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C-arylation and C-heteroarylation of icosahedral carboranes via their copper(I) derivatives *

Robert Coult, Mark A. Fox, Wendy R. Gill, Penelope L. Herbertson, J.A. Hugh MacBride and Kenneth Wade

Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE (UK)

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Abstract

Reaction between C-mono- or C,C′-di-copper(I) derivatives of 1,2-, 1,7-, or 1,12-dicarba-*closo*-dodecaborane(12) and aryl iodides in the presence of pyridine gives the corresponding C-mono- or C,C′-diaryl derivatives of 1,7- and 1,12-dicarba-*closo*-dodecaboranes(12); 1,2-dicarba-*closo*-dodecaborane(12) gives only the C-monoaryl product. Cyclic or linear arylene coupled systems are obtained when di-iodoarenes are used. Copper(I) derivatives may be generated from C-unsubstituted or C-monosubstituted carboranes using copper(I) t-butoxide when substituents incompatible with the use of C-lithio-intermediates are involved. The C-copper(I) derivative of 1,2-dicarba-*closo*-dodecaborane(12) gives 1,2-di-2′-pyridyl-1,2-dicarba-*closo*-dodecaborane(12) specifically with 2-bromopyridine. The (inferred) intermediate mono-2-pyridyl-derivative, obtained independently from 2-ethynylpyridine and the dimethylsulphide complex of decaborane, gives 1-phenyl-2,2′-pyridyl-1,2-dicarba-*closo*-dodecaborane(12) upon conversion into its copper(I) derivative and treatment with iododobenzene. However, the copper(I) derivative of 1-phenyl-1,2-dicarba-*closo*-dodecaborane(12) does not react to a significant extent with 2-bromopyridine.

1. Introduction

The icosahedral carboranes are chemical building blocks of remarkable thermal stability and high boron content, resistant to attack by most types of reagent and generally inactive towards biological systems. Despite their cost, these properties make them uniquely suitable for several specialised applications. These include incorporation of large numbers of boron atoms into tumour-seeking drugs for boron neutron capture therapy (BNCT) [1], synthesis of polymers for high temperature [2] and neutron shielding [3] purposes or for firing to form ceramics [4] related to boron carbide. Their exceptional hydrophobic character, and the unusual solubility characteristics of their ionic derivatives [5], together with their ability to form *nido* anionic species with remarkable ligand properties by treatment with alkali (*etc.*), has led to their use in preparing metal complexing agents for solvent extraction, particularly of fissionable metals where neutron capture is desirable [6], as radiochemical drugs [7], and new catalysts [8]. The non-linear optical (NLO) properties of carboranes, particularly aryl-*ortho*-carboranes, have recently been studied [9].

Most of these uses for carboranes require derivatives with reactive sites suitable for coupling reactions, *e.g.* in polymerisation, attachment to peptides for BNCT, construction of arrays of metal atoms as catalysts, or attachment of groups to modify solubility and complexing properties. The stability and diversity of synthetic reactions of aromatic groups renders them particularly suitable for these purposes, but hitherto the available range of functional aryl carboranes has been limited. We describe below a convenient general route to C-aryl and C-heteroaryl derivatives of icosahedral carboranes *via* their copper(I) derivatives.

The majority of known examples are C-aryl and C,C′-diaryl *ortho*-carboranes prepared by condensing the corresponding aryl or diaryl acetylene with com-

Correspondence to: Professor K. Wade, F.R.S.

* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

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plexes formed between decaborane and Lewis bases L (usually CH_3CN, $(CH_3)_2S$ or $(CH_3)_2N \cdot C_6H_5$).

$$R'C{\equiv}CR'' + B_{10}H_{12}L_2 \rightarrow R'R''C_2B_{10}H_{10} + 2L + H_2$$

Compatibility with this reagent system precludes built-in substituents that are acidic (*e.g.* OH, CO_2H), reducible (*e.g.* NO_2), or susceptible to nucleophilic attack (*e.g.* C_6F_5). Nucleophilic groups which form stable complexes with the decaborane unit may also complicate the reaction. Yields of *ortho*-carboranes are variable and may be reduced by side-reactions, notably hydroboration of the triple bond.

Aryl derivatives of *meta*-carboranes, whose incorporation into polymer chains leads to superior chain geometry and much greater resistance of nucleophilic deboronation compared with their *ortho*-isomers, can be made by thermal isomerisation of the latter:

$$1,2\text{-}R'R''C_2B_{10}H_{10} \xrightarrow{>350°C} 1,7\text{-}R'R''C_2B_{10}H_{10}$$

However, the reaction temperature, which depends significantly on the particular substituents, frequently exceeds 400°C. Only the most stable and unreactive substituted aryl groups can therefore be used in this preparation; indeed some groups completely suppress isomerisation at temperatures below the onset of dihydrogen evolution between BH and CH positions [10], as in the case of the bis-4-phenoxyphenyl-derivative described below. Subsequent functionalisation, *e.g.* by nitration of phenyl-derivatives [11], has the disadvantage that mixtures of ring-substitution isomers are formed.

The very high temperature, *ca.* 650°C, needed to isomerise *meta*- to *para*-carborane (and perhaps the mechanism of the reaction) rules out this route to aryl or other derivatives.

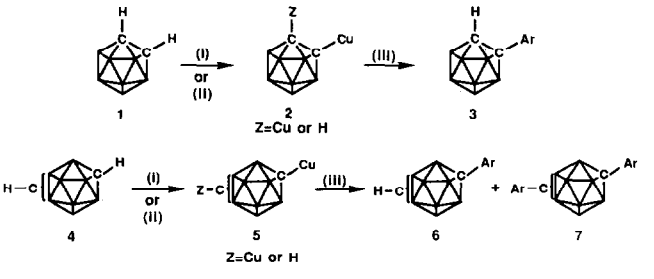
Attachment of aryl groups to the carbon atoms of *ortho*-, *meta*- or *para*-carboranes has the intrinsic difficulty that these atoms almost invariably form the nucleophilic component in polar reactions, *e.g.* with C-lithiocarboranes, whereas aryl halides do not in general undergo nucleophilic substitution in the absence of suitable "activating" groups such as nitro, which is incompatible with lithio and similar reagents, or polyhalogen substituents. *Ortho*-carborane has thus been arylated and di-arylated with polyfluorobenzenes [12], while interesting recent work [13] exploits the reactivity of chromium tricarbonyl complexes of aryl halides with nucleophiles; competing displacement of hydride as well as halide and low yields give little promise of a general synthetic procedure, however.

Mono-arylation of *ortho*- and *meta*-carboranes by reaction of their copper(I) derivatives with aryldiazonium tetrafluoroborates (an example of the Sandmeyer reaction) has been described [14], but yields are usually limited to 50% or less by concomitant formation of arylazocarboranes; we have obtained similar yields of diaryl*meta*- but not -*ortho*-carboranes under these conditions. A report [15] that phenyl and diphenyl carboranes, including *para*-carboranes, are formed in 30%–35% yield when their copper(I) derivatives react with iodobenzene in dimethylformamide proved difficult to reproduce [16] and the method has not to our knowledge been adopted.

We describe here a general procedure for C-monoarylation of *ortho*-, *meta*-, and *para*-carboranes, and for C,C'-diarylation of the last two isomers, usually in 60%–80% yield, by treatment of their copper(I) derivatives with aryl iodides in the presence of pyridine; pyridylcarboranes are similarly obtained using 2-bromopyridine.

2. Results and discussion

Suspensions of the mono- or di-copper(I) derivatives of *ortho*-, *meta*-, or *para*-carborane in 1,2-dimethoxyethane were prepared either by the conventional method of treating the corresponding lithiocarboranes (from the parent carboranes and butyllithium) with copper(I) chloride or iodide [14,17] or by treating the carboranes with a solution of copper(I) t-butoxide under conditions similar to those used by Cornforth *et al.* [18] to prepare dinitrophenylcopper reagents. Addition of pyridine and an aryl iodide and heating at reflux gave the arylcarboranes according to Scheme 1; the results are summarised in Table 1. Each reaction afforded a crystalline precipitate of a 1:1 complex of copper(I) iodide with pyridine which does not appear to correspond with any of the similar complexes previously described [19] and is the subject of further study. *Ortho*-carborane gives only the monoaryl derivative, exemplified by the 3- and 4-nitrophenyl derivatives (**3**, Ar = 3-$NO_2C_6H_4$ and 4-$NO_2C_6H_4$) (Table 1, entries 1



Scheme 1.

TABLE 1. Arylation of unsubstituted carboranes

Entry	Cu reagent (mol. ratio)	Aryl iodide	Time (h)	Mono-aryl (%) [a]	Di-aryl (%) [a]	Notes
Ortho-carborane						
1	i(1.4)	3-$NO_2C_6H_4$	42	37	0	
2	i(2)	4-$NO_2C_6H_4$	25	42	0	
Meta-carborane						
3	ii(2)	C_6H_5	48	36	40	
4	ii(1)	C_6H_5	48	57	18	b
5	i(2)	C_6H_5	46	45	32	
6	i(2)	3-ClC_6H_4	48	–	68	
7	i(2)	4-ClC_6H_4	48	–	80	c
8	i(2)	4-BrC_6H_4	48	–	65	d
9	i(2)	4-$CH_3C_6H_4$	48	–	62	e
10	i(2)	4-$NO_2C_6H_4$	90	43	34	
11	i(1)	4-$C_6H_5OC_6H_4$	48	89	–	
12	i(2)	4-$C_6H_5OC_6H_4$	72	8	75	c
13	i(1)	3-IC_6H_4	48	22 (**10**)	–	f
14	i(2)	3-IC_6H_4	86	–	5 (**9**)	f
15	i(2)	3-IC_6H_4	90	–	14 (**11**)	f
Para-carborane						
16	i(2)	4-$C_6H_5OC_6H_4$	48	25	[*ca.* 20]	

[a] Yields refer to homogeneous recrystallised or chromatographed products.
[b] Yields allow for recovered *meta*-carborane, 28%.
[c] The mono-4-chlorophenyl derivative was also characterised—see Experimental section.
[d] The coupled by-product (**8**) was also isolated in 5% yield.
[e] These diaryl derivatives were also prepared using the corresponding aryl diazonium salts, see Experimental section.
[f] Yields after separation from mixtures of oligomers; 0.5, 1 and 2 mol proportions of 1,3-di-iodobenzene were used in entries 13, 14 and 15 respectively.

and 2) and 1-phenyl-*ortho*-carborane could not be further arylated (Table 2, entries 2 and 3).

Specific mono-arylation of *ortho*-carborane under these conditions contrasts with recent work [20] on alkylation where a t-butyldimethylsilyl protecting group was found to be necessary for efficient formation of the mono-alkyl derivative without concomitant dialkylation.

Meta-carborane gives either mono- or di-aryl derivatives according to the stoichiometric proportion of reagents. Almost specific formation of either derivative was possible in some cases (*e.g.* Table 1, entries 11 and 12) but in others mixtures were formed owing, perhaps, to disproportionation of monometallated intermediates (see below) or to incomplete reaction. Separation of the mono- and diarylcarboranes by sublimation, crystallisation, or chromatography on silica gave little difficulty.

This procedure provided a 75% yield of 1,7-bis-(4-phenoxyphenyl)*meta*-carborane (*meta*-**7**, Ar = 4-$C_6H_5.O.C_6H_4$, Table 2, entry 12) which we required for study of poly-ether-ketone (PEK) polymerisation in comparison with our previous work [21] on the *ortho*-isomer. We were also able to prepare this compound in 41% yield by treating the di-copper(I) derivative of *meta*-carborane with 4-phenoxybenzenediazonium tetrafluoroborate, but we could not obtain it by thermal isomerisation of its *ortho*-carborane isomer. No

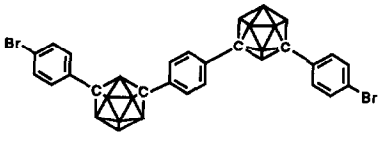
TABLE 2. Phenyl and pyridyl *ortho*-carboranes

Entry	Starting carborane	Cu reagent (mol. ratio)	Halide	Unreacted (%)	Mono-substd. (%)	Di-substd. (%)
1	Unsubstd	i(1)	2-BrC_5H_4N	37	0	43
2	1-Phenyl	ii(1)	C_6H_5I	100	–	0
3	1-Phenyl	i(1)	2-BrC_5H_4N	~ 99	–	Trace
4	1,2′-Pyridyl	i(1)	C_6H_5I	–	–	72 (**16**)

reaction occurred at 460°C while at 520°C dihydrogen pressure developed in the sealed tube and an insoluble glassy mass was formed, probably by condensation between BH and CH positions [10]. 1,7-Bis-(4-methylphenyl)*meta*-carborane was also obtained by the diazonium method in 47% yield.

We have demonstrated arylation of *para*-carborane by preparing 1,4′-phenoxyphenyl-*para*-carborane (*p*-**6**, $Ar = C_6H_5OC_6H_4$) and probably its diaryl analogue, (*p*-**7**, $Ar = C_6H_5OC_6H_4$) (Table 1, entry 16); comparison of this first experiment with the corresponding reaction of *meta*-carborane suggests that the *para*-isomer is less reactive, possibly because of lower solubility of its copper(I) derivative.

Aryl iodides are clearly more reactive than bromides under these conditions since the bis-4-bromophenyl-derivative (*meta*-**7** $Ar = 4\text{-}Br.C_6H_4$) was obtained in good yield from 4-bromoiodobenzene (Table 1, entry 8), but a second, less soluble, product proved to be the dicarborane (**8**) in which bromine has been displaced from the central phenylene group. We suspect that reaction of the bromine substituent results, at least in part, from initial halogen exchange with iodide present in the reaction mixture since the yield of coupled product (**8**) was 4.6% using copper(I) chloride but 8.5% when copper(I) iodide was used to generate the copper(I) carborane, with release of lithium iodide which is soluble in the reaction solvent.



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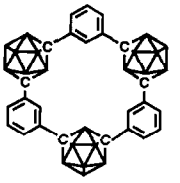

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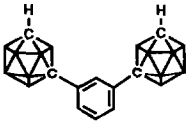
Arylene di-iodides, exemplified by 1,3-di-iodobenzene, can couple at both positions with dicopper(I) *meta*-carborane to give mixtures of oligomers from which the novel cluster-cycle (**9**) was isolated in 5% yield (Table 1, entry 14), while a similar reaction of the mono-copper carborane gave 1,3-di-*meta*-carboranylbenzene (**10**, Table 1, entry 14).



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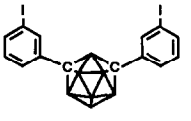

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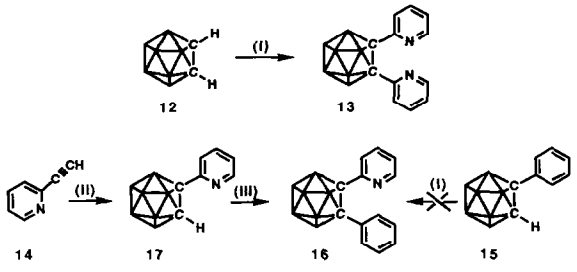
The properties of these two compounds and an X-ray crystallographic study of (**9**) have been described [22] separately. Reaction of dicopper(I) *meta*-carborane with two molecular proportions of 1,3-di-iodobenzene allowed isolation of 1,7-bis-3-(iodophenyl) *meta*-carborane (**11**). Formation and separation of other oligomers limited the purified yields of these three *meta*-phenylene derivatives.

We infer that the mechanism of coupling between C-carboranyl copper(I) reagents and aryl iodides is related to the corresponding (Ullmann) reaction of arylcopper(I) intermediates. It is a feature of the Ullmann coupling [23] that iodine is distinctly the most reactive halogen in otherwise unsubstituted arenes but that electron withdrawing functions, particularly nitro and heterocyclic ring-nitrogen atoms, facilitate reaction of bromides and chlorides, as with simple nucleophilic aromatic substitution, and that nitrogen donor molecules catalyse the reaction. The same reactivity relationships are found in the palladium-with-copper catalysed coupling of alkynes to aryl halides [24].

This comparison suggested that 2-bromopyridine might couple with copper(I) carboranes, and this is indeed the case. In remarkable contrast to mono-arylation with aryl iodides, successive treatment of *ortho*-carborane with *one* molecular proportion each of butyllithium, copper(I) chloride and 2-bromopyridine, in the presence of pyridine, gave 1,2-di-2′-pyridyl-*ortho*-carborane (**13**), in 80% yield based on the available 2-bromopyridine, together with unchanged *ortho*-carborane (Table 2, entry 1); no monopyridyl-*ortho*-carborane was detected (Scheme 2).

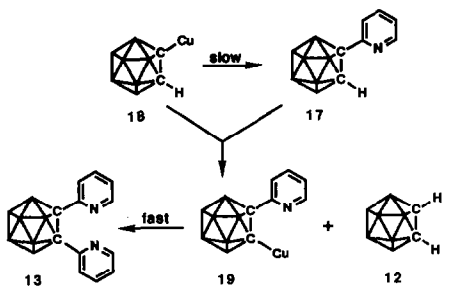
Disubstitution of *ortho*-carborane by 2-bromopyridine could be due *either* to greater reactivity of this reagent, although this would presumably not in itself account for the observed *specific* disubstitution, *or* to enhanced reactivity at C2 of the carborane following attachment of an initial 2-pyridyl group at C1. We treated the copper(I) derivative of 1-phenyl-*ortho*-carborane with 2-bromopyridine under the same conditions (Table 2, entry 3) but, as when iodobenzene was used in a similar experiment (Table 2, entry 2), very little reaction occurred although traces of the coupled



12 13 14 17 16 15

Reagents:
(I) BuLi, $(CH_3OCH_2)_2$; CuCl; 2-BrC_5H_5N; C_5H_5N;
(II) $B_{10}H_{12}[(CH_3)_2S]_2$, toluene, 80 °C
(III) BuLi, $(CH_3OCH_2)_2$; CuI; C_6H_5I; C_5H_5N;

Scheme 2.



Scheme 3.

product (**16**) were detected by mass spectrometry, showing that reactivity of the 2-bromopyridine is not the major factor.

To investigate the reactivity of mono-2′-pyridyl-*ortho*-carborane (**17**) we needed to prepare this compound by another method. To our knowledge no example of condensation of a pyridylacetylene with decaborane to give a pyridyl-*ortho*-carborane has been described in the literature, but we obtained the necessary pyridylcarborane (**17**) in 28% yield † from reaction of 2-ethynylpyridine [24] (**14**) with decaborane bis-dimethylsulphide complex [25]. Treatment of the copper(I) derivative of mono-pyridyl carborane (**17**) with iodobenzene under the usual conditions gave 1-phenyl-2,2′-pyridyl-*ortho*-carborane (**16**) in 72% yield (Table 2, entry 4). In contrast to the other coupling reactions we have described, the copper(I) derivative of the pyridylcarborane (**16**) remained in solution, which was red. When the pyridylcarborane (**17**) was treated with butyllithium followed by copper(I) iodide in 1,2-dimethoxyethane (*i.e.* as in the coupling experiment but without added pyridine) a red, then orange solution was formed which darkened through green to black during a few hours under dinitrogen at room temperature. We infer that although the copper atom of the copper derivative (**19**) is probably chelated by the pyridyl nitrogen the system does not have particular stability.

Specific di-substitution of *ortho*-carborane by equimolar quantities of butyllithium, copper(I) halide and 2-bromopyridine may be rationalised by metal exchange between the copper(I) derivative of *ortho*-carborane (**18**) and the CH position of 1-pyridyl-*ortho*-carborane (**17**) (Scheme 3). The two copper derivatives (**18**) and (**19**) can then compete for the available 2-bromopyridine and substantially faster reaction of the pyridyl compound (**19**) will lead to di-substitution. The greater reactivity of the pyridyl copper-derivative (**19**) may be directly associated with chelation but, since excess pyridine is available to complex both copper species, its solubility could be the major factor.

Solubility of the copper-derivative (**19**) of 1,2′-pyridyl-*ortho*-carborane may also explain its phenylation (Scheme 2), in contrast to the low reactivity of the corresponding derivative of 1-phenyl-*ortho*-carborane (**15**). Low solubility of the copper(I) derivative, formed, apparently, from 1,4′-nitrophenyl-*meta*-carborane (6, Ar = 4-NO_2.C_6H_4) as a bright yellow precipitate upon addition of a solution of copper(I) t-butoxide, may also account for its failure to react with an aryl iodide (4-iododiphenyl ether).

Preliminary experiments show that pyridyl derivatives of *meta*-carborane can be similarly prepared.

3. Conclusions

Although rather long reaction times are often needed, perhaps because of the low solubility of the intermediate copper(I) carborane derivatives, mono- or di-arylation of *meta*- and probably *para*-carboranes with various substituted aryl iodides can be effected in the presence of pyridine, often in excellent yield. The examples we have presented (Table 1) suggest that a very wide range of previously inaccessible C-aryl carboranes will be available in this way.

Ortho-carborane is specifically mono-arylated under the same conditions, allowing convenient preparation of functional aryl derivatives, notably nitro-compounds, which are incompatible with decaborane derivatives and not therefore directly available from the corresponding acetylenes.

Pyridyl derivatives of carboranes can be similarly obtained using 2-bromopyridine; *ortho*-carborane is specifically disubstituted by this reagent system, a result we attribute provisionally to the solubility of the intermediate copper(I) 2-pyridylcarborane derivative.

Copper(I) derivatives of C-unsubstituted or C-monosubstituted carboranes may be prepared using copper(I) t-butoxide as an alternative to butyllithium and copper(I) halides when functional groups which are not compatible with lithium (or magnesium) organometallic reagents, such as nitro-groups, are present.

We hope to be able to extend this procedure to further examples of aryl *para*-carboranes, to *ortho*-substituted aryl groups, and to a range of heterocyclic derivatives of the icosahedral carboranes.

† The major product of this reaction, which appears to form irreversibly, remains to be fully characterised but infrared studies show free acetylenic groups and suggest that both dimethylsulphide residues in the starting $B_{10}H_{12}L_2$ complex have been replaced by ethynylpyridine ligands.

4. Experimental details

4.1. 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 unless otherwise stated. Solutions were dried over anhydrous magnesium sulphate and evaporated under reduced pressure on a rotary evaporator or, where indicated, for potentially air or moisture sensitive materials by stirring under vacuum using a cold trap. Melting points were measured using capillary tubes and an electrically heated block and are uncorrected. Thin layer chromatography (TLC) was conducted on Merck DC-Plastifolien Kieselgel 60 F_{254} (Art 5735) with UV detection.

Preparative chromatography was conducted by dissolving the substrate in a suitable solvent, usually dichloromethane, adding *ca.* three times its weight of chromatographic silica (Merck silica gel 60, particle size 0.04–0.063 mm, Art. 9385) and evaporating to dryness. The resulting powder was placed on top of a dry column (length six to eight times its diameter) of silica gel (10–20 times the weight of substrate depending on separation observed by TLC) and eluted, using *ca.* 2 psi overpressure of dinitrogen, with a saturated hydrocarbon solvent containing a gradually increasing proportion of a more polar solvent, usually dichloromethane, as noted. Fractions of half the column volume, or less, were analysed by TLC before recombination.

Infrared spectra were recorded as potassium bromide discs, using a Perkin Elmer 377, 577 or 1720 X FTIR spectrometer.

Mass spectra were recorded on a VG Micromass 7070E instrument operating in the e.i. mode at 70 eV. Calculated values of M_r 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 seldom observed in practice.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ solution on a Bruker AC 250 multinuclear spectrometer operating at 250.13 MHz for ^1H, and 62.89 MHz for ^{13}C with ^1H broad band noise decoupling for the latter. ^1H and ^{13}C spectra were referenced to internal tetramethylsilane, positive δ-values to low field.

Toluene was dried by standing over sodium wire, 1,3-dimethoxyethane by refluxing and distillation over potassium and storage over sodium wire and pyridine by distillation from potassium hydroxide. Ether refers to diethyl ether, used as supplied.

Butyllithium solution was used as supplied (Aldrich) or, after storage, standardised by titration with t-butanol in toluene with 4,5-diazaphenanthrene as indicator. Carboranes were commercial materials purified by sublimation at *ca.* 70°C, 0.01 mmHg. Aryl iodides and 2-bromopyridine were used as supplied except where noted.

The following materials were prepared by published methods: purified copper(I) chloride [26]; diazonium tetrafluoroborates [27]; decaborane dimethylsulphide complex [2]; 2-ethynylpyridine [24]; 4-iododiphenyl ether [2]; 1-phenyl*ortho*carborane [28].

4.2. Preparation of copper(I) derivatives of carboranes

4.2.1. Using butyllithium

(i) The carborane (5–20 mmol) in dry 1,2-dimethoxyethane (4 cm^3 $mmol^{-1}$) was stirred under dinitrogen and butyllithium solution in hexane (1.6 M, 0.65 cm^3 or 1.30 cm^3 $mmol^{-1}$ of carborane for mono or disubstitution, respectively) was added dropwise with ice-cooling. The mixture was stirred at room temperature for 15 min and copper(I) chloride (0.2 g cm^{-3} of butyllithium solution used) or, where indicated, copper(I) iodide (0.4 g cm^{-3} of butyllithium solution), was added in one portion and the mixture, which soon formed a dark brown precipitate, was stirred for a minimum of 15 min at room temperature and pyridine (0.6 cm^3 $mmol^{-1}$ of carborane) was added.

4.2.2. Using copper(I) t-butoxide [18]

(ii) Potassium t-butoxide (0.12 g or 0.24 g $mmol^{-1}$ of carborane to be used for mono- or di-substitution, respectively) was stirred under nitrogen with dry 1,2-dimethoxyethane (4 cm^3 $mmol^{-1}$ of carborane) and copper(I) chloride (0.9 g g^{-1} of potassium t-butoxide used) was added in one portion; the mixture was stirred at room temperature for a minimum of 3 h and pyridine (5 cm^3 g^{-1} of potassium t-butoxide) was added followed by the carborane (5–20 mmol) and the mixture was stirred at room temperature for 0.5 h.

4.3. General procedure for coupling carborane copper(I) derivatives with aryl iodides

The aryl iodide (1.05 or 2.1 mmol $mmol^{-1}$ carborane for mono or disubstitution or as otherwise indicated) was added in one portion to the copper(I) carborane solution, containing pyridine, prepared by method (i) or (ii) above. The mixture was heated and stirred under nitrogen in an oil-bath at 95°C for 48–90 h or until TLC (eluted with cyclohexane containing 5%–50% dichloromethane depending on the polarity of the aryl iodide; the latter proportion is suitable for nitro-iodobenzenes) showed that the aryl iodide was

largely consumed. The cooled mixture was diluted with ether (5 cm^3 cm^{-3} of 1,2-dimethoxyethane) and allowed to stand for 2 h (or more), the precipitated copper(I) iodide–pyridine complex (etc.) was filtered off and washed with ether. The combined ethereal solution was washed with dilute hydrochloric acid (2.5 M; 10 cm^3 cm^{-3} pyridine present) and water (equal or greater volume, three times) dried and evaporated. The residual products were purified and characterised as indicated below.

4.4. Purification and characterisation of products (Table 1)

The method of copper derivative preparation, proportion of reagents, reaction times, and yields of products are shown in Table 1, to which entry numbers refer.

4.4.1. Entry 1. 1,3'-Nitrophenyl-ortho-carborane (3, Ar = 3-$NO_2 \cdot C_6H_4$)

The semi-solid product (1.59 g) from *ortho*-carborane (0.723 g) and 3-iodonitrobenzene (1.46 g) was triturated with 95% v/v aqueous methanol (5 cm^3) and the resulting ochre-yellow powder (0.760 g) was separated and recrystallised from cyclohexane to give ragged sandy yellow blades (0.492 g) m.p. 142–143°C lit. [11] 140–141°C. Found: C, 36.95; H, 5.87; N, 5.21. Calc. for $C_8H_{15}B_{10}NO_2$: C, 36.25; H, 5.70; N, 5.28.

4.4.2. Entry 2. 1,4'-Nitrophenyl-ortho-carborane (3, Ar = 4-$NO_2 \cdot C_6H_4$)

The brown semi-solid product from *ortho*-carborane (0.730 g) and 4-iodonitrobenzene (2.549 g) was extracted with boiling cyclohexane (13 cm^3), 4-iodonitrobenzene (0.381 g) was filtered off after cooling and the solution was evaporated, the residue was redissolved in dichloromethane (5 cm^3), adsorbed and chromatographed on silica (3.0 g and 30 g). Elution with cyclohexane and dichloromethane gave *ortho*-carborane (87 mg, 0%–2% CH_2Cl_2), 4-iodonitrobenzene (147 mg 6%–8% CH_2Cl_2), and 1,4'-nitrophenyl-*ortho*-carborane (498 mg, 10%–16% CH_2Cl_2), which was crystallised from ethanol to give pale yellow plates m.p. 163–165°C, lit. [11,29] 167–168°C, 164°C. Found: C, 35.59; H, 5.63; N, 5.07. Calc. for $C_8H_{15}B_{10}NO_2$ C, 36.2; H, 5.70; N, 5.28%.

4.4.3. Entry 3. 1-Phenyl-meta-carborane (m-6, Ar = C_6H_5) and 1,7-diphenyl-meta-carborane (m-7, Ar = C_6H_5)

The yellow oily product from *meta*-carborane (723 mg) and iodobenzene (1.20 cm^3) was triturated with methanol (4 cm^3) and the resulting solid (552 mg) m.p. 112–115°C raised to 118.5–120.5°C, lit. [30] 116–117°C, on recrystallisation from a 1:1 v:v mixture of ethanol and propan-2-ol was identified as 1,7-diphenyl-*meta*-carborane by comparison with an authentic sample. The methanol filtrate was evaporated and the residue sublimed at 50–55°C, 0.01 mm pressure to give tacky crystals (398 mg) m.p. 45–46°C, lit. [14] 55–56°C, after recrystallisation from pentane at *ca.* −60°C, identified as 1-phenyl-*meta*-carborane by comparison with an authentic sample.

4.4.4. Entry 4

The yellow oily product from *meta*-carborane (1.370 g) and iodobenzene (1.20 cm^3) was sublimed at *ca.* 40°C, 0.01 mm to give *meta*-carborane (389 mg), and then at 60°C to give 1-phenyl-*meta*-carborane (863 mg); recrystallisation of the residue from propanol furnished 1,7-diphenyl-*meta*-carborane (367 mg) m.p. 119–121°C.

4.4.5. Entry 5

The product from *meta*-carborane (0.725 g) and iodobenzene (0.80 cm^3) was sublimed, as in the previous experiment, to give 1-phenyl-*meta*-carborane (490 mg) and 1,7-diphenyl-*meta*-carborane (466 mg) was obtained by recrystallising the residue as before.

4.4.6. Entry 6. 1,7-bis(3-chlorophenyl)-meta-carborane (m-7, Ar = 3-ClC_6H_5)

The solid product from *meta*-carborane (1.443 g) and 3-chloroiodobenzene (5.15 g) was recrystallised from propan-2-ol to give the bis-3-chlorophenyl derivative (2.35 g) m.p. 117–118°C. Found: C, 46.05; H, 5.04; M_r (mass spectrum) 355–370. $C_{14}H_{18}B_{10}Cl_2$ requires C, 46.09; H, 4.97%, M_r 356-371. ν_{max} cm^{-1}; 3067w (ArCH); 2611s, 2588s, 2564(sh) (BH); 1676s, 1593s, 1570(sh), 1477s (Ar skel.); 1417s; 1170s; 1105s; 903s; 809s; 762s; 726 (carborane skel.); 680 (*m*-C_6H_4 o.o.p.); 423. δ^1H 1.1–3.0 (broad multiplet, rel. intensity 10, BH); 7.19–7.46 (multiplet, rel. intensity 8, ArH). δ^{13}C 78.2 (carborane C); 126.6, 128.6, 129.6, 130.2 and 132.5 (ArC).

4.4.7. Entry 7. 1,7-bis-(4-chlorophenyl)-meta-carborane (m-7, Ar = 4-ClC_6H_4)

The product from *meta*-carborane (1.445 g) and resublimed 4-chloroiodobenzene (4.801 g) was chromatographed to give the bis-(4-chlorophenyl)-derivative (2.914 g; cyclohexane, 20% ethyl acetate) m.p. 135–136.5°C from ethanol. Found: C, 46.26; H, 5.03; M_r (mass spectrum) 361–368. $C_{14}H_{18}B_{10}Cl_2$ requires: C, 46.09; H, 4.97; M_r 356-371. ν_{max} cm^{-1}: 3066 (ArCH); 2638, 2611s, 2565s (BH); 1651w, 1595w, 1494s (Ar skel.); 1104; 1075; 1017; 836s (*p*-C_6H_4 o.o.p.); 740 (carborane skel.); 514; 493; 464. δ^1H; 0.95–2.4 (broad multiplet, rel. intensity 5, BH); 7.23–7.4 (multiplet, rel.

intensity 4, ArH). $\delta^{13}C$; 7.77 (carborane C); 129.1, 129.6, 134.1, 135.7 (ArC).

In a similar experiment using 4-chloroiodobenzene as supplied the yield was 26% and 1,4'-chlorophenyl-*meta*-carborane, 31%, m.p. 64–66°C, lit. [14] 62–63°C, was also isolated.

4.4.8. Entry 8. 1,7-Bis-(4-bromophenyl)-meta-carborane (m-7, Ar = 4-BrC$_6$H$_4$) and 1,4-bis-(1,4'-bromophenyl-meta-carboran-7-yl benzene (8)

The crystalline product from *meta*-carborane (2.838 g) and 4-bromoiodobenzene (11.52 g) was washed with methanol (44 cm^3) and the resulting solid (6.095 g) was recrystallised from propan-2-ol (70 cm^3), with separation of an insoluble powder from the hot solution, to give light tan needles of the bis-bromophenyl *meta*-carborane (4.68 g) m.p. 122–124—C. Found: C, 37.00; H, 4.01; M_r (mass spectrum) 447–459. $C_{14}H_{18}B_{10}Br_2$ requires: C, 36.95; H, 3.99%; M_r, 445–459. ν_{max} cm^{-1}: 2630sh, 2597s, 2577sh (BH); 1492s, 1399s (Ar skel.); 1069s; 1012s; 850s; 832s (*p*-C$_6$H$_4$ o.o.p.); 736 (carborane skel.); 495. The material which was insoluble in propan-2-ol (305 mg) was recrystallised from toluene (*ca.* 2 cm^3) to give colourless rectangular prisms of the bis bromo phenylcarboranylbenzene (**8**) m.p. 275–276°C. Found: C, 39.67; H, 4.82; M_r (mass spectrum) 663–678. $C_{22}H_{32}B_{20}Br_2$ requires: C, 39.27; H, 4.80; M_r, 654–680. ν_{max} cm^{-1}: 3040w (ArCH); 2578vs (BH); 1508, 1484s, 1404, 1391 (Ar skel.); 1068s; 1003s; 847s, 832 (*p*-C$_6$H$_4$ × 2); 728 (carborane skel.); 499. δ^1H 1.85–3.80 (broad multiplet, rel. intensity 5, BH); 7.32–7.38 (multiplet, rel. intensity 3, ArH); $\delta^{13}C$: 77.7, 78.1 (carborane C); 123.6, 128.3, 129.8, 131.9, 134.4, 136.1 (ArC).

4.4.9. Entry 9. 1,7-Bis-(4-methylphenyl)-meta-carborane (m-7, Ar = 4-CH$_3$ · C$_6$H$_4$)

The sticky orange solid from *meta*-carborane (0.720 g) and 4-iodotoluene (2.18 g) was washed with methanol to give the almost pure bis-methylphenyl-derivative m.p. 134–136°C, raised to 138–140°C by recrystallisation from propan-2-ol, lit. [31] 141–142°C. Found: C, 58.88; H, 7.43. Calc. for $C_{10}H_{24}B_{10}$: C, 59.28; H, 7.40%.

4.4.10. Entry 10. 1,4'-nitrophenyl-meta-carborane (m-6, Ar = 4-NO$_2$ · C$_6$H$_4$) and 1,7-bis-(4-nitrophenyl)-meta-carborane (m-7, Ar = 4-NO$_2$ · C$_6$H$_4$)

The brown oily product (8.24 g) from *meta* carborane (2.81 g) and 4-iodonitrobenzene (10.0 g) was chromatographed to give first the mono-nitrophenyl-derivative (2.196 g, hexane 4%–10% dichloromethane) which was recrystallised from propan-2-ol to give colourless irregular blades m.p. 146.5–148.5°C, lit. [14] 148–149°C. Found: C, 35.75; H, 5.58; N, 5.06. Calc. for $C_8H_{15}B_{10}NO_2$: C, 36.20; H, 5.70; N, 5.28 and secondly bis-(4-nitrophenyl)-*meta*-carborane (2.586 g, hexane 24%–30% dichloromethane), which was recrystallised from butanol to give very pale yellow short needles m.p. 170–173°C. Lit. [32] 141–142°C (from heptane). Found: C, 43.31; H, 4.70; N, 6.99; M_r (mass spectrum) 382–389. Calc. for $C_{14}H_{18}B_{10}N_2O_4$: C, 43.5; H, 4.70, N, 7.25%; M_r 378–389. δ^1H: 1.80–4.00 (broad multiplet. rel. intensity 5, BH); 7.65 and 8.15 (two wings of AA'XX' multiplet, each rel. intensity 2, *para*-C$_6$H$_4$). $\delta^{13}C$: 76.66 (carborane C); 123.6 (aryl C3', 5'); 129.0 (aryl C2', 6'); 141.0 (aryl C1'); 148.1 (aryl C4').

4.4.11. Entry 11. 1,4'-phenoxyphenyl-meta-carborane (m-6, Ar = C$_6$H$_5$ · O · C$_6$H$_4$)

The product from *meta*-carbonate (1.445 g) and 4-iododiphenylether (2.98 g) was chromatographed to give the phenoxyphenyl-*meta*-carborane (2.294 g, hexane) which was recrystallised from ethanol to give colourless octahedra m.p. 86–88°C. Found: C, 54.39; H, 6.40; M_r (mass spectrum) 306–314. $C_{14}H_{20}B_{10}O$ requires: C, 53.83; H, 6.46; M_r, 304–315. ν_{max} cm^{-1}: 3057 (carborane CH); 3013w (ArCH); 2605s (BH); 1612, 1588s, 1508, 1489 (Ar skel.); 1264s, 1247s (C–O); 1202; 1171; 1154; 898; 853 (*p*-C$_6$H$_4$ o.o.p.); 752 (C$_6$H$_5$ o.o.p.); 729 (carborane skel.); 690 (C$_6$H$_5$ o.o.p.); 508; 487. δ^1H: 1.1–3.8 (broad multiplet, rel. intensity *ca.* 10, BH); 3.1 (singlet, rel. intensity *ca.* 1, carborane CH); 6.83–7.38 (multiplet, rel. intensity 9, ArH).

4.4.12. Entry 12. 1,7-Bis-(4-phenoxyphenyl)-meta-carborane (m-7, Ar = 4-C$_6$H$_5$ · O · C$_6$H$_4$)

The product from *meta*-carborane (1.533 g) and 4-iododiphenylether (6.262 g) was chromatographed to give the bis(phenoxyphenyl) derivative (3.850 g, hexane) m.p. 111–112°C after recrystallisation from propan-2-ol. Found: C, 64.63; H, 5.51; M_r (mass spectrum) 476–484. $C_{26}H_{28}B_{10}O_2$ requires: C, 65.0; H, 5.87%; M_r, 470–484. ν_{max} cm^{-1}: 3062 (ArH); 2648, 2618s, 2602s (BH); 1590s, 1506, 1490s, 1450, 1411 (Ar skel.); 1254s, 1243s (C–O); 1233; 1204; 1175s; 1162; 1079; 1072; 900; 875; 862 (*para* C$_6$H$_4$ o.o.p.); 752, 691 (C$_6$H$_5$ o.o.p.); 520; 485. δ^1H 1.1–3.9 (broad multiplet, rel. intensity 5, BH); 6.82–7.42 (multiplet, rel. intensity 9, ArH). $\delta^{13}C$ 77.8 (carborane C); 118.3, 120.0, 124.5, 129.8, 130.4, 156.2, 158.1 (ArC).

4.4.13. Entry 13. 1,3-Di-1'-meta-carboranylbenzene (10)

The product from *meta*-carborane (1.440 g) and 1,3-di-iodobenzene (3.300 g) was triturated with

methanol (5 cm^3) and the resulting solid (1.033 g) was extracted with boiling butanol (16 cm^3), cooled, filtered and evaporated; the residue was recrystallised from ethanol to give the dicarboranylbenzene [22] 398 mg, m.p. 240–244°C.

4.4.14. Entry 14. Cyclo-tris-1,7-meta-carboranylene-1',3'-phenylene (9)

The product from *meta*-carborane (2.889 g) and 1,3-di-iodobenzene (6.636 g) was chromatographed and the first fraction (1.682 g, cyclohexane) was twice recrystallised from benzene with separation of less soluble material to give rectangular prisms (60 mg) of the macrocycle (**9**) [22] m.p. 374.5–378°C. Further crystallisation gave a second crop (135 mg) of slightly lower purity.

4.4.15. Entry 15. 1,7-Bis-(3-iodophenyl)-meta-carborane (11)

The product from *meta*-carborane (1.440 g) and 1,3-di-iodobenzene (6.620 g), using copper(I) iodide in method (i), was chromatographed and the second fraction eluted by cyclohexane 0.5% ethyl acetate was freed from residual di-iodobenzene by sublimation at 0.001 mm 60°C leaving a crystalline residue of the bis-iodophenyl carborane (0.760 g) m.p. 124–125°C. Found: C, 31.89; H, 3.53; M_r (mass spectrum) 446–551. $C_{14}H_{18}B_{10}I_2$ requires: C, 30.66; H, 3.28; M_r, 541–551. δ^1H: 1.9–3.3 (broad multiplet, rel. intensity 10, BH); 7.02 (apparent triplet *J* 7.9 Hz, rel. intensity 1, H5'); 7.45 (doublet *J* 7.9 Hz, rel. intensity 1, H6'); 7.68 (doublet *J* 7.9 Hz, rel. intensity 1, H4'); 7.81 (singlet rel. intensity 1, H2').

4.4.16. Entry 16. 1,4'-Phenoxyphenyl-para-carborane (p-6, Ar = 4-$C_6H_5O \cdot C_6H_4$)

The product from *para*-carborane (0.718 g) and 4-iododiphenyl ether (2.99 g) was chromatographed, eluting with pentane only, to give first an oil (460 mg) provisionally identified as 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (IR), which remains to be further characterised, and secondly a fraction which was sublimed initially at 25°C, 0.01 mm to remove traces of 4-iododiphenyl ether and then at 60–70°C, 0.01 mmHg to give 1,4'-phenoxyphenyl-*para*-carborane (392 mg) m.p. 96–99°C. Found: C, 54.21; H, 6.58; M_r (mass spectrum) 305–315. $C_{14}H_{20}B_{10}O$ requires: C, 53.83; H, 6.46%; M_r 304–315. ν_{max} cm^{-1}: 3055 (carborane CH); 2607s (BH); 1612, 1589, 1505s, 1488s (Ar skel); 1287; 1252s, 1242sh (C–O); 1201; 1171; 1086; 872; 845 (p-C_6H_4 o.o.p.); 508; 798; 754 (C_6H_5 o.o.p.); 736 (carborane skel.); 693 (C_6H_5 o.o.p.); 578; 511; 480. δ^1H: 1.54 (carborane CH); 1.8–2.9 (broad multiplet, BH); 6.73–7.38 (multiplet, ArH).

4.4.17. Preparation of 1,7-bis-(4-methylphenyl)-meta-carborane (m-7, Ar = 4-$CH_3C_6H_4$) and 1,7-bis-(4-phenoxyphenyl)-meta-carborane (m-7, Ar = 4-$C_6H_5OC_6H_4$) using diazonium tetrafluoroborates

The procedure for conducting the reaction and separation of arylazo-byproducts using zinc and ethanoic acid was similar to the literature [14] method for monoarylation, but the proportions of butyllithium, copper(I) chloride and the diazonium salt were doubled. Thus *meta*-carborane (2.88 g) with 4-methylbenzenediazonium tetrafluoroborate (10.30 g) gave the bis-methylphenylcarborane (3.05 g, 47%) m.p. 140–141°C and with 4-phenoxybenzenediazonium tetrafluoroborate (14.20 g, prepared by diazotising 4-phenoxyaniline, adding sodium tetrafluoroborate at 0°C and drying the precipitate at 20°C, 0.01 mm) gave the bis(phenoxyphenyl)-derivative (3.95 g, 41%) m.p. 110–111°C after removal of byproduct diphenyl ether under vac. and chromatography. But for minor differences in purity both products were identical with those described above (Table 1 entries, 9 and 12).

4.4.18. Attempted Coupling of 1,4'-nitrophenyl-meta-carborane with 4-iododiphenyl ether

To a solution of copper(I) t-butoxide, prepared as in method (ii) above from potassium t-butoxide (0.70 g), was added 1,4'-nitrophenyl-*meta*-carborane (1.366 g), forming a yellow precipitate. 4-Iododiphenyl ether (1.662 g) was added and the mixture was heated (bath 95°C) for 41 h but no new product was detected by TLC (cyclohexane: dichloromethane 1:1 v/v).

4.5. Purification and characterisation of products (Table 2)

4.5.1. Entry 1. 1,2-Di-2'-pyridyl-ortho-carborane (13)

The crystalline product from *ortho*-carborane (1.443 g) and 2-bromopyridine (1.7 g, 1.0 cm^3) was sublimed at 50°C, 0.01 mm to give *ortho*-carborane (533 mg) and the residue (1.464 g) was recrystallised from ethanol to give pale yellow crystals (1.283 g) m.p. 134.5–136°C; an analytical sample of the dipyridyl-*ortho*-carborane formed slightly yellow blades m.p. 137–138°C upon a second recrystallisation from cyclohexane. Found: C, 48.07; H, 6.10; N, 9.25; M_r (mass spectrum) 286–301. $C_{12}H_{18}B_{10}N_2$ requires: C, 48.32; H, 6.08; N, 9.39%; m_r, 290–301. ν_{max} cm^{-1}: 3060, 3005w (ArCH); 2685, 2600sh, 2572s, 2558sh (BH); 1582s, 1570, 1462, 1430 (C_5H_4N skel.); 1292; 1150; 1080; 993; 828; 804; 770, 738s (2-C_5H_4N o.o.p.); 726 (carborane skel.); *ca.* 680 multiplet; 600; 577; 472; 396. δ^1H: 1.2–3.8 (broad multiplet, rel. intensity 5, BH) 7.13 (multiplet rel. intensity 1, H5'); 7.55 (multiplet rel. intensity 1, H4'); 7.65 (distorted doublet rel. intensity 1, H3'); 8.23 (multiplet

rel. intensity 1, H6′). δ^{13}C: 83.24 (carborane C); 124.1; 125.1; 136.5; 148.5 (C6′); 148.9 (C2′).

4.5.2. Entry 2. Attempted coupling of 1-phenyl-ortho-carborane with iodobenzene

The product of treatment of phenyl-*ortho*-carborane (1.13 g) with iodobenzene (0.8 cm^3) was compared by TLC (cyclohexane, 4% v/v ethyl acetate) with an authentic sample of 1,2-diphenyl-*ortho*-carborane; only 1-phenyl-*ortho*-carborane and none of the diphenyl compound was detected.

4.5.3. Entry 3. Attempted coupling of 1-phenyl-ortho-carborane with 2-bromopyridine

The product of treatment of 1-phenyl-*ortho*-carborane (0.608 g) with 2-bromopyridine (0.44 g, 0.27 cm^3) consisted (TLC, IR, mass spectrum) of a mixture of those compounds; small signals (max 3% of base *m/e* 220) at 295–298 indicated the presence of a trace of phenylpyridylcarborane, M_r 289–300.

4.5.4. Entry 4. 1-Phenyl-2,2′-pyridyl-ortho-carborane (16)

The crystalline product from 1-pyridyl-*ortho*-carborane (0.560 g) and iodobenzene (0.64 g, 0.35 cm^3) was recrystallised from ethanol (*ca.* 8 cm^3), with separation of dark insoluble material by filtration through Hyflo, to give the phenylpyridyl carborane (481 mg and a further 60 mg after partial evaporation) as ragged laths m.p. 143–144°C. Found: C, 52.42; H, 6.48; N, 4.43; m_r, 292–300. $C_{13}H_{19}B_{10}N$ requires C, 52.48; H, 6.44; N, 4.71; M_r, 289–300. ν_{max} cm^{-1}: 3093w, 3056, 3011w (ArCH); 2682, 2642, 2612s, 2594s, 2550 (BH); 1583, 1572 (C_5H_4N skel.); 1494, 1463, 1446, 1432 (Ar skel.); 1260; 1244; 1156; 1105; 1080; 995; 933; 896; 886; 875; 812; 793; 756, 743 (2-C_5H_4N and C_6H_5 o.o.p.); 728 (carborane skel.); 691 (C_6H_5 o.o.p.); 606; 583; 476; 416. δ^1H: 1.1–3.9 (broad multiplet rel. intensity 10, BH); 7.11–7.5 (multiplet rel. intensity 8, C_6H_5 and pyridyl H3, 4, 5); 8.36 (doublet *J* 5.9 Hz, rel. intensity 1, pyridyl H6).

4.5.5. 1,2′-Pyridyl-ortho-carborane (17)

To a stirred solution of decaborane dimethylsulphide complex (6.89 g) in toluene (50 cm^3) held at 80°C under dinitrogen was added 2-ethynylpyridine (2.34 g) in toluene (45 cm^3) over a period of *ca.* 5 h. After a further 3 h the mix was allowed to cool and the solution was decanted from the red resinous precipitate which was washed with a little more toluene. The solution was evaporated (bath 55°C), the residue (4.03 g) was extracted with ether (2 × 30 cm^3) and the residue after evaporation of the ether was sublimed at 0.01 mm, 60–65°C to give the crude product (2.07 g, m.p. *ca.* 85–95°C), Recrystallisation from acetonitrile at 0°C gave colourless shiny needles of the pyridyl-*ortho*-carborane (1.396 g, 28% on ethynylpyridine, 23% on decaborane – DMS) m.p. 104–105°C. Found: C, 37.41; H, 6.85; N, 6.22; M_r, 209–224. $C_7H_{15}B_{10}N$ requires: C, 38.00; H, 6.84; N, 6.33; M_r, 213–224. ν_{max} cm^{-1}: 3072 (carborane CH); 2638, 2568vs (BH); 1590s, 1574, 1467, 1435 (C_5H_4N skel.); 1283; 1152; 1100; 1073; 1052; 1020; 1012; 998; 823; 760; 734 (2-C_5H_4N o.o.p.); 722 (carborane skel.); 690; 582. δ^1H: 1.1–3.7 (broad multiplet, rel. intensity 10, BH); 5.00 (singlet, rel. intensity 1, carborane C*H*); 7.30 (multiplet rel. intensity 1, H5′); 7.50 (doublet, *J* 8 Hz, rel. intensity 1, H3′); 7.70 (multiplet, rel. intensity 1, H4′); 8.41 (doublet *J* 4.5 Hz, rel. intensity 1, H6′). δ^{13}C: 56.8 (carborane C2); 75.3 (carborane C1); 121.5; 124.3; 137.3; 148.7 (C6′); 151.0(C2′).

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