.8 (1B, d, B9), -12.2 (2B, d, B7,11), -15.5 (2B, d, B4,5), -18.3 (2B, d, B8,10), -22.6 (1B, d, B12). Calculated NMR for discrete anion $PhCb^oO^-$: ^1H: 7.87 (2H, *ortho*-aryl CH), 7.04 (1H, *para*-aryl C-H), 6.89 (2H, *meta*-aryl CH), 3.21 (2H, B3,6H), 2.53 (1H, B9H), 2.46 (2H, B7,11H), 2.42 (2H, B4,5H), 1.90 (2H, B8,10H), 1.57 (1H, B12H); ^{13}C: 164.1 (cage CO), 155.9 (*ipso* C), 137.8 (*ortho* C), 130.7 (*meta* C), 128.5 (*para* C), 94.2 (cage CPh); ^{11}B: -7.4 (2B, B3,6), -7.5 (1B, B9), -11.6 (2B, B7,11), -17.2 (2B, B4,5), -19.8 (2B, B8,10), -23.7 (1B, B12).

Protonated proton sponge salt of the 1-oxo-1,2-carborane anion (PSH^+)($PhCb^oO^-$)

This was made by the method described in the previous section with 1-hydroxy-*ortho*-carborane in place of 1-hydroxy-2-phenyl-*ortho*-carborane. NMR ($CDCl_3$)/ppm: $^1H\{^{11}B\}$: 3.91 (CH), 2.51 (2H, B3,6H), 2.32 (2H, B4,5H), 1.99 (3H, B9,7,11H), 1.82 (2H, B8,10H), 1.53 (1H, B12H). $^{13}C\{^1H\}$: 111.9 (CO), 66.8 (CH). $^{11}B\{^1H\}$: -5.9 (1B, d, J_{BH}=157 Hz, B9), -11.4 (2B, d, B3,6), -12.1 (2B, d, B4,5), -13.7 (2B, d, B8,10), -15.3 (2B, d, B7,11), -16.7 (1B, d, B12). NMR for cation in $CDCl_3$, ^1H: 7.96 (2H, aryl CH), 7.70 (4H, aryl CH), 3.16 (12H, CH_3). $^{13}C\{^1H\}$ 143.9, 135.8, 129.5, 127.2, 120.4, 118.5, 46.5. NMR ($(CD_3)_2CO$)/ppm: $^1H\{^{11}B\}$: 4.26 (CH), 2.48 (2H, B3,6H), 2.30 (2H, B4,5H), 2.02 (1H, B9H), 1.94 (2H, 7,11H), 1.78 (2H, B8,10H), 1.46 (1H, B12H); $^{13}C\{^1H\}$: 116.7 (CO), 68.7 (CH). $^{11}B\{^1H\}$: -6.1 (1B, d, B9), -11.0 (2B, d, B3,6), -12.3 (2B, d, B4,5), -14.2 (2B, d, B8,10), -15.4 (2B, d, B7,11), -17.7 (1B, d, B12). Proton and carbon NMR data corresponding to the cation are identical to those reported elsewhere. Calculated NMR for discrete anion HCb^oO^-: ^1H 3.38 (CH), 2.80 (2H, B3,6H), 2.48 (1H, B9H), 2.23 (2H, B4,5H), 2.22 (2H, B7,11H), 1.91 (2H, B8,10H), 1.31 (1H, B12H); ^{13}C: 162.6 (CO), 79.7 (CH); ^{11}B: -7.1 (1B, B9), -8.7 (2B, B3,6), -15.6 (2B, B7,11), -18.2 (2B, B4,5), -18.5 (2B, B8,10), -26.4 (1B, B12).

Triethylammonium salt of the 1-oxo-2-phenyl-1,2-carborane anion (Et_3NH^+)($PhCb^oO^-$)

Triethylamine (0.3 ml) was added dropwise to a solution of 1-hydroxy-2-phenyl-*ortho*-carborane (0.46g, 2.1 mmol), affording a white precipitate which coagulated, giving an opaque, gum-like material. The solvent was decanted off, the residue washed with fresh hexane and recrystallised from boiling hexane/toluene (4:1), affording colourless crystals identified as the Et_3NH^+ salt of $[1,2\text{-}OCB_{10}H_{10}CPh]^-$, 0.5g, 71% yield. M.p.: 125-126ºC. Analysis ($C_{14}H_{31}B_{10}NO$): C 47.2 (49.9), H 8.9 (9.2), N 3.3 (4.2). IR: 3061w (phenyl CH), 2990m (alkyl CH), 2750-2000m,br (N..H..O), 2616s, 2574s, 2555s, 2547s (BH), 1498m, 1478m, 1462m, 1451m, 1408m, 1392s, 1384s, 1358s, 1295m, 1076m, 1047m, 838m, 699m, 552m. NMR ($CDCl_3$)/ppm: $^1H\{^{11}B\}$: 7.75 (2H, d, *ortho*-aryl CH), 7.30 (3H, t, *meta* and *para*-aryl C-H), 2.69 (6H, q, CH_2), 2.61 (2H, BH), 2.36 (2H, BH), 2.28 (2H, BH), 2.11 (1H, B9H), 1.79 (1H, B12H), 1.56 (2H, B8,10H), 1.00 (9H, t, CH_3). $^{13}C\{^1H\}$: 135.0 (*ipso* aryl C), 130.8 (*ortho* aryl C), 129.9 (cage CO), 128.6 (*para* aryl C), 127.9 (*meta* aryl C), 88.5 (cage CPh). $^{11}B\{^1H\}$: -7.1 (1B, d, J_{BH}= 154, B9), -9.0 (2B, d,

J_{BH}= 146, B3,6), -12.2 (4B, d, B4,5,7,11), -16.2 (2B, d, J_{BH}= 151, B8,10), -18.3 (1B, d, J_{BH}=139, B12). NMR ($(CD_3)_2CO$)/ppm: $^1H\{^{11}B\}$: 10.5 (1H, s, NH); 7.97 (2H, d, *ortho*-aryl CH), 7.10 (1H, t, *para*-aryl C-H), 7.09 (2H, t, *meta*-aryl CH), 3.00 (6H, q, CH_2), 2.57 (2H, BH), 2.22 (2H, BH), 2.18 (2H, BH), 2.04 (1H, B9H), 1.67 (2H, B8,10H), 1.38 (1H, B12H), 1.15 (9H, t, CH_3). $^{11}B\{^1H\}$: -7.8 (1B, d, B3,6,9), -12.4 (2B, d, J_{BH}=159, B7,11), -13.2 (2B, d, J_{BH}=150, B4,5), -17.2 (2B, d, J_{BH}=142, B8,10), -20.5 (1B, d, J_{BH}=146, B12).

Attempted formation of the pyridinium salt of 1-oxo-2-phenyl-1,2-carborane anion ($C_5H_5NH^+$)($PhCb^oO^-$)

Pyridine (0.5 ml) was added to a stirred solution of 1-hydroxy-2-phenyl-*ortho*-carborane in hexane (30ml). After 10 min stirring, the solvents were removed *in vacuo*, leaving a white solid. This solid was recrystallised from hexane to afford colourless needles identified as a 3:2 adduct of 1-hydroxy-2-phenyl-*ortho*-carborane and pyridine, m.p.: 143-145ºC. Analysis ($3C_8H_{16}B_{10}O.2C_5H_5N$): C 47.8 (49.7), H 7.0 (6.7), N 3.0 (4.5). IR: 3060w (aryl CH), 2600vs, 2570s (BH), 2500-2200br (N-H..O), 1491w, 1484m, 1280 m, 1210s.

Methyl(triphenyl)phosphonium salt of the 1-oxo-2-phenyl-1,2-carborane anion (Ph_3PMe^+)($PhCb^oO^-$)

1-phenyl-*ortho*-carborane (118mg, 0.50 mmol) was dissolved in dry toluene (20mL) under nitrogen in a Schlenk tube. In a separate Schlenk tube $Ph_3P{=}CH_2$ (138mg, 0.50 mmol) was also dissolved in toluene (20ml), giving a yellow solution. The two solutions were cooled to 0ºC, and combined, under nitrogen, in a third Schlenk tube, causing the yellow colour to disappear. After 30 min stirring, approximately half the solvent was removed *in vacuo*, and the solution was placed in a freezer at -30ºC. After 48 hours at this temperature colourless block-like crystals were observed to have formed. These crystals were isolated and identified as the Ph_3PMe^+ salt of $[1,2\text{-}OCB_{10}H_{10}CPh]^-$ **1**$^-$, yield 148mg (58%). Analysis ($C_{27}H_{33}B_{10}PO$): C 64.0 (63.3), H 6.3 (6.5). IR: 3026m, 2999m, 2925m, 2834m (phenyl, methyl C-H); 2560vs,br (B-H stretch), 1489vs (CO stretch), 1451m, 1064m, 1052m, 731s, 668m.

1-Amino-2-phenyl-*ortho*-carborane $PhCb^{o}NH_2$

The compound 1-nitroso-2-phenyl-*ortho*-carborane (0.50g, 2mmol) was dissolved in dimethoxyethane (25ml) and tin powder (0.50g, 4mmol) was added. Concentrated HCl (25ml) was added dropwise and the solution stirred for 15 min, after which time the blue colour had disappeared. The solution was heated to reflux for 3 h, cooled to room temperature and diluted with diethyl ether (100ml). The solution was washed with water (3x50ml), dried (Na_2SO_4) and evaporated. The white residue was sublimed to yield 1-amino-2-phenyl-*ortho*-carborane (0.27g, 57%). Crystals suitable for X-ray crystallography were obtained by cooling a solution in hexane at -5ºC. M.p. 93.5-94.5ºC. Analysis ($C_8H_{17}B_{10}N$): C 40.1% (40.9%), H 7.4% (7.2%), N 5.4% (6.0%). MS (EI): M, 231-238 ($C_8H_{17}B_{10}N$ = 235) I.R.: 3461br, 3370br (NH), 3060w (phenyl CH), 2594s, 2564s (BH), 1605s, 1492m, 1445m, 1289m, 1249m, 1191m, 1159m, 1070s, 1033m, 1002m, 940m, 882m, 841m, 801m, 755s, 726s, 690s, 571m, 484m. NMR ($CDCl_3$)/ppm: $^{1}H\{^{11}B\}$: 7.68 (2H, d, *ortho*-aryl CH), 7.41 (1H, t, *para*-aryl C-H), 7.37 (2H, t, *meta*-aryl CH), 2.89 (2H, NH_2), 2.71 (3H, B3,6,9H), 2.52 (2H, B4,5H), 2.44 (2H, B7,11H), 2.18 (1H, B12H), 2.07 (2H, B8,10H); $^{13}C\{^{1}H\}$: 131.5 (*ortho* aryl C), 130.5 (*para* aryl C), 129.9 (*ipso* C), 128.7 (*meta* aryl C), 96.3 (cage CNH_2), 87.7 (cage CPh). ^{11}B: -2.7 (1B, d, B9), -8.3 (1B, d, B12), -9.2 (2B, d, B4,5), -10.0 (2B, d, B7,11), -10.6 (2B, d, B3,6), -12.7 (2B, d, B8,10). NMR ($(CD_3)_2CO$)/ppm: $^{1}H\{^{11}B\}$: 7.75 (2H, d, *ortho*-aryl CH), 7.46 (3H, m, meta and *para*-aryl C-H), 4.67 (2H, NH_2), 2.76 (2H, B3,6H), 2.49 (2H, B4,5H), 2.40 (1H, B9H), 2.37 (2H, B7,11H), 2.25 (1H, B12H), 1.94 (2H, B8,10H). $^{13}C\{^{1}H\}$: 132.5 (*ortho* aryl C), 131.2 (*para* aryl C), 129.8 (*ipso* C), 129.4 (*meta* aryl C), 103.2 (cage CNH_2), 90.3 (cage CPh). ^{11}B: -3.3 (1B, d, B9), -9.6 (3B, d, B4,5,12), -10.8 (4B, d, B3,6,7,11), -14.0 (2B, d, B8,10). NMR calculated (NH_2 towards) ppm: ^{1}H: 7.89 (2H, *ortho*-aryl CH), 7.60 (1H, *para*-aryl C-H), 7.53 (2H, *meta*-aryl C-H), 3.18 (1H, B9H), 3.10 (2H, B4,5H), 3.07 (2H, B3,6H), 2.90 (2H, B7,11H), 2.78 (1H, B12H), 2.59 (2H, B8,10H), 2.13 (2H, NH_2). ^{13}C: 141.0 (*ipso* C), 139.4 (*ortho* aryl C), 136.8 (*para* aryl C), 134.7 (*meta* aryl C), 101.5 (cage CNH_2), 93.8 (cage CPh). ^{11}B: -1.0 (1B, B9), -7.5 (1B, B12), -10.2 (2B, B4,5), -10.5 (2B, B7,11), -12.3 (2B, B3,6), -13.7 (2B, d, B8,10). NMR calculated (NH_2 away) ppm: ^{1}H: 7.85 (2H, *ortho*-aryl CH), 7.58 (1H, *para*-aryl C-H), 7.49 (2H, *meta*-aryl C-H), 3.12 (2H, B3,6H), 3.00 (1H, B9H), 2.95 (2H, B4,5H), 2.92

(2H, B7,11H), 2.80 (1H, B12H), 2.66 (2H, B8,10H), 2.21 (2H, NH_2). ^{13}C: 141.2 (*ipso* C), 139.6 (*ortho* aryl C), 136.4 (*para* aryl C), 134.0 (*meta* aryl C), 101.8 (cage CNH_2), 96.1 (cage CPh). ^{11}B: -3.1 (1B, B9), -7.5 (1B, B12), -9.7 (2B, B4,5), -10.5 (2B, B7,11), -12.5 (2B, d, B8,10), -14.3 (2B, B3,6).

Crystals of the 1:1 1-amino-2-phenyl-*ortho*-carborane:hmpa adduct suitable for X-ray crystallography were obtained from a solution of 1:1 ratio mixture of 1-amino-2-phenyl-*ortho*-carborane:hmpa in hexane.

1-Fluoro-2-phenyl-*ortho*-carborane $PhCb^oF$

The compound 1-phenyl-*ortho*-carborane (0.66g, 3mmol) was dissolved in dry diethyl ether, cooled in an ice bath and lithiated with a solution of n-BuLi (2.5M in hexanes, 1.6 mL, 3mmol), giving a clear yellow solution which was allowed to warm slowly to room temperature. The solution was cooled again before the addition of NFBS （N-fluorobenzenesulfonamide, 0.95g, 3mmol), to give a brown solid in a clear yellow solution. The solid was removed by filtration and the liquid transferred to a separating funnel and washed with distilled water. The organic layer was isolated and the solvent removed under reduced pressure to give a yellow oil. The oil was sublimed under vacuum, giving a white solid consisting of a mixture of unreacted 1-phenyl-*ortho*-carborane and the fluorinated product. These compounds were separated by preparative tlc with cyclohexane as solvent to isolate the white crystalline product, 1-fluoro-2-phenyl-*ortho*-carborane, yield 170mg (24%). M.p. 87 -88ºC. Analysis ($C_8H_{15}B_{10}F$): C 40.7 (40.3), H 6.5 (6.3). MS (EI): M, 234-240 ($C_8H_{15}B_{10}F$ = 238). IR: 3070w (phenyl CH), 2645m, 2576s (B-H), 1494m, 1447m, 1250m, 1232s, 1193m, 1070s, 1029s, 1002m, 933m, 783m, 750m, 723s, 683s, 571s, 479s. NMR ($CDCl_3$)/ppm: $^1H\{^{11}B\}$: 7.71 (2H, d, *ortho*-aryl CH), 7.45 (1H, t, *para*-aryl C-H), 7.40 (2H, t, *meta*-aryl CH), 2.95 (2H, BH), 2.65 (2H, BH), 2.44 (2H, BH), 2.30 (1H, B9H), 2.22 (1H, B12H), 2.12 (2H, B8,10H); $^{13}C\{^1H\}$: 130.8 (*ortho* aryl C), 130.5 ((*ipso*, *para* aryl C), 128.8 (*meta* aryl C), 107.8 (J_{CF} = 314 Hz, cage CF), 80.5 (cage CPh). $^{11}B\{^1H\}$: -5.8 (1B, d, J_{BH}=149 Hz, B9), -10.5 (1B, d, J_{BH}=151, B12), -11.8 (2B, d, B7,11), -12.0 (2B, d, B3,6), -12.8 (2B, d, J_{BH}=148, B4,5), -13.8 (2B, d, J_{BH}=156, B8,10). ^{19}F: -149. Calculated NMR (B3LYP/6-311G*//MP2/6-

31G*) ^{1}H: 7.93 (2H, *ortho*-aryl CH), 7.62 (1H, *para*-aryl C-H), 7.52 (2H, *meta*-aryl CH), 3.46 (2H, B3,6H), 3.15 (2H, B4,5H), 2.91 (1H, B9H), 2.82 (1H, B12H), 2.81 (2H, B7,11H), 2.66 (2H, B8,10H); ^{13}C: 139.3 (*ortho* aryl C), 138.2 (*ipso* C), 137.2 (*para* aryl C), 134.5 (*meta* aryl C), 117.6 (cage CF), 88.5 (cage CPh). ^{11}B: -5.0 (1B, B9), -9.0 (1B, B12), -12.0 (2B, B7,11), -13.4 (2B, B4,5), -13.8 (2B, B8,10), -14.1 (2B, B3,6). ^{19}F: -138.

1-Mercapto-2-phenyl-*ortho*-carborane $PhCb^{o}SH$ and 1,1'-bis(2-phenyl-*ortho*-carboranyl)trisulfide $PhCb^{o}S_3Cb^{o}Ph$

Under nitrogen, 1-phenyl-*ortho*-carborane (4.4g, 20mmol) and powdered sulfur (1.28g, 40mmol) were added to a stirred solution of sodium hydride with 60% paraffin (0.96g) in dimethoxyethane (monoglyme, 40ml). The mixture was refluxed for 10h, cooled and diluted with methanol (50ml). The solvents were removed in vacuo and the residue was diluted with water (20ml) and then extracted with 2x10ml of benzene. The combined benzene extracts were dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The yellow residue was recrystallized from 40-60 pet. ether to form crystals identified as the trisulfide (0.2g, 3.7%). M.p. 160 -161ºC. Analysis ($C_{16}B_{20}H_{30}S_3$): C 35.5 (36.0), H 5.7 (5.6), S 18.3 (18.0), B 40.4 (40.5). MS (EI): M, 524-538 ($C_{16}H_{30}B_{20}S_3$ = 535). IR: 3059w (phenyl CH), 2597s, 2584s, 2573s (B-H), 1493m, 1449s, 1077m, 1062m, 771m, 759m, 738m, 732m, 728m, 691s, 492m.

The solvent was removed from the mother liquor to give 1-mercapto-2-phenyl-*ortho*-carborane, (0.82g, 16%). M.p. 67 -68ºC. Analysis ($C_8H_{16}B_{10}S$): C 38.3 (38.1), H 6.7 (6.4), S 12.8 (12.7). MS (EI): M, 248-255 ($C_8H_{16}B_{10}S$ = 252). IR: 3050w (phenyl CH), 2574s (B-H), 1491m, 1445m, 1076m, 1062m, 1001m, 972m, 767m, 752m, 721m, 684s, 563m, 490m. NMR ($CDCl_3$)/ppm: ^{1}H: 7.66 (2H, d, *ortho*-aryl CH), 7.54 (1H, t, *para*-aryl C-H), 7.35 (2H, t, *meta*-aryl CH), 3.37 (1H, SH), 4.0-1.0 (10H, BH); ^{13}C{^{1}H}: 131.6 (*ortho* aryl C), 131.2 (*ipso* aryl C), 130.9 (*para* aryl C), 128.7 (*meta* aryl C), 86.6 (cage CPh), 84.8 (cage CS). ^{11}B{^{1}H}: -1.3 (1B, d, B9), -2.5 (1B, d, B12), -6.9 (2B, d, B8,10), -8.0 (6B, d, B3,6,4,5,8,10). Calculated NMR (B3LYP/6-311G*//MP2/6-31G*) ^{1}H: 7.84 (2H, *ortho*-aryl CH), 7.64 (1H, *para*-aryl C-H), 7.54 (2H, *meta*-aryl CH), 3.13 (2H, B3,6H), 3.12 (1H, B9H), 3.11 (2H, B4,5H), 2.98 (1H, B12H), 2.96 (3H, B7,11H, SH),

2.79 (2H, B8,10H); ^{13}C: 141.0 (*ipso* C), 139.8 (*ortho* aryl C), 137.1 (*para* aryl C), 134.5 (*meta* aryl C), 85.3 (cage CPh), 79.8 (cage CS). ^{11}B: -1.7 (1B, B9), -3.0 (1B, B12), -7.9 (2B, B4,5), -9.3 (2B, B7,11), -10.2 (2B, B8,10), -12.3 (2B, B3,6).

Protonated proton sponge salt of the 1-thio-2-phenyl-1,2-carborane anion $(PSH^+)(PhCb^oS)^-$

A solution of 1-mercapto-2-phenyl-*ortho*-carborane (0.252g, 10 mmol) in hexane (15ml) was added to a solution of 0.214g (10mmol) proton sponge in hexane (10ml). An immediate off-white precipitate was formed, filtered off and washed with hexane. The solid was recrystallized from toluene to give pale yellow crystals identified as the salt. (0.38g, 82% yield). M.p.: 189-190ºC. Analysis ($C_{22}H_{34}B_{10}N_2S$): C 56.3 (56.7), H 7.4 (7.3), N 5.5 (6.0). MS (ES): M^+, 247-253 ($C_8H_{15}B_{10}S^-$ = 251), M^-, 215 ($C_{14}H_{19}N_2$ = 215). IR: 3680-3120m,br (NH), 3062w (phenyl CH), 2932w (methyl CH), 2604s, 2588s, 2566s (BH), 1468m, 1451m, 1168m, 1010m, 969m, 893m, 871m, 838m, 775s, 771s, 699m, 409m. NMR ($(CD_3)_2SO$)/ppm: ^{1}H{^{11}B}: 7.61 (2H, d, *ortho*-aryl CH), 7.39 (1H, t, *para*-aryl C-H), 7.37 (2H, t, *meta*-aryl CH), 2.71 (2H, B3,6H), 2.60 (2H, B4,5H), 2.24 (2H, B7,11H), 2.10 (1H, B9H), 1.83 (2H, B8,10H), 1.56 (1H, B12H). ^{13}C{^{1}H}: 119.7 (cage CS), 133.9 (ipso C), 131.4, 128.8, 126.9 (aryl CH), 91.8 (cage CPh). ^{11}B{^{1}H}: -4.8 (1B, d, B9), -6.5 (4B, d, B3,6,4,5), -10.3 (2B, d, B7,11), -12.8 (3B, d, B8,10,12). NMR for cation in $(CD_3)_2SO$ ^{1}H: 8.10 (2H, aryl CH), 8.08 (2H, aryl CH), 7.74 (2H, t, aryl CH), 3.14 (12H, CH_3). ^{13}C{^{1}H} 144.5, 134.8, 128.8, 127.6, 121.8, 118.9, 45.7. NMR ($(CD_3)_2CO$)/ppm: ^{1}H{^{11}B}: 7.74 (2H, d, *ortho*-aryl CH), 7.33 (3H, t, *para*-aryl and *meta*-aryl CH), 2.82 (2H, B3,6H), 2.74 (2H, B4,5H), 2.34 (2H, B7,11H), 2.23 (1H, B9H), 1.95 (2H, B8,10H), 1.70 (1H, B12H). ^{11}B{^{1}H}: -4.4 (1B, d, B9), -6.2 (4B, d, B3,6,4,5), -10.0 (2B, d, B7,11), -12.5 (3B, d, B8,10,12). Calculated NMR for discrete anion $PhCb^oS^-$: ^{1}H: 7.86 (2H, *ortho*-aryl CH), 7.19 (2H, *meta*-aryl C-H), 7.08 (1H, *para*-aryl CH), 3.30 (2H, B3,6H), 3.17 (2H, B4,5H), 2.71 (2H, B7,11H), 2.68 (1H, B9H), 2.11 (2H, B8,10H), 1.76 (1H, B12H); ^{13}C: 157.3 (cage CS), 150.0 (*ipso* C), 140.6 (*ortho* C), 131.0 (*meta* C), 130.9 (*para* C), 105.3 (cage CPh); ^{11}B: -4.1 (1B, B9), -6.7 (2B, B3,6), -6.8 (2B, B4,5), -10.2 (2B, B7,11), -14.7 (2B, B8,10), -16.2 (1B, B12).

Triethylammonium salt of the 1-thio-2-phenyl-1,2-carborane anion (Et_3NH^+)($PhCb^oS)^-$

A solution of 1-mercapto-2-phenyl-*ortho*-carborane (0.126g, 5mmol) in hexane (10ml) was treated with 4 drops of dry triethylamine which slowly produced a white precipitate. After 30 min the solid was filtered off, washed with fresh hexane and dried *in vacuo* to give the salt. (0.13g, 74% yield) M.p.: 107-109ºC. Analysis ($C_{14}H_{31}B_{10}NS$): C 48.2 (48.4), H 8.9 (8.9), N 3.7 (4.0), B 30.6 (31.1), S 9.1 (9.0). IR: 3063w (phenyl CH), 2971m (alkyl CH), 2650-2000m,br (N..H..S), 2619s, 2609s, 2592s, 2581s, 2567s, 2545s (BH), 1472m, 1447s, 1398m, 1358s, 1072m, 1002m, 889s, 874s, 770m, 693m. NMR (C_6D_6)/ppm: ^{1}H: 7.75 (2H, d, *ortho*-aryl CH), 7.37 (3H, t, *meta* and *para*-aryl C-H), 2.92 (6H, q, CH_2), 4.0-1.0 (10H, BH), 1.24 (9H, t, CH_3). ^{11}B{^{1}H}: -4.4 (1B, d, B9), -7.1 (2B, d, B3,6), -9.7 (4B, d, B4,5,7,11), -11.6 (3B, d, B8,10,12). NMR ($CDCl_3$)/ppm: ^{13}C{^{1}H}: 133.4 (*ipso* aryl C), 131.9 (*ortho* C), 129.4 (*para* aryl C), 127.8 (*meta* aryl C), 100.3 (cage CS), 88.7 (cage CPh), 45.6 (CH_2), 8.4 (CH_3).

1-Hydroxy-7-phenyl-*meta*-carborane $PhCb^mOH$:

A solution of 1-phenyl-*meta*-carborane (2.2g, 10mmol) in anhydrous diethyl ether (20ml) was treated dropwise with 7.1ml (10mmol) butyllithium in hexanes (1.61M) under a dry nitrogen atmosphere at 0ºC. After 30 minutes stirring at refluxing temperature, a dry solution of 2.42g (10mmol) benzoyl peroxide in toluene (20ml) was added to the solution at 0ºC. The cloudy solution was refluxed for 2 h, cooled to ambient temperature, and distilled water (30ml) was added slowly. The organic layer was separated, washed with water and then extracted with 20% aqueous sodium hydroxide. The alkali extracts were combined, acidified with dilute HCl, and the precipitate was extracted with diethyl ether. The combined ether extracts were dried over $MgSO_4$, filtered, and the ether was removed in *vacuo* to leave an oily residue. It was vacuum distilled at 155ºC/0.02mmHg to give a clear oil which slowly turned solid. This solid was identified as pure 1-hydroxy-7-phenyl-*meta*-carborane, yield 0.55g (47%). M.p.: 71-72ºC. Analysis ($C_8H_{16}B_{10}O$) C 40.4 (40.7), H 7.0 (6.8), B 45.6 (45.8). MS (EI): M, 232-239 ($C_8H_{16}B_{10}O$ = 236). IR: 3570-3050s,br (OH), 2611s, 2602s, 2579s (BH), 1493m, 1448m, 1205s, 1194s, 1070m, 1027s, 868m, 806m, 742m, 692s. NMR ($CDCl_3$)/ppm: ^{1}H: 7.54 (2H, d, *ortho*-aryl CH), 7.45 (1H, OH), 7.26 (2H, t, *meta*-aryl C-H), 7.21 (1H, t, *para*-aryl CH), 4.1-1.0 (10H, BH);

$^{13}C\{^{1}H\}$: 134.6 (*ipso* aryl C), 128.8 (*para* aryl C), 128.4 (*ortho* C), 127.8 (*meta* aryl C), 101.3 (cage COH), 75.0 (cage CPh). $^{11}B\{^{1}H\}$: -6.1 (1B, d, B5), -11.0 (2B, d), -12.8 (7B, d).

Attempted formation of the protonated proton sponge salt of the 1-oxo-7-phenyl-1,7-carborane anion (PSH^{+}) $PhCb^{m}O^{-}$

A solution of proton sponge (0.104g, 0.48 mmol) in hexane (10 ml) was added dropwise to a solution of 1-hydroxy-7-phenyl-*meta*-carborane (0.114g, 0.48 mmol) in hexane (10ml), affording a white precipitate which coagulated to give a gum-like material. This was filtered off, washed with fresh hexane and recrystallized from a 1:1 hexane : toluene mixture. The resulting crystals appeared to contain a 3:1 ratio adduct of carborane : proton sponge from elemental analysis and NMR spectroscopy. M.p.: 127-128ºC. Analysis ($3C_8H_{16}B_{10}O{\cdot}C_{14}H_{18}N_2$) C 49.6 (49.4), H 7.4 (7.2), N 2.9 (3.0). IR: 3058w (phenyl CH), 2938w (methyl CH), 2598s, 2590s (BH), 1900-1400w,br (N…H…O), 1491m, 1472m, 1448m, 1218s, 1205s, 1185s, 1168s, 1159s, 1108m, 1072s, 1027s, 1002m, 869m, 748m, 697m.

1-Mercapto-7-phenyl-*meta*-carborane, $PhCb^{m}SH$

Using a dry ice bath at –40ºC, iron(III) nitrate nonahydrate (0.1g) and sodium metal (0.56g, 20mmol) were slowly added to 50ml of liquid ammonia with stirring for 30 min. A solution of 1-phenyl-*meta*-carborane (2.20g, 10mmol) in hexane (20ml) and, after 1 h, 0.32g (10mmol) of powdered sulfur were added to the ammonia solution. The mixture was left to evaporate for 8 h at ambient temperature. Ethanol (10ml) and water (50ml) were added to the solid residue and the organic solvents were removed using a rotary evaporator. The blue-black aqueous layer was filtered with activated charcoal, acidified with dilute HCl, and the products were extracted with hexane. The combined hexane extracts were washed with 10% potassium hydrogen carbonate solution, dried over $MgSO_4$ and filtered. The organic solvent was removed in vacuo to give an oily residue, which was vacuum distilled at 100ºC/0.05 mm Hg to give the desired thiol. Yield 1.97g (78%). M.p.: 43-44ºC. Analysis ($C_8H_{16}B_{10}S$) C 37.8 (38.1), H 6.5 (6.4), B 42.2 (42.9), S 12.7 (12.7). MS (EI): M, 248-255 ($C_8H_{16}B_{10}S$ = 252). IR: 3060w (phenyl CH), 2604s,

2592s, 2563s (BH), 1496m, 1491m, 1449m, 1090m, 1081m, 1003s, 852s, 808m, 790m, 757m, 740s, 732s, 691s, 660m, 577m. NMR ($CDCl_3$)/ppm: ^{1}H: 7.46 (2H, d, *ortho*-aryl CH),), 7.32 (1H, t, *para*-aryl CH), 7.30 (2H, t, *meta*-aryl C-H, 3.48 (1H, SH), 4.1-1.0 (10H, BH). ^{13}C{^{1}H}: 134.6 (*ipso* aryl C), 128.9 (*ortho* aryl C), 128.5 (*para* C), 127.7 (*meta* aryl C), 79.4 (cage CPh), 74.2 (cage CS). ^{11}B{^{1}H}: -3.5 (1B, d, B5), -7.1 (1B, d, B12), -8.5 (2B, d), -9.5 (4B, d), -11.4 (2B, d, B2,3).

Attempted formation of the protonated proton sponge salt of the 1-thio-7-phenyl-1,7-carborane anion (PSH^+) ($PhCb^mS^-$)

A solution of proton sponge (0.214g, 1 mmol) in hexane (10 ml) was added dropwise to a solution of 1-mercapto-7-phenyl-*meta*-carborane (0.252g, 1 mmol) in hexane (10ml). A yellow precipitate appeared after 30 min. This was filtered off and washed with fresh hexane. This solid was identified as a 1:1 carborane:proton sponge adduct. Yield 0.43g (92%). M.p. 120-121ºC. Analysis ($C_{22}H_{34}B_{10}SN_2$): C 56.2 (56.7), H 7.3 (7.3), B 22.8 (23.2), S 6.8 (6.9). IR: 3015w (phenyl CH), 2949w (methyl CH), 2632m, 2600s, 2568s (B-H), 1492m, 1464m, 1446m, 1182m, 1170m, 1166m, 1099m, 1072m, 1030m, 1017m, 1007m, 888m, 843s, 818m, 810m, 787m, 772s, 759m, 742m, 697m.

X-ray crystallography

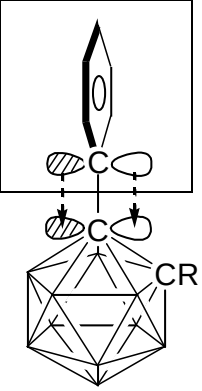
Data were collected on a Stoe-Siemens four-circle diffractometer for $PhCb^oOH{\cdot}0.5H_2O$ (**1**) and $PhCb^oS_3Cb^oPh$ (**5**), on Bruker SMART CCD diffractometers for $Ph_3PMe^+PhCb^oO^-$ (**2**) and $PhCb^oNH_2$ (**3**), and on a Rigaku AFC6S four-circle diffractometer for $PhCb^oNH_2{\cdot}OP(NMe_2)_3$ (**4**); Mo*K*α radiation (λ = 0.71073 Å) was used for **1**, **2** and **3**, and Cu*K*α radiation (λ = 1.54184 Å) for **4** and **5**. Crystal data and refinement information are given in Table 3. The structures were solved by direct methods and refined on all unique F^2 values.[43] Hydrogen atoms bonded to N and O were refined with geometrical restraints, while all other H atoms were treated with a riding model. The crystal structures of **4** and **5** are non-centrosymmetric, and the enantiopole parameter was refined to a value insignificantly different from the ideal zero in each case.[44]

CCDC reference numbers 000000–000000.

See http://www.rsc.org/suppdata/dt/00/00000000/ for crystallographic data in CIF or other electronic format.

Calculations

All *ab initio* computations were carried out with the Gaussian 98 package.[45] All geometries discussed here were optimised at the HF/6-31G* level of theory with no symmetry constraints unless otherwise stated. Frequency calculations were computed on these optimised geometries at the HF/6-31G* level for imaginary frequencies. Optimisation of these geometries were then carried out at the MP2/6-31G* level of theory. Calculated NMR shifts at the GIAO-B3LYP/6-311G* level were obtained from MP2-optimized geometries. Theoretical ^{11}B chemical shifts at the GIAO-B3LYP/6-311G*//MP2/6-31G* level were referenced to B_2H_6 (16.6 ppm[46]) and converted to the usual $BF_3.OEt_2$ scale: $\delta(^{11}B) = 102.83 - \sigma(^{11}B)$. The ^{13}C and ^{1}H chemical shifts were referenced to TMS: $\delta(^{13}C) = 184.81 - \sigma(^{13}C)$; $\delta(^{1}H) = 32.28 - \sigma(^{1}H)$. ^{19}F chemical shifts were referenced to HF and converted to the usual $CFCl_3$ scale; $\delta(^{19}F) = 185\ 2 - \sigma(^{19}F)$. The NMR shifts for the benzylidene anion were determined at the GIAO-B3LYP/6-31G* level from the X-ray geometry with hydrogens optimized at the HF/6-31G* level. Relative energies were computed at the MP2/6-31G* level with ZPE (calculated at HF/6-31G*) corrections scaled by 0.89. All model geometries with fixed torsional angles at C2-C1-Y-H were optimized initially at HF/6-31G* followed by MP2/6-31G*. Cartesian coordinates and total energies of the MP2/6-31G* optimized geometries described in this study are in the ESI.



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