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Transmission of electronic effects by icosahedral carboranes; skeletal carbon-13 chemical shifts and ultraviolet–visible spectra of substituted aryl-*p*-carboranes (1,12-dicarba-*closo*-dodecaboranes)

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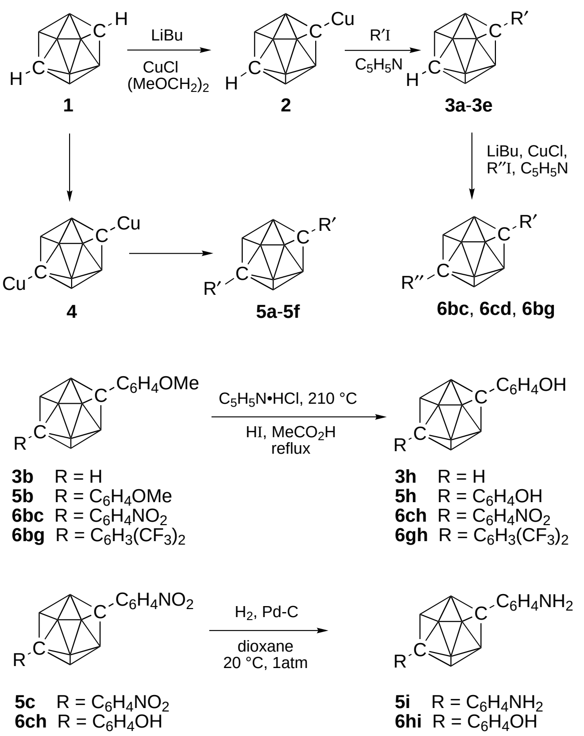
A series of *para*-carboranes (1,12-dicarba-*closo*-dodecaboranes) substituted at one or both carbon atoms by phenyl groups bearing a range of electron-releasing or -withdrawing substituents (X = NMe_2, NH_2, OH, OMe, Me, CF_3 or NO_2), principally at the *para* positions, has been prepared. The carbon-13 NMR shifts of the monoaryl compounds $(4\text{-}XC_6H_4)CB_{10}H_{10}CH$ showed a linear increase in shielding of the unsubstituted (antipodal) cage carbon, C12, and a linear decrease at the substituted position, C1, with increasing electron-donating power of the substituent represented by its Hammett σ_P value. Purely inductive, σ_I, or resonance σ_R, parameters gave less satisfactory plots. The diaryl series of 4-nitrophenyl derivatives showed the same relationships. Calculations of electron densities showed that the ^{13}C NMR shifts correspond with charge density in the tangential p orbitals. The UV absorptions of the monoaryl *p*-carboranes have substantial red-shifts compared with the corresponding substituted benzenes, while those of the 4-nitrophenyl compounds having 4-dimethylamino or 4-oxide anion substituents in the second phenyl group extend into the visible. The colour is attributed to changes in the nitro $n \longrightarrow \pi^*$ absorption rather than conjugation or intermolecular charge transfer. Two anhydrous polymorphs and a hydrate of the (18-crown-6)potassium salt of this nitrophenoxide have been identified (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane). The results establish that *p*-carborane transmits electronic effects, perhaps as a formally unsaturated system or possibly in a similar manner to the staffanes (bicyclo[1.1.1]pentanes) and other formally saturated hydrocarbon linkages.

In this study we have prepared a series of *C*-phenyl- and symmetric or unsymmetric *C*,*C*′-diphenyl-*para*-carboranes (1,12-dicarba-*closo*-dodecaboranes) bearing a variety of electron-releasing or -withdrawing substituents, principally at the *para* positions of the phenyl groups (see Scheme 1). Comparison of NMR and ultraviolet/visible spectra and X-ray crystallographic[1] structural data for 1,12-diphenyl-*p*-carborane **5a**, 1,12-bis(4-methylphenyl)-*p*-carborane **5f**, 1,12-bis(4-nitrophenyl-*p*-carborane **5c**, 1-(4-hydroxyphenyl)-12-(4-nitrophenyl)-*p*-carborane **6ch** and 1-(4-dimethylaminophenyl)-12-(4-nitrophenyl)-*p*-carborane **6cd** has shed light on changes in electron density and in π-orbital energies, resulting from interaction between the aryl substituents and the carborane cage, and between two aryl substituents through the cage.

The electronic structures of icosahedral *closo* carboranes have been described as three-dimensional aromatic systems[2] and the implications for electronic interaction with substituents has been of particular interest since the first studies of these compounds some 30 years ago. The results, some seemingly contradictory, underline the notable difference between the carboranes and any group encountered in organic chemistry.

It was soon apparent from the acidity of the carboranes and their *C*-carboxylic acids,[3] and from the reactions of various derivatives such as carboranyl ketones,[4] that the icosahedral carborane isomers behave as strongly electron-withdrawing groups in the sequence *ortho* ≫ *meta* > *para* towards carbon substituents.



Scheme 1 **a** Ph, **b** C_6H_4OMe-4, **c** $C_6H_4NO_2$-4, **d** $C_6H_4NMe_2$-4, **e** $C_6H_4CF_3$-4, **f** C_6H_4Me-4, **g** $C_6H_3(CF_3)_2$-3,5, **h** C_6H_4OH-4 and **i** $C_6H_4NH_2$-4; R′, R″ = aryl. atm = 101 325 Pa. Throughout this paper, the back three vertices have been omitted from the icosahedral skeleton, for clarity

The UV spectra[5] of *C*,*C*′-diphenyl and *C*-monophenyl derivatives of *o*- and *m*-carboranes differ little from that of benzene, showing no conjugation, and although the relatively enhanced absorption intensity of the diphenyl compound revealed interaction between the phenyl groups it was concluded[5] that carboranyl substituents on benzene behave as purely inductive electron-withdrawing groups similar to CF_3; the ^{19}F and ^{13}C NMR spectra of *o*- and *m*-carborane derivatives have been similarly interpreted.[6,7] The formation of *p*- as well as *m*-nitrophenyl derivatives (the latter being formed almost specifically in nitrations of trifluoromethylbenzene[8]) in the nitration[7,9] of *C*-phenylcarboranes shows that this cannot be a complete description and our results may have a bearing on this point as noted below.

A remarkably general effect of substituents at B or C bearing

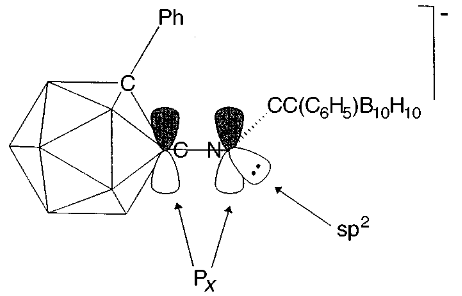


Fig. 1 Orbital alignment of bis(2-phenyl-*o*-carboranyl)amide anion; the cation is potassium complexed by 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and one molecule of diethylene glycol dimethyl ether [$(MeOCH_2CH_2)_2O$]

non-bonding electron pairs is specifically increased shielding of the resonance of the opposite, or *antipodal*, atom of *closo* carboranes. Hermánek *et al.*[10] have attributed this effect to increased electron density in the tangential, cage-bonding, p orbitals of the antipodal atom resulting from transmission of electron density from a substituent p orbital through the tangential p-orbital system to refocus at the opposite position. Calculated electron-density changes in the *radial* sp hybrid bond of the antipodal atom, which affect its reactivity in substitution reactions, do not correspond with the NMR shift.

X-Ray crystallographic evidence confirms π-bonding interaction between *o*-carborane and its carbon substituents having electron pairs in p orbitals, and particularly those that are negatively charged such as the anion of 1-hydroxy-2-phenyl-*o*-carborane,[11] whose C–O bond length is only 1.245 Å, typical of C=O. The crystal conformation of the anion bis(2-phenyl-*o*-carboran-1-yl)amide[12] $(PhCB_{10}H_{10}C)_2N^-$ (Fig. 1), the plane of whose trigonal nitrogen atom (with non-bonding electron pairs in p and sp^2 orbitals) lies normal to the planes containing the cage C–C bonds, shows that the nitrogen p orbital interacts with the cage carbon $2p_x$ orbital (of both cages). These orbitals make major contributions to the cage C–C bonds, which explains the observed extension of these bonds concomitant with *exo*-π bonding;[13] calculations at the AM1 level show the expected increase in charge density in the tangential orbitals of the antipodal boron atoms.

Antipodal shielding by the phenyl group has been recorded by comparing the ^{13}C NMR shifts of *p*-carborane with those of its *C*-phenyl and *C,C′*-diphenyl derivatives[14] and a corresponding study of the methyl derivatives[7] shows that this group also has a shielding effect at the antipodal carbon, presumably by hyperconjugation if the Hermánek mechanism applies.

p-Carborane provides a unique system for studying transmission of electronic effects into, and through, the icosahedral cage since synthetically convenient carbon-substituents have the antipodal relationship which the NMR results suggest is likely to maximise interaction. These compounds have the advantage that antipodal effects are accurately observable by ^{13}C resonances which (despite some broadening by cage boron) are sharper than those of ^{11}B. Further, *p*-carborane is expected to give particularly good correspondence between charge density and shielding values since perturbation, by paramagnetic effects, of diamagnetic shielding, upon which this correspondence depends is likely to be minimal in the very highly symmetric environment of the cage carbon. This expectation is confirmed by our results.

To maximise possible electronic interaction between two aryl substituents *through* the *p*-carborane unit we have placed electron-releasing and -withdrawing ('push-pull') substituents (*e.g.* NMe_2 and NO_2) at the aryl *para* positions. The resulting interactions, which lead to development of colour in some examples, have also been studied by UV spectrometry and by comparing the X-ray crystallographic bond parameters[1] of symmetric and unsymmetric diaryl-*p*-carboranes. Correlation of our experimental results with calculated electron densities (AM1 program) has, we believe, given new insight into the electronic nature of the *p*-carboranyl group in particular, and probably of the other carborane isomers. Finally, we consider the significance of our findings in the search for materials with new optical and electronic properties.

Preparative Work

We have developed an efficient procedure for coupling the *C*-copper(I) derivatives of *o*-, *m*- and *p*-carborane with aryl iodides or suitably reactive (heterocyclic) bromides[15,16] in the presence of pyridine* and have now used it to prepare the monoaryl-*p*-carboranes **3a**–**3e**, Scheme 1, using equimolar proportions of the reagents, and symmetric diaryl-*p*-carboranes **5a**–**5f** with 2 : 1 molar proportions. In practice, varying amounts of the corresponding diarylcarboranes are usually also formed with the monosubstitution products (with unchanged *p*-carborane); separation of the mono- and di-aryl compounds is readily achieved by vacuum sublimation in most examples (see Experimental section). Unsymmetrical diaryl-*p*-carboranes **6bc**, **6cd** and **6bg** were formed in good yield from monoaryl derivatives **3b**, **3d** by a second lithiation and arylation sequence; the nitrophenyl group must be added in the second step since it reacts with butyllithium. As with the analogous *m*-carborane,[15] 1-(4-nitrophenyl)-*p*-carborane **3c** formed a bright yellow precipitate, presumably of the copper(I) derivative, when it was treated with copper(I) *tert*-butoxide and pyridine in 1,2-dimethoxyethane but no coupling with 4-iodoanisole was observed at reflux temperature; the monosubstituted carborane **3c** was recovered after acidification.

Hydroxyphenyl-*p*-carboranes **3h**, **5h** and **6ch** were obtained by demethylating the corresponding methoxy-compounds by heating them to 210 °C in fused pyridine hydrochloride, but the 3,5-bis(trifluoromethyl) derivative **6bg** failed to react. Further, we found that reaction times for complete demethylation were not always reproducible. An alternative reagent, which gave the bis(trifluoromethyl)phenol **6gh**, is a mixture of equal volumes of constant-boiling (57%) hydriodic and acetic (ethanoic) acids at reflux temperature.

Reduction of the nitro-derivatives **5c** and **6ch** to the amines **5i** and **6hi** was effected virtually quantitatively by hydrogenation over 5% palladium on carbon in 1,4-dioxane at ambient temperature and pressure. We have found this method generally superior† to reduction of nitrophenylcarboranes by other methods, including zinc and acetic acid[9b] which usually gives some of the corresponding azo-compound as a persistent impurity.

A yellow monohydrate of the (18-crown-6)potassium salt of the nitrophenol **6ch** precipitates when aqueous potassium hydroxide is added to an ethanolic solution of the nitrophenol and 18-crown-6. Warming under high vacuum gives an orange-yellow anhydrous form, which is also precipitated in *ca.* 30% yield by mixing dry toluene solutions of the nitrophenol, and of equimolar proportions of potassium *tert*-butoxide and 18-crown-6. After a few hours at room temperature the filtrate deposits garnet-red crystals (sadly not suitable for X-ray crystallography) having the same composition as that of the orange-yellow form and which, like the latter, quickly revert to the yellow hydrate upon exposure to moist air.

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* Michl and co-workers[17] have effected coupling between *p*-carboranyl-copper(I) and aryl iodides using chloride bis(triphenylphosphine)-palladium(II) as catalyst. We have observed efficient phenylation of this copper intermediate with idobenzene using triphenylphosphine instead of pyridine, and suggest that catalysis by the palladium complex may be due to exchange with this ligand rather than to the palladium.

† 1,7-Bis(3-nitrophenyl)-*m*-carborane is an exception which gives several products under these conditions; all are destroyed by hydrogenation at higher temperatures.

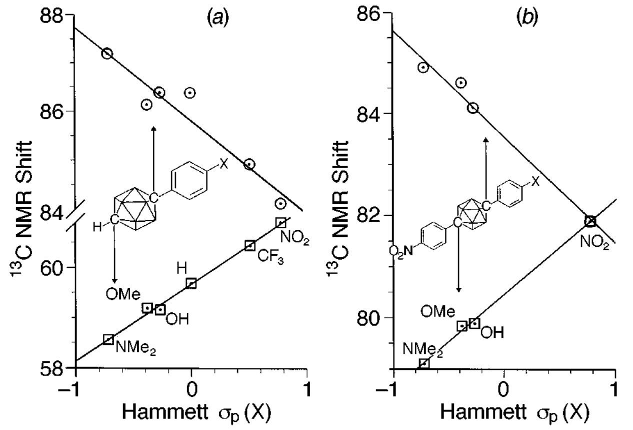


Fig. 2 Variation of cage carbon chemical shift of *p*-carboranes with σ_p of the 4-X phenyl substituents: (*a*) monosubstituted, (*b*) disubstituted

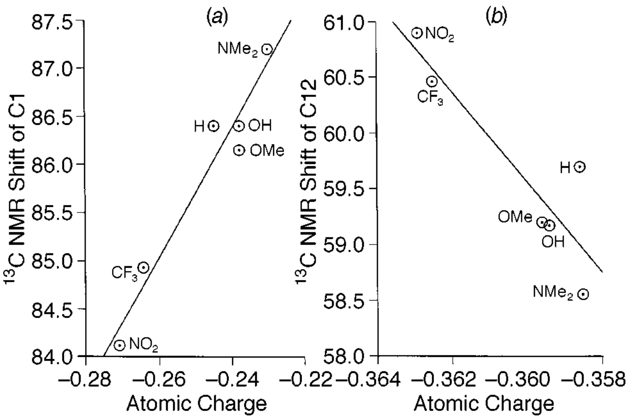


Fig. 3 Variation of cage carbon chemical shift of substituted monophenyl-*p*-carboranes with calculated atomic charge: (*a*) C1, (*b*) C12

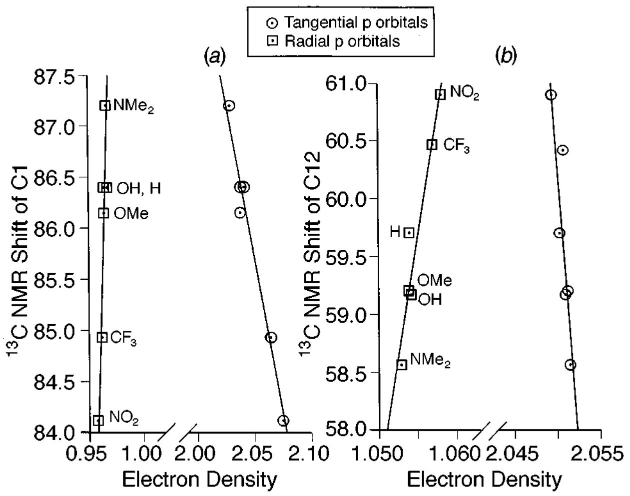


Fig. 4 Variation of cage carbon chemical shift of substituted monophenyl-*p*-carboranes with calculated electron density in tangential and radical orbitals: (*a*) C1, (*b*) C12

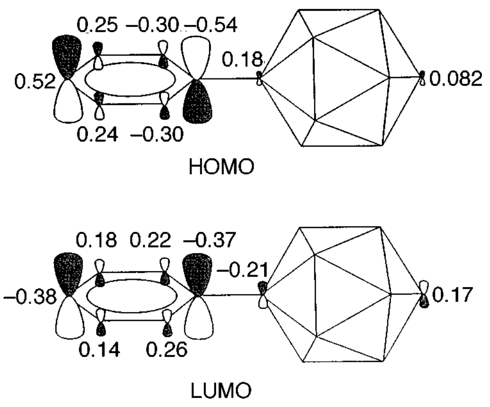


Fig. 5 Atom coefficients of 2p orbitals for carbon atoms of 1-phenyl-*p*-carborane frontier MOs

NMR Studies of Mono- and Di-aryl-*p*-carboranes and Calculated Charge Densities

The ^{13}C NMR spectra of a series of *C*-monoaryl-*p*-carboranes **3a**–**3e** in which the aryl group is phenyl *para*-substituted by a range of groups varying from strongly electron withdrawing (nitro) to strongly electron donating (dimethylamino) confirm our expectation that antipodal effects can be accurately observed in this way. Fig. 2(*a*), lower plot, shows a remarkably sharp linear relation between the substituent electronic effect, represented by the Hammett σ_p value,[18] and the ^{13}C NMR shift of the antipodal carbon (C12). The slope of the line corresponds with the anticipated increase in nuclear shielding (lower δ value) with increasing electron-releasing power of the substituent. We had expected that this would arise from increased electron density (and shielding) at the substituted carbon C1 transmitted through the tangential p orbitals of the cage to C12, but Fig. 2(*a*), upper plot, shows the reverse effect since shielding of C1 *decreases* with the electron-releasing effect of the substituent; again there is a reasonably close linear relationship with σ_p.

To confirm that the NMR shielding is responding as expected to electron-density changes, we calculated the atomic charges on the carbon atoms of the series **3a**–**3e** using the AM1 molecular orbital program (geometries were fully optimised using MOPAC).[19] Fig. 3(*a*) shows the total atomic charge on the substituted carbon C1 plotted against ^{13}C shift; the relationship is a reasonably good straight line whose slope clearly supports our expectation that the highest negative charge corresponds with the most shielded resonance. Thus the calculated charges confirm our remarkable conclusion that there is an *inverse* linear relation between substituent electron-donating power and negative charge density at the carbon, C1, directly bonded to the substituted phenyl group.

The calculated total atomic charges at the antipodal carbon C12, Fig. 3(*b*), show substantially higher charge at this position for every compound **3a**–**3e** with relatively little variation within the series, but the slope of the, once again, linear relation is towards more shielding at *lower* total negative charge. Hermánek *et al.*[10] have shown that NMR shielding of the nuclei of cage atoms responds to electron density in the tangential p orbitals, rather than in the s and p orbitals which form the radial bonds, and when the former contribution is plotted against ^{13}C shift of C12, Fig. 4(*b*) right-hand plot, the steep slope of the roughly linear relation lies in the expected direction of more shielding at higher electron density.

We note that the tangential p-orbital component of electron density at C1, Fig. 4(*a*) right-hand plot, varies in the same sense as the total charge [Fig. 3(*a*)] used in the argument above, although the radial p component, left-hand line, shows a small change in the opposite direction. It is interesting that, at C12, the small changes in tangential p-orbital electron density [Fig. 4(*b*)] override considerably larger ones in the opposite sense in the radial p and total, s plus p, orbital densities in determining the ^{13}C NMR shift.

Fig. 5 shows the atom coefficients of the 2p orbitals of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of 1-phenyl-*p*-carborane; its 4-dimethylamino- and 4-nitro-derivatives show a similar pattern. The coefficients of the boron atomic orbitals (AOs) are all very small. For each compound the majority of the corresponding lower, filled MOs resemble the HOMOs in

Table 1 Charge on the carboranyl residue $HCB_{10}H_{10}C$ of systems $HCB_{10}H_{10}C(C_6H_4X\text{-}4)$

Compound	X	Charge
3d	NMe_2	−0.128
3a	H	−0.032
3h	OH	−0.031
3b	OMe	−0.031
3e	CF_3	−0.013
3c	NO_2	−0.004

having an *antibonding* interaction between the cage and aryl carbon atoms (level 24 is exceptional in having the eight carbon AOs in phase) so that there is little π character, the π-bond order is 0.047 for the phenyl derivative **3a**, in these bonds in the ground state (but more when the LUMO is populated in the first excited state). The overall effect is evidently to repel charge from the substituted cage carbon to the antipodal position, leading to the reciprocal response of these atoms to σ_p of the aryl 4-substituent indicated by the ^{13}C resonances. A similar effect has been noted in the ^{13}C NMR spectra of 4-substituted *p*-terphenyls.[20]

The charge on the carborane cages of the monosubstituted derivatives is shown in Table 1 (that on the aryl groups is equal and opposite); the electron-withdrawing effect of the 4-nitrophenyl group does not quite balance that of the carborane unit.

To investigate the corresponding polarisation of *C*,*C′*-diaryl-*p*-carboranes we recorded the ^{13}C NMR spectra of these compounds with the same substituents (less trifluoromethyl and unsubstituted phenyl) as those of the monosubstituted series and 4-nitrophenyl as the second group, compounds **5c**, **6bc**, **6cd** and **6ch**. Fig. 2(*b*) shows that plots of the ^{13}C shift of the cage atoms against the Hammett σ_p value of the substituents give straight lines very similar to those of the monosubstituted series but with rather higher gradients, corresponding with greater polarisation towards the nitrophenyl group. We have not performed the corresponding electron-density calculations for all of these larger molecules, but those for the (dimethylamino)-nitro-derivative **6cd** support polarisation very similar to that of the monosubstituted series, enhanced by the 4-nitrophenyl group.

The electronic effect of substituents can be divided[18] into inductive (σ_I) and resonance (σ_R) contributions and it might be expected that antipodal effects, transmitted through p orbitals, would respond more to σ_R than to σ_I. Plots of the ^{13}C NMR shifts of compounds **3a**–**3f**, or of the calculated electron densities on carbon, against either of these parameters gave very much less satisfactory linear correlation than with σ_p, which is based on the acidities of substituted benzoic acids,[18] so that the *p*-carborane cage evidently responds to the combination of inductive and resonance effects in very much the same way as does the carboxylate group.

Ultraviolet and Visible Spectra

The (dimethylamino)nitro-compound **6cd** is orange both in the crystalline state and in solution, and the anion of the colourless hydroxynitro-analogue **6ch** is bright yellow, so that this compound behaves as an indicator similar to 4-nitrophenol. This part of the study was undertaken primarily to elucidate the origin of this visible absorption. To examine the effect of the second aryl substituent we first measured the spectra of the colourless monoaryl-*p*-carboranes **3a**–**3e** in a solvent [tetrahydrofuran (thf)] which can also dissolve the less soluble diaryl derivatives.

The spectrum of the phenol **3h** shows a relatively intense band at 240 nm and a weaker one, which clearly retains characteristic vibrational structure in this solvent, centred at 276 nm. Since the carboranyl chromophore has no absorption beyond *ca.* 210 nm (close to the solvent cut-off) these bands can be assigned with reasonable confidence as the ^1L_a and ^1L_b benzene-like absorptions,[21,22] respectively. The corresponding bands of 1-phenyl-*p*-carborane are at 220 and 260 nm, the former just observable within the solvent window, but the other monoaryl compounds show only one band, the ^1L_a absorption having shifted to coalesce with the longer-wavelength ^1L_b band, a pattern common in disubstituted benzenes. Table 2 shows the wavelengths and intensities of the absorptions and their differences (Δλ,Δε) from the spectra[22] of the corresponding monosubstituted benzenes (phenol, nitrobenzene, *etc.*; positive Δ shows the carborane at higher value) assuming that the single bands are due principally to the ^1L_a absorption.

Table 2 Absorptions (in thf) of $HCB_{10}H_{10}C(C_6H_4X\text{-}4)$ and differences (Δ) from C_6H_5X

	X				
	H	OH	O^-	NO_2	NMe_2
^1L_a					
λ	220	240	284	264	278
Δλ	16	29	48	12	27
ε	13 400	14 000	16 000	14 800	26 400
Δε	4 600	7 800	6 600	4 800	12 400
^1L_b					
λ	260	276			
Δλ	6	6			
ε	310	1 000			
Δε	60	−450			
$n \longrightarrow \pi^*$					
λ^a				332	
$\Delta\lambda^a$				2	
ε				360	
Δε				240	

[a] Point of inflection in both spectra.

The spectrum of the nitro-derivative **3c** shows a distinct inflection at 332 nm, similar to that of nitrobenzene,[22,23] which we correspondingly assign as the $n \longrightarrow \pi^*$ transition of the nitro-group.

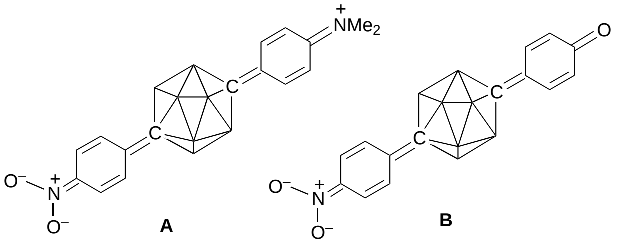
On the basis of these assignments, *p*-carborane as a second substituent on all of the 4-substituted benzenes produces a pronounced shift to longer wavelength, and enhanced intensity, except for that of the ^1L_b band of the phenol **3h**; our supposition that the single absorptions are essentially ^1L_a bands is strengthened if ^1L_b is similarly diminished in the other derivatives. The intensity changes are presumably associated with differences in the vibrational distortion which allows observation of these symmetry-forbidden transitions.

Detailed conclusions from the wavelength changes require analysis of the energies of the states arising by configuration interaction between the degenerate pairs of ground and excited π states, a formidable computational task, but we infer that the general bathochromic shift produced by *p*-carborane substitution reflects narrowing of the $\pi \longrightarrow \pi^*$ gap by lowering the energies of the π* orbitals more than those of the π, or, less probably for an intrinsically electron-withdrawing substituent, by raising the π level more than the π*.

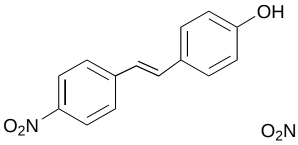
Substitution of the second CH position of *p*-carborane by another aryl group extends absorption into the visible region for the two examples, **6cd** and the anion of **6ch**, with the strongest ‘push-pull’ substituent pairs, and we considered three possible reasons for this effect. First, the possibility that the *p*-carborane cage extends conjugation between the aryl groups in a manner similar to that expected for a *p*-phenylene or ethene linkage, so that quinonoid electron distributions **A** and **B** contribute to the ground states. This situation is expected to lead to a substantial red-shift of the $\pi \longrightarrow \pi^*$ absorption

Table 3 Absorption spectral data for mono- and di-aryl-*p*-carboranes

			λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	
Compound	Donor substituent	Acceptor substituent	$\pi \longrightarrow \pi^*$	$n \longrightarrow \pi^*$
3c	None	$C_6H_4NO_2$	264 (14 800)	332 (360)
3h	C_6H_4OH-4	None	240 (14 000) 276 (1000)	—
6ch	C_6H_4OH-4	$C_6H_4NO_2$-4	242 (20 900) 270 (17 600)	*ca.* 350 (weak)
3d	$C_6H_4NMe_2$-4	None	278 (26 400)	—
6cd	$C_6H_4NMe_2$-4	$C_6H_4NO_2$-4	280 (38 700)	(obscured)
Anion				
3h	$C_6H_4O^-$-4	None	284 (16 000)	—
6ch	$C_6H_4O^-$-4	$C_6H_4NO_2$-4	282 (26 300)	351 (2800)



A **B**



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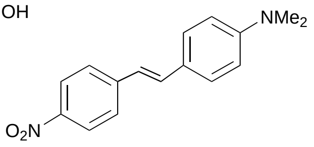

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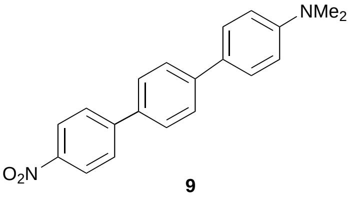

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compared with *p*-carborane monosubstituted by either of the aryl groups.

Secondly, the colour might arise by *intermolecular* charge transfer between donor and acceptor groups. In this case the intensity would be concentration dependent and mixtures of the carboranes monosubstituted by the same groups should show a similar effect; the donor and acceptor groups would also need to be close together in the crystalline state.

Thirdly we considered the possibility that the colour of these nitrophenyl derivatives is due to the nitro $n \longrightarrow \pi^*$ transition, which gives incipient colour to many nitro-compounds, shifted towards the visible region. This shift almost certainly requires lowering of the π* level of the 4-nitrophenyl-*p*-carborane moiety by the donor aryl substituent since the energy of the (highest) non-bonding orbital of aromatic nitro-compounds[23] is generally insensitive to substituents. Relating this point to *p*-carborane substitution of nitrobenzene (Table 2), the small (2 nm) red-shift of the inflection where the $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ bands overlap is probably due principally to the higher intensity of the shorter-wavelength band which, assuming similar band profiles, will shift the point of inflection to longer wavelength. The $n \longrightarrow \pi^*$ spacing, and hence the π* level, are therefore seemingly little changed by the carborane substituent so that its +12 nm $\pi \longrightarrow \pi^*$ shift is presumably associated with raising of the π-energy level.

The spectra distinguish clearly between these three causes for visible absorption. Conjugation through the cage is ruled out by the absence of a significant red-shift of the principal absorption band when a complementary donor or acceptor group is added to a monosubstituted system, Table 3. The absorption of the mono(dimethylamino)-compound **3d** at 278 nm is shifted only 2 nm to longer wavelength in the nitroamino derivative **6cd** and that of the monophenoxide anion of **3h** at 284 nm shifts an equal amount towards the blue by addition of the acceptor nitro-group. These wavelengths contrast with those of the analogous compounds with the substituted phenyl groups connected by conjugating ethene or *p*-phenylene links. Thus the longest-wavelength absorptions[24] of 4-monosubstituted *trans*-stilbenes are hydroxy 301 (ε 27 000), dimethylamino 349 (33 400), and nitro 351 nm (28 000 dm^3 mol^{-1} cm^{-1}), whereas those of the donor–acceptor disubstituted examples **7** and **8** are 382 (34 500) and 432 nm (22 800 dm^3 mol^{-1} cm^{-1}) respectively.[25] The terphenyl **9** absorbs at 385 nm (ε not recorded),[26] over 100 nm to longer wavelength than the corresponding *p*-carborane derivative **6cd**.

The spectrum of a mixture of the monosubstituted nitro- **3c** and dimethylaminophenyl- **3d** *p*-carboranes shows no shift of the long-wavelength tail of the, additive, absorption towards the visible compared with those of the individual components, and the absorption of the nitroamine **6cd** does not deviate significantly from Beer's law. The colour of this compound cannot therefore be attributed to intermolecular charge transfer, which is also precluded by the X-ray crystallographic data[1] which show that the nitro and dimethylamino groups are not adjacent in the (coloured) crystal. Further, comparison of the bond lengths of the diphenyl derivative **5a**, the ditolyl **5f** and the dinitro **5c** with those of the push-pull substituted compounds **6cd** and **6ch** shows no evidence of contribution by quinonoid electron distributions. In benzene derivatives this effect is, however, only noticeable in extreme examples like 1-dimethylamino-4-nitrobenzene[27] and most *p*-phenylene derivatives with push-pull substituents show no significant quinonoid distortion of the benzene ring,[28] so that the absence of this trend in these carborane-linked systems does not preclude conjugative interactions although the UV spectra almost certainly do so.

The spectrum of the yellow anion of the nitrophenol **6ch** shows a distinct inflection at *ca.* 351 nm, intensity 2800 dm^3 mol^{-1} cm^{-1} and the tail of the long-wavelength band extends beyond 450 nm, *i.e.* well into the visible region, as does that of the orange nitroamine **6cd** although no inflection is discernible owing, apparently, to the broader profile of the $\pi \longrightarrow \pi^*$ band. We infer that the nitro $n \longrightarrow \pi^*$ transition is shifted by rather more than the *ca.* 19 nm between the inflections, judging by the slopes of the curves, to longer wavelength, and intensified *ca.* 10 times, when the nitrophenyl-*p*-carborane is substituted by the phenoxide donor group in **6ch**, and that a similar effect gives rise to the colour of the nitroamine **6cd**.

Infrared Spectra of Solid Salts of 1-(4-hydroxyphenyl)-12-(4-nitrophenyl)-*p*-carborane 6ch

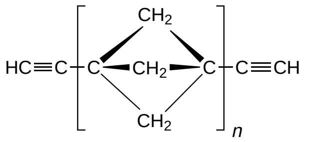
As noted in Section 2 the (18-crown-6)potassium salt of the nitrophenol **6ch** forms a yellow hydrate and has orange-yellow and garnet-red anhydrous forms whose infrared spectra have a majority of bands in common but differ in the absorptions associated with the nitro-group. The orange-yellow compound shows bands at 1350 cm^{-1} (symmetric N–O stretch) and 1525 (asymmetric stretch) and a doublet 1596, 1603 cm^{-1}, assigned as a benzene-ring deformation, which are very close to the corresponding bands of the mono- or di-(nitrophenyl)-*p*-carboranes at 1348, 1523 and 1596, 1604 cm^{-1}. The red form shows a similar symmetric stretch at 1345 cm^{-1} but bands at 1501 and 1516 cm^{-1} replace the 1525 cm^{-1} absorption of the isomer while the frequency of the ring deformation doublet is reduced to 1587, 1591 cm^{-1}. Neither compound shows any significant (*e.g.* carbonyl stretching) absorption between 1604 cm^{-1} and the B–H stretching band (which reproducibly appears as a singlet at 2610 cm^{1} for the orange-yellow and as a triplet at 2588, 2602, 2616 cm^{-1} for the red form) attributable to the C=O group of a quinonoid tautomer with structure **B**. We infer that an oxygen atom of the nitro-group co-ordinates potassium in the red but not the orange-yellow or the hydrated form. Their insolubility and/or moisture sensitivity has hitherto precluded further spectrometric study of these compounds.

Conclusion

The ^{13}C NMR spectra of mono- and di-aryl-*p*-carboranes provide unequivocal evidence for electronic interaction, involving transfer of electron density, from a *C*-aryl group, and in particular its *para* substituent, to the remote carbon atom of the *p*-carborane cage; this interpretation of the spectra is supported by charge-density calculations.

None of the substituents [with the possible exception of 3,5-bis(trifluoromethylphenyl)] in this study is more electronegative than the *p*-carborane cage, 4-nitrophenyl being only a little less so (Table 1). Unless there is a discontinuity in the smooth (linear) relationship between cage-carbon electron density and substituent electronegativity, it may be expected that the cage will be electron donating towards more strongly electron-attracting groups, such as the Wheland cation moieties of the intermediates in nitration of *C*-phenylcarboranes, which may have a bearing on the observed high proportion of *para* substitution, although we suspect that other effects (which we hope to discuss in a future paper) also operate here. We note, however, that our results refer to *p*-carborane while the nitration experiments were done with the *o* and *m* isomers. It appears that the *p*-carborane cage, and by inference the other isomers, behave as ‘electron sinks’ absorbing, and probably releasing, electron density in proportion to the supply or demand of its substituents.

The ultraviolet absorptions of the monoaryl *p*-carboranes (Table 2) show that the π-energy levels of the aryl groups are strongly influenced by the *p*-carboranyl group, giving substantial shifts to longer wavelength. Comparison of these spectra with those of the disubstituted derivatives, particularly where ‘push-pull’ substitution gives rise to visible absorption, reveals interaction between the two aryl chromophores through the carborane bridge. The spectra also show that the effect is distinct from resonance interaction between chromophores connected by π-electron bridges (ene, polyene or arylene for example) and the NMR results do not correlate with purely inductive parameters. We suggest that the electronic coupling is related to those observed[29] (by photoelectron spectrometry) between chromophores connected by ‘staffane’ (bicyclo[1.1.1]-pentylidene) or oligo-staffane, *e.g.* **10**, and related formally saturated bridges, which are predicted to be capable of electron and energy transfer over considerable distances by mutual interaction of the π orbitals of the terminal chromophores with the σ and σ* orbitals of the bridge.[30]



10

Michl and co-workers,[31] as well as Hawthorne’s group,[32] have prepared di- and tetra-*p*-carborane chains and pointed out their structural relationship to the series of oligomeric propellanes such as [*n*]staffanes which have attracted interest, particularly in the field of novel materials, as transparent rigid-rod molecules capable of transmitting electronic effects. Our results provide the first spectroscopic evidence that the *p*-carborane unit also provides electronic connection between terminal π systems.

Whether or not electronic effects are transmitted through carboranes by a similar mechanism to that of the staffanes, their remarkable thermal and chemical stability, combined with the available synthetic methods whereby they can be coupled together[31,32] and to aromatic and other carbon groups or heteroatoms, gives them a potential advantage for materials applications over strained hydrocarbon systems such as [*n*]staffanes which are available only in low yields and decompose between 200 and 300 °C.[33]

We are currently examining further electronic properties, including second harmonic generation (SHG), of these compounds as well as the synthesis and properties of more complex assemblies of *p*-carborane units. The remarkable polarisation of the cage revealed by our NMR results and charge-density calculations give these studies particular interest.

Experimental

General

Reactions with butyllithium were conducted under dry oxygen-free dinitrogen in glassware dried by heating to *ca.* 120 °C and cooling under a dry nitrogen purge. Stirring refers to the use of a magnetic stirrer. Solutions were dried over anhydrous sodium sulfate and evaporated under reduced pressure on a rotary evaporator. Melting points were measured in capillary tubes in an electrically heated block. Thin-layer chromatography (TLC) was conducted on Merck DC-Plastifolien Kieselgel 60 F_{254} (Art 5735) with UV detection.

Infrared spectra were recorded as potassium bromide discs, using a Perkin-Elmer 1720 X FTIR spectrometer, mass spectra on a VG Micromass 7070E instrument operating in the electron impact (EI) mode at 70 eV (1.12×10^{-17} J). Calculated values of *M* show the full isotope range $^{10}B_n$ to $^{11}B_n$ including a ^{13}C contribution where this is likely to have observable intensity; the less-probable combinations are not always observed in practice. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ solution on a Bruker AMX 500 spectrometer operating at 500 MHz for ^{1}H, 125.8 MHz for ^{13}C and 160.5 MHz for ^{11}B except where stated: ^{1}H spectra at 250 MHz, ^{13}C at 62.9 MHz and all the ^{19}F spectra, at 235.3 MHz, were run on a Bruker AC 250. The ^{1}H and ^{13}C shifts are referenced to tetramethylsilane, ^{11}B and ^{19}F to external boron trifluoride–diethyl ether.

1,2-Dimethoxyethane was dried by refluxing and distillation over potassium and storage over sodium wire, and pyridine by distillation after standing over potassium hydroxide. Diethyl ether was used as supplied. Butyllithium solution was used as supplied (Aldrich) or, after storage, standardised by titration with Bu^{s}OH in toluene with 4,5-diazaphenanthrene as indicator. Carboranes were commercial materials purified by sublimation at *ca.* 70 °C (0.01 mmHg, *ca.* 1.33 Pa). Copper(I) chloride was purified as described by Whitesides *et al.*[34] (a larger proportion of dilute H_2SO_4 was used so as to form a pourable suspension). 4-(Dimethylamino)iodobenzene was prepared by the method of Bayer[35] and sublimed at 45 °C (0.01 mmHg).

General procedure for coupling reactions with aryl iodides

A solution of the carborane (5–20 mmol) in 1,2-dimethoxyethane (4 cm^3 per mmol of carborane) was stirred and a solution (1.6 or 2.5 mol dm^{-3}) of butyllithium in hexanes (1.05, or 2.05 mol for mono- or di-substitution, respectively) was added slowly followed by dry pyridine (0.6 cm^3 per mmol of carborane) and purified copper(I) chloride (*ca.* 1.2 or 2.2 mol, weighed in air, without delay). Vigorous stirring was maintained and the mixture was heated at the reflux temperature for *ca.* 30 min. The aryl iodide (1.05 or 2.05 mol) was added, and the mixture, which was usually dark purple-red but became lighter as the reaction proceeded, was heated under gentle reflux (oil-bath 95–100 °C) for 16–60 h. The mixture was allowed to cool, diluted to *ca.* 5 times its volume with ether (not dry; addition of a few drops of water at this stage may be advantageous) and set aside for a few hours (conveniently overnight). The solid (complexed copper salts) was separated and washed with ether (and retained for re-extraction in some preparations), and the solution shaken first with dilute (1 mol dm^{-3}) hydrochloric acid (*ca.* 20 cm^3 per cm^3 of pyridine used) and then three times with water, and the organic layer was separated, dried, and evaporated. The product was purified by sublimation and/or recrystallisation or chromatography, as indicated.

1-Phenyl-*p*-carborane 3a and 1,12-diphenyl-*p*-carborane 5a. The solid residue from reaction of *p*-carborane (2.88 g, 20 mmol) and iodobenzene (4.18 g, 20.5 mmol) during 20 h under the general conditions described above was sublimed at room temperature, 0.01 mmHg, to recover *p*-carborane (0.52 g, 22%) and then at 30 °C to give the monophenyl derivative (2.29 g, 52%), m.p. 99–100 °C (from MeOH) (lit.,[36] 99–100 °C) [Found: C, 43.75; H, 7.3%; *M* (mass spectrum) 212–222. Calc. for $C_8H_{16}B_{10}$: C, 43.6; H, 7.3%; *M* 212–223]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 220 (13 400) and 260 (310). $\tilde{\nu}_{max}$/cm^{-1} 3057 (carborane CH); 3024w (aryl CH); 2599vs (BH); 1582, 1495, 1446 (phenyl skeleton); 1139; 1083; 1022; 1003; 909; 893; 831; 773. 692 (phenyl out of plane); 741 (carborane skeleton); 673; 607; 583; 490. $\delta_H\{^{11}B\}$ 7.21 (3 H, m, phenyl H2,4,6), 7.18 [2 H, t, *J*(HH) 7.5, phenyl H3,5], 2.78 [1 H, sextet, *J*(HH) 3.5 Hz, carborane CH], 2.53 (5 H, br s, H on B2–6) and 2.29 (5 H, br s, H on B7–11). $\delta_C\{^1H\}$ 136.7 (phenyl C1), 128.2 (phenyl C4), 128.0 (phenyl C2,6), 126.9 (phenyl C3,5), 86.4 (carborane C1) and 59.7 (carborane CH). $\delta_B\{^1H\}$ −9.17 (B2–6) and −11.85 (B7–11).

Recrystallisation of the sublimation residue from propan-2-ol gave 1,12-diphenyl-*p*-carborane (1.07 g, 18%), m.p. 214–215 °C (lit.,[33] 202–203 °C from hexane) [Found: C, 55.75; H, 6.9%; *M* (mass spectrum) 285–299. Calc. for $C_{14}H_{20}B_{10}$: C, 55.75; H, 6.8%; *M* 288–299]. $\tilde{\nu}_{max}$/cm^{-1} 3056w, 3040w (phenyl CH); 2604vs (BH); 1597, 1579, 1498, 1445 (phenyl skeleton); 1261; 1187w; 1108w; 1085; 1029; 1002; 914; 790; 755, 691 (phenyl out of plane); 729 (carborane skeleton); 646; 602; 485. $\delta_H\{^{11}B\}$ 7.17 [4 H, d, *J*(HH) 7.5, phenyl H2,2′,6,6′], 7.13 [2 H, t, *J*(HH) *ca.* 7.5 Hz, phenyl H3,3′,5,5′] and 2.56 (10 H, s, BH). $\delta_C\{^1H\}$ 136.3 (phenyl C1,1′); 128.4 (phenyl C4,4′), 128.1 (phenyl C2,2′,6,6′), 127.2 (phenyl C3,3′,5,5′) and 82.8 (carborane C). $\delta_B\{^1H\}$ −9.22.

1-(4-Methoxyphenyl)-*p*-carborane 3b and 1,12-bis(4-methoxyphenyl)-*p*-carborane 5b. The crystalline residue (6.69 g) from reaction of *p*-carborane (3.03 g, 21 mmol) and resublimed 4-iodoanisole (5.05 g, 21.6 mmol) was sublimed at 38 °C, 0.01 mmHg, for 3 h to recover 4-iodoanisole (265 mg, with traces of the required arylcarborane) and then at 76 °C to give the *methoxyphenyl derivative* (4.13 g, 79%), m.p. 99.5–101 °C [Found: C, 42.45; H, 7.05%; *M* (mass spectrum) 246–253. $C_9H_{18}B_{10}O$ requires C, 43.1; H, 7.25%; *M* 242–253]. $\tilde{\nu}_{max}$/cm^{-1} 3060w (carborane CH); 3005w (aryl CH); 2958w, 2932w, 2903w, 2835w (methoxy CH); 2613vs (BH); 1613, 1578w, 1515, 1461 (aryl skeleton); 1439; 1301; 1262; 1183; 1139; 1087; 1038; 1023; 843 (aryl out of plane); 809; 738 (carborane skeleton); 567; 527. $\delta_H\{^{11}B\}$ 7.14 (2 H, m, aryl H2,6), 6.69 (2 H, m, aryl H3,5), 3.75 (3 H, s, methoxy), 2.76 (1 H, br s, carborane CH), 2.52 (5 H, br s, H on B2–6) and 2.28 (5 H, br s, H on B7–11). $\delta_C\{^1H\}$ (62.9 MHz) 159.6 (aryl C4), 129.3 (aryl C1), 128.2 (aryl C2,6), 113.2 (aryl C3,5), 86.4 (carborane C1), 59.2 (carborane CH) and 55.2 (methoxy). $\delta_B\{^1H\}$ −12.4 (B2–6) and −15.2 (B7–11).

Recrystallisation of the sublimation residue from cyclohexane with separation of a little dark insoluble matter gave off-white flakes of the *bis*(*methoxyphenyl*) *derivative* (508 mg, 7%), m.p. 236–238 °C [Found: C, 53.75; H, 6.75%; *M* (mass spectrum) 354–358. $C_{16}H_{24}B_{10}O_2$ requires C, 53.9; H, 6.8%; *M* 348–359]. $\tilde{\nu}_{max}$/cm^{-1} 3005w (aryl CH); 2958w, 2932w, 2904w, 2836w (methoxy CH); 2616vs (BH); 1611, 1512, 1462, 1440 (aryl skeleton); 1300; 1260; 1183; 1085; 1029; 918; 835 (aryl out of plane); 796w; 756w (carborane skeleton); 588; 525. δ_H 7.17 (4 H, m, aryl H2,2′,6,6′), 6.71 (4 H, m, aryl H 3,3′,5,5′), 3.76 (6 H, s, methoxy) and 3.7–1.2 (*ca.* 10 H, BH). $\delta_C\{^1H\}$160.2 (aryl C4,4′), 129.3 (aryl C1,1′), 128.9 (aryl C2,2′,6,6′), 113.9 (aryl C3,3′,5,5′), 84.5 (carborane C) and 55.9 (methoxy). $\delta_B\{^1H\}$ −12.70.

1-(4-Nitrophenyl)-*p*-carborane 3c and 1,12-bis(4-nitrophenyl)-*p*-carborane 5c. The ether-soluble product (2.40 g) isolated by the standard procedure from the reaction of *p*-carborane (1.47 g, 10.2 mmol) and 1-iodo-4-nitrobenzene (5.23 g, 21.0 mmol) during 48 h was chromatographed on silica (50 g), eluted with pentane containing 8% v/v of dichloromethane, to give the *mononitrophenyl derivative* (1.04 g, 39%) as just perceptibly yellow flakes, m.p. 171.5–172 °C (from benzene) [Found: C, 35.9; H, 5.85; N, 5.05%, *M* (mass spectrum) 261–268. $C_8H_{15}B_{10}NO_2$ requires C, 36.2; H, 5.7; N, 5.3%; *M* 257–268]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 264 (14 800) and 332 (infl.) (360). $\tilde{\nu}_{max}$/cm^{-1} 3110w, 3085w (aryl CH); 3059w (carborane CH); 2611vs (BH); 1605, 1596 (aryl skeleton); 1523s (NO_2); 1496; 1406; 1348s (NO_2); 1290; 1141; 1112; 1091; 1015; 866; 848 (aryl out of plane); 739 (carborane skeleton); 695; 681; 491; 448. δ_H(250 MHz) 8.03 (2 H, m, aryl H3,5), 7.38 (2 H, m, aryl H2,6), 2.88 (1 H, s, carborane CH) and 1.8–1.3 (*ca.* 10 H, m, BH). $\delta_C\{^1H\}$ (62.9 MHz) 147.6 (aryl C4), 143.0 (aryl C1), 128.2 (aryl C3,5), 123.2 (aryl C2,6), 84.1 (carborane C1) and 60.9 (carborane CH). $\delta_B\{^1H\}$ −12.7 (B2–6) and −14.9 (B7–11).

The solid (copper salts, *etc.*) separated after dilution of the reaction mixture with ether was extracted with dichloromethane (100 cm^3), the solution was shaken with dilute hydrochloric acid (2 mol dm^{-3}, 50 cm^3), filtered through Hyflo and the organic layer dried and evaporated. The residue (1.94 g) was dissolved in toluene and chromatographed as before to give a further sample of the mononitro-compound (108 mg, 4%) followed by the *bis*(*nitrophenyl*)*derivative* (1.16 g, 30%) eluted by pentane containing 25% v/v of dichloromethane; an additional crop (306 mg, 8%) was obtained by similar elution of the first chromatogram. Recrystallisation from benzene furnished pale yellow laths, m.p. 317–319 °C [Found: C, 43.3; H, 4.7; N, 6.9%; *M* (mass spectrum) 382–389. $C_{14}H_{18}B_{10}N_2O_4$ requires C, 43.5; H, 4.7; N, 7.25%; *M* 378–389]. $\tilde{\nu}_{max}$/cm^{-1} 3109w, 3077w, 3054w (aryl CH); 2619s (BH); 1604, 1595 (aryl skeleton); 1521s (NO_2); 1494; 1407; 1347s (NO_2); 1291; 1252; 1123; 1111; 1081; 1013; 918; 860; 843s (aryl out of plane); 777; 751 (carborane skeleton); 686; 598; 527; 480; 462. $\delta_H\{^{11}B\}$ 8.07 (4 H, m, aryl H3,3′,5,5′), 7.42 (4 H, m, aryl H2,2′,6,6′) and 2.68 (10 H, s, BH). $\delta_C\{^1H\}$ 147.9 (aryl C4,4′), 142.2 (aryl Cl,1′), 128.3 (aryl C3,3′,5,5′), 123.4 (aryl C2,2′,6,6′) and 81.9 (carborane C). $\delta_B\{^1H\}$ −9.11.

1-(4-Dimethylaminophenyl)-*p*-carborane 3d and 1,12-bis(4-dimethylaminophenyl)-*p*-carborane 5d. The white solid from reaction of *p*-carborane (2.88 g, 20 mmol) and 1-(dimethylamino)-4-iodobenzene[32] (4.94 g, 20 mmol) during 24 h was separated from traces of *p*-carborane (*ca.* 100 mg) by sublimation at room temperature (0.01 mmHg), and of the starting iodo-compound (94 mg) at 50 °C. Since sublimation of the carborane derivative proved very slow up to 85 °C the residue was recrystallised from propan-2-ol with separation of colourless insoluble material (85 mg) to give, including a second crop of equal purity, the *monoamino-compound* (4.30 g, 82%), m.p. 179.5–180.5 °C [Found: C, 45.9; H, 8.15; N, 4.9%; *M* (mass spectrum) 258–266. $C_{10}H_{21}B_{10}N$ requires C, 45.6; H, 8.05; N, 5.3%; *M* 255–266]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 278 (26 400). $\tilde{\nu}_{max}$/cm^{-1} 3101w (aryl CH); 3062 (carborane CH); 2991w, 2906, 2862w, 2815 (methyl CH); 2606vs (BH); 1614, 1530 (aryl skeleton); 1483; 1446; 1373 (C–N); 1237; 1200; 1137; 1086; 1008; 950; 828; 799 (aryl out of plane); 735 (carborane skeleton); 581; 555; 513. $\delta_H\{^{11}B\}$ 7.04 (2 H, m, aryl H2,6), 6.46 (2 H, m, aryl H3,5), 2.87 (6 H, s, methyl), 2.68 (1 H, s, carborane CH), 2.50 (5 H, br s, H on B2–6) and 2.24 (5 H, br s, H on B7–11). $\delta_C\{^1H\}$ 150.2 (aryl C4), 127.7 (aryl C2,6), 124.9 (aryl C1), 111.3 (aryl C3,5), 87.22 (carborane Cl) and 58.6 (carborane CH). $\delta_B\{^1H\}$ −9.05 (B2–6) and −11.94 (B7–11).

The material which was insoluble in propan-2-ol was recrystallised from 1,2-dichlorobenzene and washed with ethanol to give colourless prisms of the *diamine* (58 mg, 0.8%), m.p. > 300 °C [Found: C, 55.85; H, 7.85; N, 6.75%; *M* (mass spectrum) 378–387. $C_{18}H_{30}B_{10}N_2$ requires C, 56.5; H, 7.9; N, 7.3%; *M* 374–387]. $\tilde{\nu}_{max}$/cm^{-1} 3098w, 3045w (aryl CH); 2991w, 2906, 2891, 2861w, 2815 (methyl CH); 2603s (BH); 1611, 1529, 1483, 1446 (aryl skeleton); 1373 (C–N); 1237; 1200; 1084; 951; 915; 810 (aryl out of plane); 740 (carborane skeleton); 600; 570; 512. The compound was too insoluble for NMR measurements.

1-(4-Trifluoromethylphenyl)-*p*-carborane 3e and 1,12-bis(4-trifluoromethylphenyl)-*p*-carborane 5e. The mobile oil, which solidified slowly, from the reaction of *p*-carborane (2.52 g, 17.5 mmol) and 1-iodo-4-trifluoromethylbenzene (4.95 g, 18.2 mmol) during 16 h was sublimed at 26 °C, 0.01 mmHg, to recover *p*-carborane (110 mg) and then at 50 °C to give the *monoaryl derivative* (2.52 g, 50%), m.p. 93.5–94.5 °C (from MeOH) [Found: C, 37.4; H, 5.25%; *M* (mass spectrum) 280–290. $C_9H_{15}B_{10}F_3$ requires C, 37.65; H, 5.25%; *M* 280–291]. $\tilde{\nu}_{max}$/cm^{-1} 3077 (carborane CH); 2961w, 2936w, 2856w (aryl CH); 2613vs (BH); 1624, 1582w, 1516w (aryl skeleton); 1411; 1329 (CF_3); 1164; 1121; 1069; 1016; 856 (aryl out of plane); 739 (carborane skeleton); 600; 503; 410. $\delta_H\{^{11}B\}$ 7.35 (2 H, m, aryl CH), 7.25 (2 H, m, aryl CH), 2.74 (1 H, br s, carborane CH), 2.43 (5 H, br s, H on B2–6) and 2.24 (5 H, br s, H on B7–11). $\delta_C\{^1H\}$ 140.3 (aryl C1), 130.6 [q, *J*(CF) 32.7, aryl C4], 127.6 (aryl C2,6), 125.1 [q, *J*(CF) 3.8, aryl C3,5], 123.7 [q, *J*(CF) 272.9 Hz, CF_3], 84.9 (carborane Cl) and 60.5 (carborane CH). $\delta_B\{^1H\}$ −12.70 (B2–6) and −15.10 (B7–11). δ_F −63.28.

The sublimation residue was recrystallised from butan-1-ol with separation of insoluble matter to give the *diaryl derivative* (663 mg, 9%) as a white powder, m.p. 238–241 °C [Found: C, 43.75; H, 4.4%; *M* (mass spectrum) 422–435. $C_{16}H_{18}B_{10}F_6$ requires C, 44.4; H, 4.2%; *M* 422–436]. $\tilde{\nu}_{max}$/cm^{-1} 2961w, 2935w, 2856w (aryl CH); 2622s (BH); 1617, 1583w, 1518w (aryl skeleton); 1411; 1322 (CF_3); 1166; 1129; 1062; 1019; 920; 868; 833 (aryl out of plane); 749 (carborane skeleton); 609; 504; 437; 408. $\delta_H\{^{11}B\}$ 7.42 (4 H, m, aryl CH), 7.30 (4 H, m, aryl CH) and 2.60 (10 H, br s, BH). $\delta_C\{^1H\}$ 139.6 (aryl C1,1′), 130.8 [q, *J*(CF) 32.7, aryl C4], 127.6 (aryl C2,2′,6,6′), 125.2 [q, *J*(CF) 3.8, aryl C3,3′,5,5′], 123.7 [q, *J*(CF) 271.7 Hz, CF_3] and 82.1 (carborane C). $\delta_B\{^1H\}$ −12.63. δ_F −63.28.

1,12-Bis(4-methylphenyl)-*p*-carborane 5f. The solid product from *p*-carborane (1.44 g, 10 mmol) and freshly sublimed 4-iodotoluene (4.36 g, 20 mmol) during 20 h was chromatographed on silica to give the *ditolyl derivative* (2.72 g, 84%), eluted by hexane containing 5% v/v ethyl acetate, m.p. 232–233 °C (from cyclohexane) [Found: C, 59.35; H, 7.75%; *M* (mass spectrum) 319–326. $C_{16}H_{24}B_{10}$ requires C, 59.2; H, 7.5%; *M* 316–328]. $\tilde{\nu}_{max}$/cm^{-1} 3033w (aryl CH); 2955w, 2916w (methyl CH); 2603s (BH); 1507, 1443w (aryl skeleton); 1077; 1028w; 821 (aryl out of plane); 741 (carborane skeleton); 598w; 492. $\delta_H\{^{11}B\}$ 7.15 (4 H, m, aryl CH), 7.10 (4 H, m, aryl CH), 2.64 (10 H, br s, BH) and 2.29 (6 H, s, methyl). $\delta_C\{H\}$ 138.2 (aryl C1,1′), 133.5 (aryl C4,4′), 128.7 (aryl C2,2′,6,6′), 126.9 (aryl C3,3′,5,5′), 82.4 (carborane C) and 20.7 (methyl). $\delta_B\{^1H\}$ −9.22.

1-(4-Methoxyphenyl)-12-(4-nitrophenyl)-*p*-carborane 6bc. The crystalline residue (2.86 g) from reaction of 1-(4-methoxyphenyl)-*p*-carborane (2.02 g, 8.06 mmol) with 1-iodo-4-nitrobenzene (2.02 g, 8.11 mmol) during 20 h was recrystallised from butan-1-ol to give white flakes of the *methoxynitro-compound* (2.11 g, 71%), m.p. 206–207 °C [Found: C, 47.8; H, 5.6; N, 3.4%; *M* (mass spectrum) 374–367. $C_{15}H_{21}B_{10}NO_3$ requires C, 48.45; H, 5.7; N, 3.75%; *M* 374–367]. $\tilde{\nu}_{max}$/cm^{-1} 3110w, 3078w (aryl CH); 2935w, 2832w (methoxy CH); 2616s (BH); 1605, 1596 (aryl skeleton); 1527s (NO_2); 1511; 1495; 1461; 1438; 1349s (NO_2); 1301; 1259; 1183; 1082; 845 (aryl out of plane); 821; 804; 752; 741 (carborane skeleton); 684; 600; 573; 524; 492; 450. $\delta_H\{^{11}B\}$ 8.05 (2 H, m, $C_6H_4NO_2$, H3,5), 7.43 (2 H, m, $C_6H_4NO_2$ H2,6), 7.15 (2 H, m, C_6H_4OMe, H2,6), 6.72 (2 H, m, C_6H_4OMe, H3,5), 3.76 (3 H, s, OCH_3), 2.69 (5 H, br s, H on B7–11) and 2.61 (5 H, br s, H on B2–6). $\delta_C\{^1H\}$ (62.9 MHz) 159.8 (C_6H_4OMe, C4), 147.7 ($C_6H_4NO_2$, C4), 142.8 ($C_6H_4NO_2$, C1), 128.2 (multiplet unresolved, $C_6H_4NO_2$, C3,5; C_6H_4OMe, C1,2,6), 123.3 ($C_6H_4NO_2$, C2,6), 113.4 (C_6H_4OMe, C3,5), 84.2 (carborane C1) and 80.0 (carborane C12). $\delta_B\{^1H\}$ −12.60, −12.35 (B2–6 and B7–11).

1-(4-Dimethylaminophenyl)-12-(4-nitrophenyl)-*p*-carborane 6cd. The solid (copper salts, *etc.*) precipitated by addition of ether to the reaction mixture obtained from 1-(4-dimethylaminophenyl)-*p*-carborane (1.23 g, 4.68 mmol) and 1-iodo-4-nitrobenzene (1.20 g, 4.82 mmol) during 23 h was washed with dilute hydrochloric acid (2 mol dm^{-3}, 4 × 10 cm^3) and then with ethanol (2 × 8 cm^3), dried, and extracted with hot chloroform (6 × 15 cm^3). The extract was evaporated and the residue (1.17 g) combined with that obtained from the ether solution of the reaction products (0.71 g) and recrystallised from toluene to give orange prisms of the *dimethylaminonitro-compound* (1.23 g, 69%), m.p. 285–286.5 °C [Found: C, 50.35; H, 6.4; N, 7.2%; *M* (mass spectrum) 374–388. $C_{16}H_{24}B_{10}N_2O_2$ requires C, 50.0; H, 6.3; N, 7.3%; *M* 374–388]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 280 (38 700). $\tilde{\nu}_{max}$/cm^{-1} 3110w, 3086w, 3054w, 2998w (aryl CH); 2908w, 2864w, 2820w (methyl CH); 2611s (BH); 1610, 1597 (aryl skeleton); 1523s (NO_2); 1493; 1444; 1406w; 1369 (C–N); 1347s (NO_2); 1288; 1238; 1201; 1174; 1110; 1084; 1015; 1003; 951; 916; 866; 845, 835 (aryl out of plane); 807; 746; 739 (carborane skeleton); 683; 599; 561; 515; 488; 457. $\delta_H\{^{11}B\}$ 8.04 (2 H, m, $C_6H_4NO_2$, H3,5), 7.42 (2 H, m, $C_6H_4NO_2$, H2,6), 7.06 (2 H, m, $C_6H_4NMe_2$, H3,5), 6.48 (2 H, m, $C_6H_4NMe_2$, H2,6), 2.91 (6 H, s, methyl), 2.67 (5 H, br s, H on B7–11) and 2.58 (5 H, br s, H on B2–6). $\delta_C\{^1H\}$ 150.4 ($C_6H_4NMe_2$, C4), 147.7 ($C_6H_4NO_2$, C4), 143.1 ($C_6H_4NO_2$, C1), 128.5 ($C_6H_4NO_2$, C3,5), 127.7 ($C_6H_4NMe_2$, C2,6), 123.7 ($C_6H_4NMe_2$, C1), 123.2 ($C_6H_4NO_2$, C2,6), 111.4 ($C_6H_4NMe_2$, C3,5), 85.0 (carborane C1) and 79.1 (carborane C12). $\delta_B\{^1H\}$ −9.43, −8.90 (B2–6 and B7–11).

1-[3,5-Bis(trifluoromethyl)phenyl]-12-(4-methoxyphenyl)-*p*-carborane 6bg. The crystalline product from reaction of 1-(4-methoxyphenyl)-*p*-carborane (1.12 g, 4.48 mmol) and 1-iodo-3,5-bis(trifluoromethyl)benzene (1.73 g, 5.09 mmol) during 24 h was recrystallised from ethanol to give colourless crystals of the *bis*(*trifluoromethyl*) *compound* (1.99 g, 96%), m.p. 117–118 °C [Found: C, 44.15; H, 4.35%; *M* (mass spectrum) 458–465. $C_{17}H_{20}B_{10}F_6O$ requires C, 44.15; H, 4.35%; *M* 454–465]. $\tilde{\nu}_{max}$/cm^{-1} 3098w, 3066w, 3005w, 2966w (aryl CH); 2936w, 2908w, 2837w (methoxy CH); 2615s (BH); 1615, 1516, 1465 (aryl skeleton); 1377 (CF_3); 1287; 1276; 1198; 1182; 1132; 1085; 903 (aryl isolated H out of plane); 845 (1,4-substituted aryl out of plane); 821w; 745w (carborane skeleton); 700; 683; 658; 631; 574; 522; 413. δ_H(250 MHz) 7.77 [1 H, s, $C_6H_3(CF_3)_2$, H4], 7.68 [2 H, s, $C_6H_3(CF_3)_2$, H2,6], 7.15 (2 H, m, C_6H_4OMe, H2,6), 6.71 (2 H, m, C_6H_4OMe, H3,5), 3.75 (3H, s, OCH_3) and 3.5–1.5 (10 H, br m, BH). $\delta_C\{^1H\}$ (62.9 MHz) 159.8 (C_6H_4OMe, C4), 138.7 [$C_6H_3(CF_3)_2$, C1], 131.7 [q, *J*(CF) 33.7, $C_6H_3(CF_3)_2$, C3,5], 128.2 (C_6H_4OMe, Cl,2,6), 127.4 [$C_6H_3(CF_3)_2$, C2,6], 127.1 [q, *J*(CF) 272.9 Hz, CF_3], 125.0 [$C_6H_3(CF_3)_2$, C4], 113.4 (OCH_3), 84.1 (carborane C1) and 79.2 (carborane C12). $\delta_B\{^1H\}$ −12.56 (br s, B2–6 and B7–11). δ_F −63.41.

1,12-Bis(4-hydroxyphenyl)-*p*-carborane 5h. (*a*) *Using pyridine hydrochloride.* 1,12-Bis(4-methoxyphenyl)-*p*-carborane (540 mg) was mixed with pyridine hydrochloride (6.5 g) and heated to 200–212 °C (bath temperature) with stirring and occasional shaking for 2 h, when all the solid had dissolved. The cooled mixture was extracted with dilute hydrochloric acid (1 mol dm^{-3}, 30 cm^3) and the insoluble material washed with water and dried at 78 °C, 0.01 mmHg, to give the *dihydroxy-compound* (486 mg, 98%) as a light brown powder. Recrystallisation from ethanol using charcoal gave lustrous white plates, m.p. 290–291 °C, or square prisms, m.p. 291–292 °C (from acetonitrile) [Found: C, 50.95; H, 6.1%; *M* (mass spectrum) 320–331. $C_{14}H_{20}B_{10}O_2$ requires C, 51.05; H, 6.1%; *M* 320–331]. $\tilde{\nu}_{max}$/cm^{-1} 3363s (br) (OH); 2610s (BH); 1613, 1599, 1513s, 1458 (aryl skeleton); 1384; 1299; 1244s (C–O); 1182; 1123; 1082; 1016; 918; 838 (aryl out of plane); 811; 750; 591; 514; 437. δ_H([$^2H_8$]thf) 8.45 (2 H, s, OH), 7.05 (4 H, m, aryl H2,2′,6,6′), 6.54 (4 H, m, aryl H3,3′,5,5′) and 4.0–1.3 (*ca.* 10 H, br m, BH). $\delta_C\{^1H\}$ (thf) 158.0 (aryl C4,4′), 127.9 (aryl C2,2′,6,6′), 126.9 (aryl C1,1′), 114.5 (aryl C3,3′,5,5′) and 81.8 (carborane C). $\delta_B\{^1H\}$ (thf) −13.39.

(*b*) *Using hydriodic and acetic acids.* Bis(4-methoxyphenyl)-*p*-carborane (500 mg), hydriodic acid (55% solution, 10 cm^3) and acetic acid (10 cm^3) were stirred and heated under reflux for 24 h, with periodic shaking to wash down solid which collected above the liquid surface, when all the solid had dissolved. The mixture was allowed to cool to room temperature and the resulting solid collected on a glass sinter, washed with water and dried at 78 °C, 0.01 mmHg, to give the *diphenol* (439 mg, 95%), m.p. 290–291 °C, identical (IR spectrum) with that obtained by method (*a*).

1-(4-Hydroxyphenyl)-*p*-carborane 3h. 1-(4-Methoxyphenyl)-*p*-carborane (450 mg) was heated with pyridine hydrochloride (5.1 g) as in method (*a*) above for 0.5 h and the product (365 mg, 86%), isolated as before, recrystallised from cyclohexane using charcoal and dried at room temperature, 0.01 mmHg, to give a cyclohexane solvate of the *phenol* of reproducible (three experiments) composition, m.p. 188–189 °C [Found: C, 42.4; H, 7.2%; *M* (mass spectrum) 228–239 and 84. $C_8H_{16}B_{10}O\cdot 0.14C_6H_{12}$ requires C, 42.8; H, 7.2%; *M* 228–239 and 84]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 240 (14 000) and 276 (1000); (thf with one drop 2% methanolic KOH added to *ca.* 4 cm^3) 284 (16 000). $\tilde{\nu}_{max}$/cm^{-1} 3266s (br) (OH); 3059 (carborane CH); 3032w (aryl CH); 2925, 2851w (cyclohexane CH); 2613 (BH); 1616, 1600, 1516, 1449 (aryl skeleton); 1372; 1249 (C–O); 1185; 1088; 1015; 899; 847 (aryl out of plane); 827; 812; 737 (carborane skeleton); 709; 658w; 582w; 561; 517. $\delta_H\{^{11}B\}$ 7.07 (2 H, m, aryl H2,6), 6.62 (2 H, m, aryl H3,5), 4.92 (1 H, s, OH), 2.75 (1 H, br s, carborane CH), 2.50 (5 H, br s, H on B2–6), 2.27 (5 H, br s, H on B7–11) and 1.43 (1.64 H, s, cyclohexane). $\delta_C\{^1H\}$ (62.9 MHz) 155.5 (aryl C4), 129.6 (aryl C1), 128.4 (aryl C2,6), 114.7 (aryl C3,5), 86.2 (carborane C1), 59.2 (carborane CH) and 26.7 (cyclohexane). $\delta_B\{^1H\}$ −9.12 (B2–6) and −11.86 (B7–11).

1-[3,5-Bis(trifluoromethyl)phenyl]-12-(4-hydroxyphenyl)-*p*-carborane 6gh. 1-[3,5-Bis(trifluoromethyl)phenyl]-12-(4-methoxyphenyl)-*p*-carborane (360 mg) was heated with hydriodic acid (10 cm^3) and acetic acid (5 cm^3) as in method (*b*) above. The cooled mixture was extracted with ether (50 cm^3), the extract washed successively with water (3 × 80 cm^3), sodium hydrogencarbonate solution (2.5%, 50 cm^3), sodium thiosulfate solution (5%, 50 cm^3) and water (50 cm^3), dried and evaporated. The crystalline residue of the *phenol* (321 mg, 92%) m.p. 156–157 °C, showed only one TLC spot (R_f 0.3 on silica, cyclohexane–ethyl acetate 9 : 1) [Found: C, 42.7; H, 4.1%; *M* (mass spectrum) 444–451. $C_{16}H_{18}F_6O$ requires C, 42.85; H, 4.05%; *M* 440–452]. $\tilde{\nu}_{max}$/cm^{-1} 3329s (br) (OH); 2614vs, 2585 (BH), 1618, 1515, 1472, 1445 (aryl skeleton); 1380, 1279 (C–O and OH); 1237; 1181; 1142; 1133; 1113; 1086; 903, 881 (aryl isolated H out of plane); 847 (1,4-substituted aryl out of plane); 817; 744 (carborane skeleton); 709; 700; 683; 659; 638w; 569; 526; 460w. $\delta_H\{^{11}B\}$ 7.76 [1 H, s, $C_6H_3(CF_3)_2$, H4], 7.68 [2 H, s, $C_6H_3(CF_3)_2$, H2,6], 7.11 (2 H, m, C_6H_4OH, H2,6), 6.65 (2 H, m, C_6H_4OH, H3,5), 4.97 (1 H, br s, OH), 2.68, 2.62 (5 H, 5 H, br s, H on B2–6 and B7–11). $\delta_C\{^1H\}$ 155.9 (C_6H_4OH, C4), 138.7 [$C_6H_3(CF_3)_2$, C1], 131.5 [q, *J*(CF) 34.0, $C_6H_3(CF_3)_2$, C3,5], 128.5 (C_6H_4OH, C1), 128.4 [C_6H_4OH, C2,6], 127.4 [$C_6H_3(CF_3)_2$, C2,6], 122.8 [q, *J*(CF) 272.9 Hz, CF_3], 114.9 (C_6H_4OH, C3,5), 84.0 (carborane C1) and 79.3 (carborane C12). $\delta_B\{^1H\}$ −8.88, −9.36 (B2–6 and B7–11). δ_F −63.34. Attempted demethylation by method (*a*) was unsuccessful.

1-(4-Hydroxyphenyl)-12-(4-nitrophenyl)-*p*-carborane 6ch. 1-(4-Methoxyphenyl)-12-(4-nitrophenyl)-*p*-carborane (820 mg) was heated with pyridine hydrochloride (8.67 g) during 2 h as in method (*a*) above and the product similarly isolated by filtration to give the *hydroxy-derivative* (754 mg, 96%), m.p. 244–248 °C, after recrystallisation from methanol using charcoal [Found: C, 46.6; H, 5.15; N, 3.65%; *M* (mass spectrum) 352–361. $C_{14}H_{19}B_{10}NO_3$ requires C, 47.05; H, 5.35; N, 3.9%; *M* 349–361]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 242 (20 900), 270 (17 600) and *ca.* 350 (infl., weak); (thf with one drop 2% methanolic KOH added to *ca.* 4 cm^3) 282 (26 300) and 351 (infl.) (2800). $\tilde{\nu}_{max}$/cm^{-1} 3543 (OH); 3113w, 3080w (aryl CH); 2612s (BH); 1599, 1513, 1496, 1456w, 1433 (aryl skeleton); 1524s, 1348s (NO_2); 1323w; 1291w; 1275; 1255; 1179; 1112; 1083; 1014; 918; 869; 845 (aryl out of plane); 817; 740 (carborane skeleton); 684; 668; 599; 569; 522; 486. $\delta_H\{^{11}B\}$ ([$^2H_8$]thf) 8.52 (1 H, s, OH), 8.08 (2 H, m, $C_6H_4NO_2$, H3,5), 7.53 (2 H, m, $C_6H_4NO_2$, H2,6), 7.06 (2 H, m, C_6H_4OH, C2,6), 6.58 (2 H, m, C_6H_4OH, C3,5), 2.60, 2.50 (5 H, 5 H, H on B2–6 and B7–11). $\delta_C\{^1H\}$ (thf) 158.2 (C_6H_4OH, C4), 147.9 ($C_6H_4NO_2$, C4), 142.1 ($C_6H_4NO_2$, C1), 128.2 ($C_6H_4NO_2$, C3,5) 127.8 (C_6H_4OH, C3,5), 126.5 (C_6H_4OH, C1), 122.9 ($C_6H_4NO_2$, C2,6), 114.6 (C_6H_4OH, C3,5), 84.6 (carborane C1) and 79.8 (carborane C12). $\delta_B\{^1H\}$ (thf) −11.88 (B2–6) and −12.29 (B7–11).

The (18-crown-6)potassium salt of 1-(4-hydroxyphenyl)-12-(4-nitrophenyl)-*p*-carborane. (*a*) *Aqueous conditions.* The phenolic carborane (95 mg) and 18-crown-6 (80 mg) in warm ethanol (2.0 cm^3) were added dropwise to potassium hydroxide (17 mg) in water (1.5 cm^3). The bright yellow microcrystalline precipitate, collected after heating briefly to *ca.* 100 °C and standing overnight at room temperature, was washed with aqueous ethanol (1 : 1 v/v) and dried at room temperature, 0.01 mmHg, to give the monohydrate of the *crown potassium salt* (125 mg, 69%), m.p. 270–271 °C (decomp.) (Found: C, 46.05; H, 6.25; N, 2.55. $C_{14}H_{18}KNO_3\cdot C_{12}H_{24}O_6\cdot H_2O$ requires C, 46.05; H, 6.55; N, 2.05%). $\tilde{\nu}_{max}$/cm^{-1} 3447 (br) (OH); 3057w, 3021w (aryl CH); 2899 (multiplet unresolved, crown CH); 2610s (BH); 1603, 1596, 1497, 1472 (aryl skeleton); 1457 (CH_2); 1525s, 1350s (NO_2); 1283; 1250; 1175; 1111s; 1082; 1016w; 962; 915w; 866w; 845 (aryl out of plane); 742 (carborane skeleton); 686; 646w; 602w; 569; 527; 441. The compound is not sufficiently soluble for NMR measurements; on warming under vacuum. It becomes orange-yellow and, at 78 °C, 0.01 mmHg, loses weight corresponding with one water molecule. The orange-yellow anhydrous form reverts to the yellow hydrate upon exposure to the atmosphere.

(*b*) *Anhydrous conditions.* The phenolic carborane (427 mg) in warm (*ca.* 55 °C) toluene (10 cm^3) was added by syringe under dinitrogen to potassium *tert*-butoxide (141 mg) and 18-crown-6 (338 mg) in toluene (5 cm^3). A granular precipitate started to form in the orange-brown solution after *ca.* 1 min and filtration under dinitrogen after 2 h at room temperature gave an orange-yellow powder (240 mg, 30%) identical with that obtained by drying the product of the previous experiment. After a further 3 h the filtrate started to deposit ragged garnet-red crystals which were collected under dinitrogen after 24 h and washed with toluene to give the *isomeric anhydrous salt* (*ca.* 480 mg, 60%) (Found: C, 47.2; H, 6.5; N, 2.05. $C_{14}H_{18}B_{10}KNO_3{\cdot}C_{12}H_{24}O_6$ requires C, 47.35; H, 6.4; N, 2.1%). $\tilde{\nu}_{max}/cm^{-1}$ 3057, 3021 (aryl CH); 2893 (multiplet unresolved, crown CH); 2616, 2602, 2588 (BH); 1591, 1587, 1516, 1501 (aryl skeleton); 1457w (CH_2); 1345 (NO_2); 1285; 1249; 1171; 1109s; 1081; 991w; 961; 915w; 884w; 863w; 845, 837 (aryl out of plane); 743w (carborane skeleton); 688w; 569; 495. The dark red anhydrous form is quickly converted into the yellow hydrate, identical (IR spectrum) with that obtained in the previous experiment, upon exposure to the atmosphere.

1,12-Bis(4-aminophenyl)-*p*-carborane 5i. A stoppered Buchner flask containing 1,12-bis(4-nitrophenyl)-*p*-carborane (272 mg) in 1,4-dioxane (50 cm^3) and palladium on carbon (5%, 240 mg) was twice evacuated and filled with dihydrogen from a supply at atmospheric pressure. The mixture was stirred vigorously under dihydrogen at room temperature for 24 h, the flask evacuated and filled with dinitrogen and the catalyst separated by filtration on Hyflo and washed with dioxane. The filtrate was evaporated and the chalky-white residue recrystallised from butan-1-ol to give feathery blades of the *diamine* (168 mg, 90%), m.p. *ca.* 320 °C (subl., decomp.) [Found: C, 51.6; H, 6.85; N 8.3%; *M* (mass spectrum) 318–329. $C_{14}H_{22}B_{10}N_2$ requires C, 51.5; H, 6.8; N, 8.6%; *M* 318–329]. $\tilde{\nu}_{max}/cm^{-1}$ 3451, 3363 (NH_2); 3206w (overtone); 3058w, 3038w (aryl CH); 2598s, 2583 (BH); 1624s (NH_2); 1516s, 1430w (aryl skeleton); 1292; 1189; 1137w; 1080; 916; 832 (aryl out of plane); 750 (carborane skeleton); 601; 584; 515; 466w. $\delta_H([^2H_8]thf)$ 6.97 (4 H, m, aryl C2,2′,6,6′), 6.45 (4 H, m, aryl C3,3′,5,5′), 4.72 (4 H, br s, NH_2) and 4.0–0.7 (*ca.* 10 H, br m, BH). $\delta_C\{^1H\}$ (thf) 148.6 (aryl C4,4′), 127.4 (aryl C2,2′,6,6′), 124.0 (aryl C1,1′), 113.0 (aryl C3,3′,5,5′) and 82.6 (carborane C). $\delta_B\{^1H\}$ (thf) −13.49.

1-(4-Aminophenyl)-12-(4-hydroxyphenyl)-*p*-carborane 6hi. 1-(4-Hydroxyphenyl)-12-(4-nitrophenyl)-*p*-carborane (267 mg) was hydrogenated, as in the previous preparation, using palladium on carbon (5%, 212 mg) in 1,4-dioxane (25 cm^3). The theoretical volume of dihydrogen was absorbed in *ca.* 2.5 h and after 5.5 h the product was isolated as before and recrystallised from aqueous ethanol (1 : 1 v/v) to give colourless plates of the hydrated *aminophenol* (200 mg, 82%), m.p. 260–262 °C [Found: C, 49.4; H, 6.55; N, 3.9%; *M* (mass spectrum) 320–331. $C_{14}H_{21}B_{10}NO{\cdot}0.5H_2O$ requires C, 49.95; H, 6.6; N, 4.2%; *M* 319–331]. $\tilde{\nu}_{max}/cm^{-1}$ 3533s (br) (OH); 3457s (br), 3365s (br) (NH_2); 3066w, 3038w, 3018w (aryl CH); 2610s (BH); 1623 (NH_2); 1515, 1429w (aryl skeleton); 1331w; 1290; 1266; 1190; 1181; 1081; 917; 836, 832 (aryl out of plane); 750 (carborane skeleton); 601w; 585; 517. $\delta_H\{^{11}B\}$ 7.10 (2 H, m, C_6H_4OH, H2,2′,6,6′), 7.01 (2 H, m, $C_6H_4NH_2$, H2,2′,6,6′), 6.64 (2 H, m, C_6H_4, H3,3′,5,5′), 6.47 (2 H, m, $C_6H_4NH_2$, H3,3′,5,5′), 5.25 (1 H, br s, OH), 3.65 (2 H, br s, NH_2), 2.57 (10 H, br s, BH) and 1.62 (*ca.* 1 H, br s, H_2O). $\delta_C\{^1H\}$ 155.6 (C_6H_4OH, C4), 146.5 ($C_6H_4NH_2$, C4), 129.2 ($C_6H_4NH_2$, C1), 128.6 (C_6H_4OH, C2,6), 128.1 ($C_6H_4NH_2$, C2,6), 126.7 (C_6H_4OH, C1), 114.8 (C_6H_4OH, C3,5), 114.3 ($C_6H_4NH_2$, C3,5), 82.7 (carborane C1) and 81.6 (carborane C12). $\delta_B\{^1H\}$ −9.27 (br s, B2–6 and B7–11).

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