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Preparation of C-2-pyridyl derivatives of icosahedral carboranes via copper(I) intermediates

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Abstract

The C-mono- or C,C'-di-2-pyridyl derivatives of 1,7- and 1,12-dicarba-closododecaborane(12) are obtained in good yield by treatment of the corresponding dicarba-closo-dodecaborane(12) copper(I) derivatives with 2-bromopyridine in the presence of pyridine. (In contrast, earlier work showed that only the 1,2-di-2'-pyridyl derivative is formed from 1,2-dicarba-closo-dodecaborane(12) under the same conditions.) With 2,6-dibromopyridine the dicopper(I) derivative of 1,7-dicarba-closo-dodecaborane(12) gives the tripyridylene macrocycle (14) in up to 10% yield. The pyridyl compounds are considerably weaker bases than pyridine, but 1,12-di-2'-pyridyl-1,12-dicarba-closo-dodecaborane(12), for example, slowly gives the N,N'dimethylpyridinium salt with trimethyloxonium tetrafluoroborate.

*Keywords:* Carboranes; Pyridyl; Macrocycle; Copper

1. Introduction

Derivatives of the icosahedral carboranes and their *nido*-anions formed by removal of one boron atom have received considerable attention in the recent literature because of fundamental interest in their nature and properties and an expanding range of studies of their potential applications in the fields of heat-stable polymers [1,2], ceramics [1,3], non-linear optical [4] and electronic [5] materials, nuclear fuel processing [1] and medicine [6]. Recent studies of general interest include the effects of π-bonding interactions between cage carbon and substituent atoms [7] and the synthesis and inclusion complexes of macrocyclic arrays [8] of icosahedra such as (1) [9] and (2) [10].

Boron neutron capture therapy (BNCT) requires non-toxic boron-rich compounds able to concentrate in tumour tissue, which can then be selectively destroyed by short-range α-particles released by fission of ^{10}B nuclei under thermal neutron irradiation. A variety of nitrogen and sulphur heterocyclic derivatives of, usually, *ortho*carborane bearing isoxazole [11], thiazolidine [12], phenothiazine [13] and pyrimidine [14], including a

thymidine nucleoside [15] and thiouracil [16], and porphine [17–19] ring-systems have been investigated clinically [20], by measurement of cellular boron uptake [21] and its subcellular distribution [22], and by many related studies. The last type, incorporating four carborane units, also shows promising activity, without irradiation, against HIV-1 and -2 viruses [23]. A pair of $nido$-$C_2B_9H_{10}$ units linked through the nitrogen atoms of pyrazole-4-carboxylic acid form a stable dicarbollide ligand [24] for radio-metals and the complexes, when conjugated to a tumour-specific antigen, allow excellent radio-imaging with ^{57}Co and offer potential for radio-therapy.

Heterocyclic derivatives of *ortho*-carborane can be made by condensation of decaborane complexes with alkynyl derivatives of the ring-system, and, with other cage isomers, by coupling the components, often using alkylation or acylation reactions with haloalkyl [17], hydroxy-alkyl [25], aminoalkyl [16] or carboxy [19], as well as alkenyl [18], functional carboranes. Heterocyclic substituents have also been constructed from similar reactive groups attached to the cage, despite the disadvantage that several synthetic steps may be needed after incorporation of the relatively expensive carborane unit; thus a 4-pyridyl*ortho*carborane has been obtained from a 1,5-dicarbonyl side chain intermediate [26]; 2,3-dihy-

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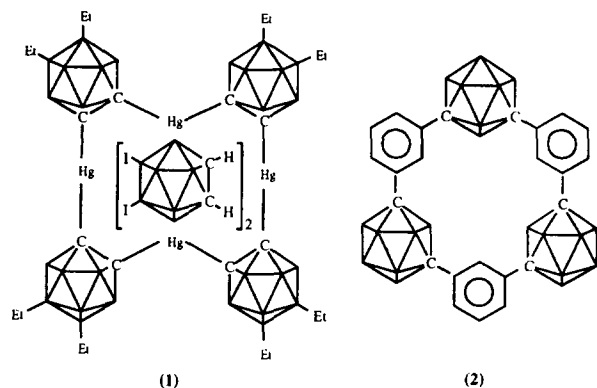
Diagrams (1) and (2).

drobenzothiazolyl-*meta*-carboranes, from C-formyl precursors, have been studied as a thermally stable polymer system [27].

Direct attachment of *N*-alkyldihydropyridine, and its benzo-derivatives, to carboranyl carbon is effected by nucleophilic addition of C-lithiocarboranes to *N*-alkylpyridinium salts [28]. The analogous aromatic systems are available in principle by nucleophilic displacement of halogen from suitably reactive heterocyclic halides by these lithium reagents, and we have observed a number of successful coupling reactions of this type [29], but other attempts have failed, with loss of the carborane. The reaction is evidently crucially dependent on the conditions, including the choice of solvent, and we plan to report our results when we have defined the conditions needed for general application of this method.

Recently we have shown [30] that C-2-pyridyl derivatives of *ortho*carborane are formed from carborane copper(I) intermediates with 2-bromopyridine, and we here report the application of this reaction to the preparation of C-2-pyridyl derivatives of *meta*- and *para*-carboranes.

2. Results and discussion

Our previous studies [30] showed that arylation with aryl iodides of *ortho*-carborane (unlike that of its *meta*-

and *para*-isomers) via the copper(I) derivatives, gives only mono-substitution, but that 1,2-di-2′-pyridyl-*ortho*carborane is formed specifically when 2-bromopyridine is used (leaving half the carborane unchanged if one molecular proportion of reagent is employed).

We attribute the failure of the second arylation step in the case of *ortho*carboranes to the steric effect of the initial substituent operating in an oligomeric monocopper(I) derivative of low solubility, whereas the corresponding compound from 2-pyridyl*ortho*carborane is observed to be soluble [30] and, we infer, less hindered by oligomerisation because one coordination site on copper is occupied by chelation with the adjacent 2-pyridyl group. (Attempts to isolate and structurally characterise crystalline samples of copper derivatives of carboranes have so far been unsuccessful). The soluble pyridyl copper complex is consequently likely to be more reactive than either its monoaryl analogue or the starting dicopper(I) *ortho*carborane, which we also assume to be oligomeric, and so can undergo specific di-substitution (through copper-proton exchange if starting from monocopper(I) carborane). Our observations that the copper(I) derivative of monopyridyl*ortho*carborane can be phenylated with iodobenzene while that of phenyl*ortho*carborane does not react at significant rate with 2-bromopyridine are consistent with this interpretation [30].

On the basis of this argument we expected that the copper(I) derivatives of *meta*- and *para*-carboranes would react with 2-bromopyridine in the same way as they do with aryl iodides, since an initial 2-pyridyl group cannot chelate the second copper atom, so that their mono or di-2-pyridyl derivatives should be preparable by using appropriate stoichiometric proportions of reagents.

This prediction is confirmed; treatment of monocopper(I) *meta*carborane (4) with an equimolar proportion of 2-bromopyridine gives 1-(2′-pyridyl)*meta*carborane (5) in 57% yield, after sublimation, along with 11% of the less volatile 1,7-di(2′-pyridyl)*meta*carborane (6), and traces of unchanged carborane (3), Scheme 1. Similarly, successive treatment of *meta*carborane (3) with two molar proportions each of butyllithium, copper(I) chlo-
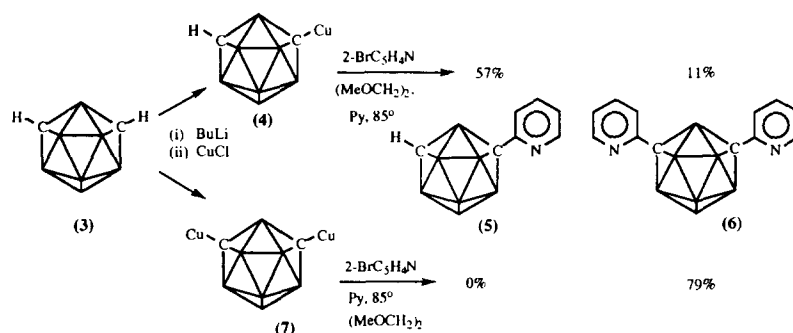
Scheme 1.
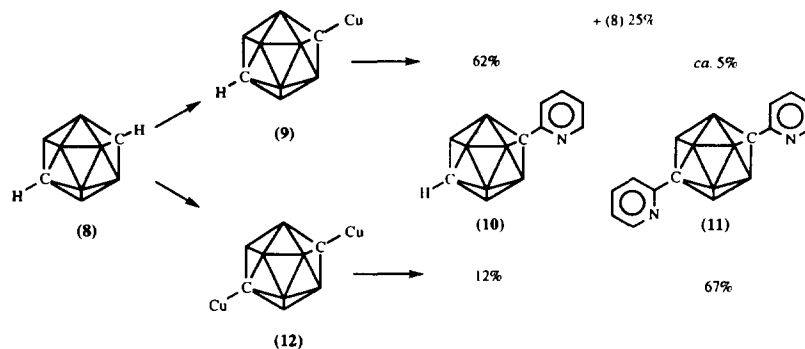
Scheme 2.

ride and 2-bromopyridine (in the presence of pyridine) gives the dipyridyl product (6) in 79% yield.

Although preliminary work noted in our previous communication [30] gave only modest yields of 4-phenoxyphenyl derivatives of *para*carborane, substitution with 2-bromopyridine proves to be efficient. Indeed, further experiments [31] involving mono- and di-arylation of *para*carborne with substituted iodobenzenes have shown that this cage isomer often gives better results than the *ortho* or *meta* isomers in these reactions.

Under the conditions used for *meta*carborane we isolated by sublimation 1,-(2'-pyridyl)*para*carborane (10) in ca. 62% yield, along with 25% of unchanged *para*carborane, although in this example subsequent recrystallisation was needed to free the derivative from a small proportion of disubstituted compound (11), Scheme 2. Using two molar proportions of the reagents we obtained the disubstituted carborane (11), 67% yield, along with the monopyridyl compound (10), (12%), by sublimation of the recrystallisation residues.

We have described [10] the formation of the trimeric phenylenecarborane macrocycle (2) in about 5% yield by condensation of 1,3-di-iodobenzene with dicopper-(I)*meta*carborane (7); the corresponding reaction with 2,6-dibromopyridine (13), Scheme 3, gives the analogous pyridine compound (14) in yields approaching 10%, together with a relatively complex mixture of oligomers.

An X-ray crystallographic study [32] of the macrocycle (14), has confirmed the structure.

The distance between the nitrogen atoms of the macrocycle (14) is approximately 5.5 Å, and their distance from the centre of the molecule, i.e. the required lengths of three bonds to a central trigonally coordinated metal atom, is about 3.2 Å, too long for any significant bonding interaction to a first row transition metal atom such as copper. The higher yield in the case of the heterocyclic species (14) cannot therefore be due to a simple template effect, although interaction between terminal carboranylcopper and bromopyridyl groups may assist cyclisation.

We have started to investigate the metal complexes of the pyridylcarboranes and of their deboronated *nido*-anions [33], but we note at this stage that they are relatively weak bases owing to the strong electron-withdrawing effect of the carborane cages, particularly in the case of the *ortho*-isomer and that of the macrocycle (14), with effectively two carborane substituents to each pyridine ring. Thus while all three monopyridyl-carboranes are soluble in concentrated hydrochloric acid (ca. 12M), the *ortho*-isomer separates on dilution to ca. 9M acid, but the *meta* and *para*-compounds are soluble in 6M but not 3M aqueous acid. The macrocycle (14) dissolves in concentrated sulphuric, but not hydrochloric, acid, and the proton NMR of the solution is consistent with protonation; the unprotonated compound separates, unchanged, upon addition of a small amount of water.

Alkylation of the pyridine nitrogen of these com-
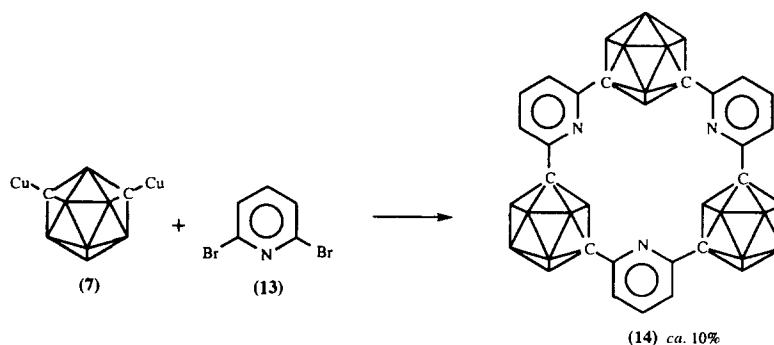
Scheme 3.
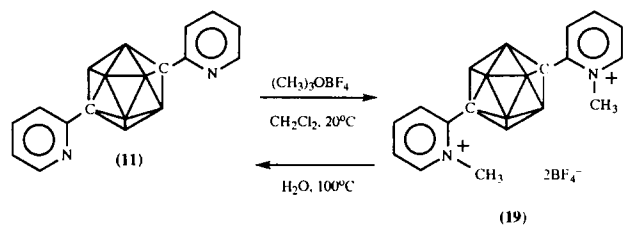
Scheme 4.

pounds is evidently hindered by the carborane cage, since, for example, when the dipyridyl *para*carborane (11) was treated with an excess of trimethyloxonium tetrafluoroborate in dichloromethane at room temperature for 20 h most of the compound was recovered, and only 23% yield of the bis(*N*-methylpyridinium) tetrafluoroborate (19) was obtained, Scheme 4. The salt (19) is stable to the atmosphere, but despite its insolubility is rapidly demethylated by boiling water.

Further studies of quaternisation of the pyridine rings of these compounds, and possibly subsequent pyridine ring-opening reactions to form a range of unsaturated functional C_5-derivatives of the three carborane isomers, extension of the method to the 4-pyridyl analogues are currently under way, as well as the complexation and deboronation [33] studies noted above.

3. Conclusions

Condensation of the C-copper(I) derivatives of *meta* and *para*carboranes with 2-bromopyridine under the conditions described previously [30] gives good yields of either mono- or disubstituted C-2-pyridylcarboranes. In contrast, the corresponding reaction of *ortho*carborane gives only the dipyridyl product.

The macrocyclic trimeric pyridyl*meta*carborane (14) is formed in the corresponding reaction of *meta*carborane with 2,6-dibromopyridine. The more efficient cyclisation observed in this case than in the corresponding reaction of 1,3-di-iodobenzene suggests that this step may be assisted by a copper-pyridine interaction.

Although the basicity and nucleophilic reactivity of carboranylpyridines are lower than those of pyridine because of the electronic and steric effects of the carborane cages, protonation and methylation on nitrogen can be effected, and we expect the compounds will form the basis of a new range of carborane derivatives.

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 sodium sulphate and evaporated under reduced pressure on a rotary evaporator. Melting points were measured for samples 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 were recorded on a VG Micromass 7070E instrument operating in the e.i. mode at 70 eV. Calculated values of Mr 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 except where otherwise stated, on a Varian Gemini 200 spectrometer operating at 199.98 MHz for ^1H, and 50.29 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; ^{11}B spectra on a Bruker AMX 500 at 160.46 MHz were referenced to external BF_3-etherate.

1,2-Dimethoxyethane was dried 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 s-butanol in toluene with 4,5-diazaphenanthrene as indicator. Carboranes were commercial materials purified by sublimation at ca. 70°C, 0.01 mmHg. 2-Bromopyridine was used as supplied, and 2,6-dibromopyridine was sublimed at ca. 40°C, 0.01 mmHg; copper(I) chloride was purified as described by Whitesides [34].

4.2. General procedure for coupling reactions with 2-bromopyridine

A solution of the carborane (5–20 mmol) in 1,2-dimethoxyethane (4 cm³ per mmol of carborane) was stirred and a solution (1.6 M or 2.5 M) of butyllithium in hexanes (1.05, or 2.05 mol for mono or di-substitution, respectively) was added slowly (with cooling in the case of larger scale preparations) followed by dry pyridine (6 cm³ per mmole of carborane) and purified copper(I) chloride, or dry copper(I) iodide where stated (ca. 1.2 or 2.2 mol, weighed in air, without delay for the chloride, and under a counter-current of dry dinitrogen). Vigorous stirring was maintained and the mixture was heated at the reflux temperature for ca. 30 min. When copper(I) iodide was used the more volatile solvent (hexane) was distilled off with the help of a gentle stream of dinitrogen until a homogenous liquid phase

(with solid precipitate) was obtained. 2-Bromopyridine (1.05 or 2.05 mol) was added, and the mixture, which was usually dark purple-red but becoming lighter as the reaction proceeded, was heated under gentle reflux (oil bath 95–100°C) for 16–60 h.

Progress of the reaction was monitored by applying a sample of the reaction mixture to TLC sheet with chloroform as eluent (unsubstituted carboranes were not detected). Completion was shown by consumption of all, or most, of the bromopyridine, or absence of further change.

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 the solution was shaken first with dilute (1 M) 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, as indicated.

4.3. 1-2'-pyridyl-meta-carborane (5)

The oily product (2.12 g) formed during 45 h from metacarborane (1.45 g) and one proportion of the reagents as described above, crystallised spontaneously and sublimed at 0.01 mm Hg at room temperature for 30 min, to remove traces of metacarborane, and then sublimed at the same pressure at 45°C to give the monopyridylcarborane (1.27 g, 57%) m.p. 80–82°C. Found: C, 37.29; H, 6.81; N, 5.89; M_r, 209–224. $C_7H_{15}B_{10}N$ requires: C, 37.99; H, 6.84; N, 6.33%; M_r 213–224. ν_{max} cm^{-1}: 3059 (carborane CH); 2667, 2599vs, 2570 (BH); 1589, 1573, 1466s, 1431 (C_5H_4N skel.) 1274; 1157; 1084; 1042; 997; 881; 825; 736 br (C_5H_4N o.o.p. and carborane skel.); 686. δ^1H: 1.5–3.8 broad multiplet rel. intensity ca. 10, BH); 3.07 (singlet rel. intensity ca. 1, carborane CH); 7.22 (doublet of doublets, J 4.0 and 2.4 Hz rel. intensity 1.0, pyridine H5); 7.39 (doublet, J 4.0 Hz pyridine H3); 7.60 (triplet of doublets, J 4.0, 4.0, 1.0 Hz rel. intensity 1.0, pyridine H4); 8.48 (doublet of doublets J ca. 2.4, 1.0 rel. intensity 1.0, pyridine H6). $\delta^{13}C$: 55.01 (carborane C7); 78.90 (weak, broad, carborane, C1); 121.87, 123.49, 136.77, 148.76; 152.58 (pyridine C2). $\delta^{11}B$ − 15.3 (br. singlet rel. intensity 2, B2 and B3); − 13.6 (br. singlet rel. intensity 2, B8 and B11); − 10.9 (br. singlet rel. intensity 4, B4, B6, B9 and B10); − 8.4 (br. singlet rel. intensity 1, B12); − 4.6 (br. singlet rel. intensity 1, B5). These assignments are supported by the [^{11}B–^{11}B]-COSY spectrum, which revealed the following couplings: δ − 10.9 with each of the others; − 13.6 with − 15.3; and − 8.4 with − 13.6.

The sublimation residue (320 mg, 11%) was identified (IR) as 1,7-di-2'-pyridyl metacarborane.

4.4. 1,7-Di-2'-pyridyl-meta-carborane (6)

(a) The oily product (1.55 g) formed during 60 h from metacarborane (0.73 g) and two mol of the reagents, using in this case copper(I) iodide, crystallised readily on scratching and was recrystallised (at ca. 5°C) from ethanol (ca. 5 cm^3) to give sandy crystals of the dipyridyl derivative (0.65 g), m.p. 115–117°C; a further crop (0.37 g, total yield 69%) of comparable purity was obtained by evaporation of the mother-liquor. Found: C, 48.24; H, 6.19; N, 9.11; M_r 285–301. $C_{12}H_{18}B_{10}N_2$ requires: C, 48.32; H, 6.08; N, 9.39%; M_r 290–301. ν_{max} cm^{-1}: 3090w, 3055w, 3010w (CH): 2647, 2600vs (BH); 1583, 1572, 1463, 1431 (pyridine skel.); 1271; 1153w; 1089; 1045w; 995; 908w; 878w; 855; 821; 751, 741 (CH o.o.p. and carborane skel.); 681; 613w; 491w. δ^1H: 1.0–4.5 (br. multiplet rel. intensity ca. 10, BH); 7.24 (doublet of doublets of doublets, J 7.4, 4.8, 1.1 Hz rel. intensity 1.0, pyridine H5); 7.50 (doublet of triplets, J 8.0, 1.1, 1.0 Hz rel. intensity 1.0, pyridine H3); 7.63 (doublet of doublets of doublets, J 8.0, 7.4, 1.8 Hz rel. intensity 1.0, pyridine H4); 8.51 (doublet of doublets of doublets J 4.8, 1.8, 1.0 Hz rel. intensity 1, pyridine H6). $\delta^{13}C$: 78.67 (carborane C) 121.90, 123.47, 136.74, 148.80; 152.64 (pyridine C2). $\delta^{11}B\{^1H\}$: − 13.9 (br. singlet rel. intensity ca. 1, B2 and B3); − 11.5 (br. singlet rel. intensity ca. 3, B4, B6, B8, B9, B10 and B11); − 6.6 (br. singlet rel. intensity ca. 1, B5 and B12).

(b) In a similar experiment using copper(I) chloride during 48 h, the oily product (3.78 g) from metacarborane (1.44 g) was chromatographed on silica with a mixture of equal volumes of cyclohexane and dichloromethane as eluent to give the dipyridyl derivative (6) (2.38 g 79%) m.p. 114–117°C.

4.5. 1,2'-Pyridyl-para-carborane (10)

The pale yellow crystalline product (2.04 g) formed during 16h from paracarborane (1.43 g) and 1 mol of the reagents was sublimed at ca. 30°C, 0.01 mmHg, to remove unchanged para-carborane (0.35 g) and then sublimed at the same pressure at 60°C to give the monopyridyl-derivative (1.37 g, 62% or 83% after allowance for recovered starting material), m.p. 113–115°C containing (by ^{1}HNMR) traces of dipyridylcarborane. The analytical sample crystallised as needles m.p. 116–117°C from methanol containing 10% v/v of water. Found: C, 37.44; H, 6.88; N, 6.27; M_r 212–224. $C_7H_{15}B_{10}N$ requires: C, 37.99; H, 6.84; N, 6.33%; M_r 213–224. ν_{max} cm^{-1}: 3044, 3014w (carborane and pyridine CH); 2596vs (BH); 1588, 1575, 1468, 1431 (pyridine skel.); 1292w; 1271; 1149; 1089; 1059; 1033;

997; 904w; 842; 784; 754 (pyridyl o.o.p); 734 (carborane skel.); 689; 616; 588w; 493. δ^1H: 0.8–4.1 (br. multiplet rel. intensity ca. 10, BH); 2.83 (br. singlet rel. intensity ca. 1, carborane CH); 7.13 (doublet of doublets of doublets J 7.5, 4.8, 0.9 Hz rel. intensity 1.0, pyridine H5); 7.22 (doublet J 7.8 Hz and small coupling unresolved rel. intensity 1.0, pyridine H3); 7.52 (triplet of doublets J ca. 7.7, 7.7, 1.9 Hz rel. intensity 1.0, pyridine H4); 8.40 (doublet of doublets of doublets J 4.8, 1.9, 0.9 Hz rel. intensity 1.0, pyridine H6). δ^{13}C: 60.94 (br. carborane C12); ca. 87.3 (br. weak, carborane C1); 121.52; 123.65; 137.03; 149.08; 154.10 (pyridine C2). δ^{11}B{^{1}H} − 15.24 (br. singlet rel. intensity 1.0, B7, B8, B9, B10 and B11); − 12.80 (br. singlet rel. intensity 1.0, B2, B3, B4, B5 and B6).

4.6. 1,12-Di-2'-pyridyl-para-carborane (11)

The brown crystalline product (1.49 g) formed during 60 h from *para*carborane (0.73 g) with 2 mol of the reagents, (using copper(I) iodide) was dissolved in chloroform (25 cm^3), and the solution was filtered through a short column of chromatographic silica (6 g), which was washed with a further 75 cm^3 of chloroform. Evaporation of the solution and two recrystallisations of the residue from 1-butanol afforded light brown crystals of the dipyridylcarborane (1.00 g, 67%) m.p. 247–251°C (subl.). Found: C, 48.44; H, 6.21; N, 9.20; M$_r$ 284–301. 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}: 3092w, 3053, 3009w (CH); 2615vs(BH); 1585, 1571, 1465, 1437 (pyridine skel.); 1295w; 1277; 1237w; 1162w; 1096; 1050w; 996; 959w; 929; 808; 747 (pyridyl o.o.p.); ca. 728 (sh., carborane skel.); 678; 622w; 607; 483. δ^1H: 1.4–4.1 (br. multiplet rel. intensity ca. 10, BH); 7.24 (doublet of doublets of doublets J 7.3, 4.6, 1.0 Hz rel. intensity 1.0, pyridine H5); 7.35 (doublet J 8.0 Hz, rel. intensity 1.0, pyridine H3); 7.54 (doublet of doublets of doublets J 8.0, 7.3, 1.8 Hz, rel. intensity 1.0, pyridine H4); 8.42 (doublet J 4.6 Hz, rel. intensity 1.0, pyridine H6). δ^{13}C: 83.96 (br., weak, carborane C); 121.11; 123.19; 136.51; 148.65; 153.52 (weak, pyridyl C2). δ^{11}B{^{1}H}: − 13.02.

4.7. Cyclo-tris-1,7-meta-carboranylene-2',6'-pyridylene (14)

Meta-carborane (2.80 g) was treated during 148h with 2 mol of the reagents, using copper(I) iodide, as described in 4.2 but with 2-bromopyridine replaced by 2,6-dibromopyridine (in a 2-fold excess, which was found to give a better yield of the macrocyclic product). The semi-solid product (9.75 g), isolated as before, was dissolved in dichloromethane (70 cm^3) and the solution

was filtered using Hyflo, chromatographic silica (Merck, Art. 9385, 27 g) was added, and the solvent was evaporated. The resulting powder was placed on top of a dry column of chromatographic silica (100 g, as above) and eluted, under ca. 2 psi overpressure of dinitrogen, with cyclohexane (5 fractions of 50 cm^3) and then with addition of an increasing proportion (1% v/v per 5 fractions) of ethyl acetate (ethyl ethanoate). Fractions 5 to 11 inclusive were combined, (after TLC analysis, R_f 0.7 in cyclohexane 5% v/v ethyl acetate, cf. 2,6-dibromopyridine, R_f 0.45), evaporated, and the residue (0.60 g) was recrystallised from xylene (30 cm^3, mixed isomers) to give the cyclic trimer (0.43 g, 10%, including a second crop, 61 mg, obtained after evaporation to ca. 8 cm^3) as a white microcrystalline powder m.p. > 400°C (decomp.). Found: C, 37.76; H, 6.13; N, 6.04; M$_r$ 642–661. C$_{21}$H$_{39}$B$_{30}$N$_3$ requires: C, 38.34; H, 6.39; N, 5.98%; M$_r$ 633–664. ν_{max} cm^{-1}: 3065w, 2927w (CH); 2677, 2605vs (BH); 1588, 1578, 1454, 1410 (pyridine skel.); 1295; 1273; 1235; 1168; 1110; 1027; 996; 907w; 874; 833 (pyridine o.o.p.); 810w; 782w; 735 (carborane skel.); 710 (pyridine o.o.p.); 649w; 619w. δ^1H (d$_8$-THF): 0.8–4.8 (br. rel. intensity ca. 10, BH); 7.44 (doublet J 7.8 Hz pyridine H3, H5); 7.72 triplet J 7.8 Hz pyridine H4). δ^1H (H$_2$SO$_4$): 0.8–2.7 (br. rel. intensity ca. 10 BH); 6.94 (doublet J 8.4 Hz, rel. intensity 2.0, pyridine H3, H5); 7.50 (triplet J 8.4 Hz, rel. intensity 1.0, pyridine H4); δ^{13}C (d$_8$-THF): 79.10 (carborane C), 122.95 (pyridine C3, C5); 139.52 (pyridine C4); 152.67 (pyridine C2, C6); δ^{11}B (THF): − 6.0 (rel. intensity ca. 2 B5, B12); − 10.9 (rel. intensity ca. 8, B2, B3, B4, B6, B8, B9, B10, B11).

4.8. Methylation of 1, 12-di-pyridyl-para-carborane (11) with trimethyloxonium tetrafluoroborate

The dipyridylcarborane (158 mg) in dichloromethane (5 cm^3) was treated with trimethyloxonium tetrafluoroborate (262 mg, 3.3 mol) for 20 h at room temperature under dinitrogen. The solution was then filtered, and the filtrate evaporated to give unchanged dipyridylcarborane (95 mg, 60%). The solid obtained by the filtration was treated with a solution of DMF in ether 1:9 v/v and washed with dichloromethane to give a white powder (62 mg, 23%). Found: C, 28.96; H, 3.97; N, 5.03. C$_{14}$H$_{24}$B$_{12}$F$_8$N$_2$ requires: C, 33.47; H, 4.78; N, 5.58%. ν_{max} cm^{-1} 3253–2921 (multiplet, CH); 2627vs, 2611 (BH); 1613, 1601, 1528, 1449 (pyridine skel.) 1360; 1299; 1235; 1222; 1082vs (br.BF$_4$); 992 (pyridine o.o.p.): 880w; 799 (pyridine o.o.p.); 754 (carborane skel.); 669; 622; 601; 533; 521; 491.

The starting compound was re-formed (IR) when a sample of the product was boiled with water for ca. 1 min.; it is insoluble in common NMR solvents.

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