ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 587 (1999) 67–73

Journal of Organometallic Chemistry

Synthesis of new arylcarboranes as precursors for oligomers

Beate Förster, Josep Bertran, Francesc Teixidor *, Clara Viñas

Institut de Ciència de Materials de Barcelona, CSIC, Campus UAB, E-08193 Bellaterra, Spain

Received 19 February 1999

Abstract

Some new aryl *o*-carboranes have been synthesized. From methyl 3-iodo-5-(trimethylsilyl-ethynyl)-benzoate (**1**) or butyl 3-(3,3-diethyltriazeno)-5-ethynyl-benzoate (**2**), 5-ethynyl-3-iodo-benzoates (**3a**, **3b**) were obtained, which after the reaction with the decaborane–acetonitrile complex led to the corresponding 5-(1′-(1′,2′-dicarba-*closo*-dodecaboranyl))-3-iodo-benzoates (**4a**, **4b**). Furthermore, the methyl 3-iodo-5-(trimethylsilyl-ethynyl)-benzoate (**1**) is the starting material for the synthesis of a bis-carborane. Compound **1** is modified to the methyl 3,5-bis(trimethylsilyl-ethynyl)-benzoate (**5**), which is deprotected to give the methyl 3,5-bis(ethynyl)-benzoate (**6**). Compound **6** reacted with the decaborane–acetonitrile complex to the methyl 3,5-bis(1′-(1′,2′-dicarba-*closo*-dodecaboranyl))-benzoate (**7**), which was partially degraded to the bis(tetramethylammonium)-3,5-bis(7′-(7′,8′-dicarba-*nido*-undecaboranyl))methoxycarbonylphenyl (**8**).

Keywords: *o*-Carboranes; Arylcarboranes; Oligomers

1. Introduction

The icosahedral carboranes $C_2B_{10}H_{12}$ may be regarded as excellent molecular building blocks with remarkable chemical stability and high boron content [1]. When they are substituted by suitable functionalized groups, they can be used in many applications. They serve as precursors for boron–carbide type ceramics [2], in the cancer treatment by boron neutron capture therapy (BNCT) [3], as polymers for high-temperature applications [4], in neutron shielding purposes [5], in connection with their non-linear optical (NLO) properties [6], as ligands in metallaborane catalysts [4,7], as metal complexing agents for solvent extraction [8] and as carriers for radioactive metals in radioimmunodetection and radioimmunotherapy [9].

With the aim of finding a convenient and controllable pathway to carboranylbenzene oligomers, we have begun an exploratory research leading to these compounds. These results are presented in this paper. Basically two pathways are considered, one in which ethynylbenzene oligomers are produced leaving the cluster formation as the very last step, and a second alternative that consists of introducing the cluster in the early stages, followed by their oligomerization. A discussion suggesting the first as the better choice is included.

2. Results and discussions

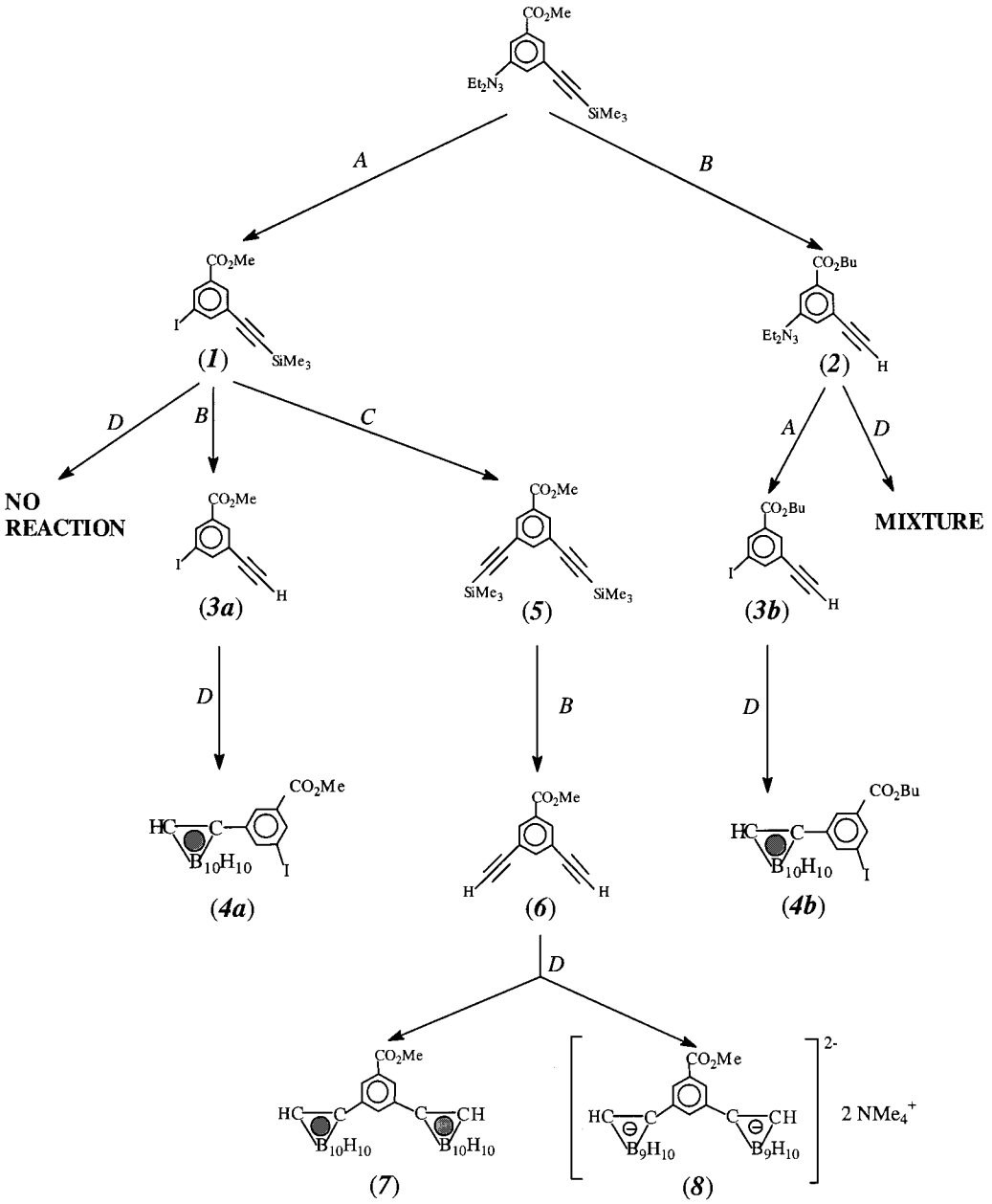
The methyl-3-(3,3-diethyltriazeno)-5-(trimethylsilyl-ethynyl)-benzoate is a monomer that contains a diethyltriazene group and a terminal ethynyl moiety protected by a trimethylsilyl group. It also contains an ester group, which is a very versatile function. This is a good starting material to synthesize oligomers that have periodic segments, the chain growth being able to take place at both ends. This idea has been used in the synthesis of alkane oligomers [10] and polyurethane segments [11].

Starting with methyl-3-(3,3-diethyltriazeno)-5-(trimethylsilyl-ethynyl)-benzoate, the formerly described methyl 3-iodo-5-(trimethylsilyl-ethynyl)-benzoate (**1**) [12] and butyl 3-(3,3-diethyltriazeno)-5-ethynyl-benzoate (**2**) have been prepared. These compounds are good precursors for oligomers and macrocycles [12,13].

* Corresponding author. Tel.: +34-3-5801853; fax: +34-3-5805729.

E-mail address: teixidor@icmab.es (F. Teixidor)

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00277-6



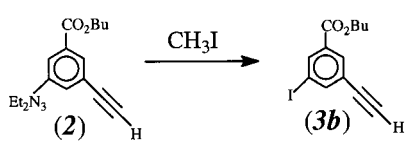
Scheme 1. General procedure for the synthesis of the new aryl-*o*-carboranes.

The reagents for these syntheses are based on terminal acetylenes protected as the corresponding trimethylsilyl derivative and aryl iodide precursors based on a dialkyltriazene, respectively. They allow for the stepwise synthesis of well-defined sequences of phenylacetylene units with the possibility to control the chain length and the functional group placement.

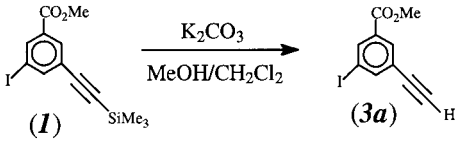
We have used the same strategy, shown in Scheme 1, in the synthesis of new aryl-*o*-carboranes. Four reactions, A, B, C and D, have been carried on to synthesize the compounds. Reactions A and B are deprotecting ones, C is a coupling reaction, and D corresponds to the *o*-carborane derivatives formation.

2.1. Triazene group deprotection (A)

Removal of the triazene groups to introduce the iodide is carried out with an excess of methyl iodide in an autoclave at 110°C for 17 h [12,14] (see Scheme 2).



Scheme 2. Triazene group removal and iodide insertion (A).



Scheme 3. Trimethylsilylacetylene group deprotection (B).

2.2. Trimethylsilylacetylene group deprotection (B)

The deprotection at the acetylenic group is carried out in good yield by a catalytic amount of a weak base like potassium carbonate in the presence of methanol using dichloromethane as a co-solvent to improve the solubility of the ester [12,15] (see Scheme 3).

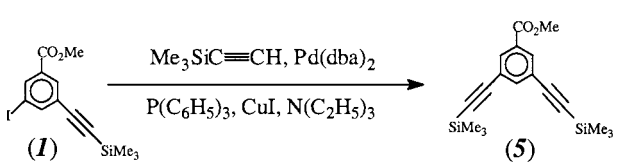
The iodide group in the starting material **1** also offers the possibility to synthesize a selected diacetylene compound **5**.

2.3. Coupling of acetylenic groups in the aromatic ring (C)

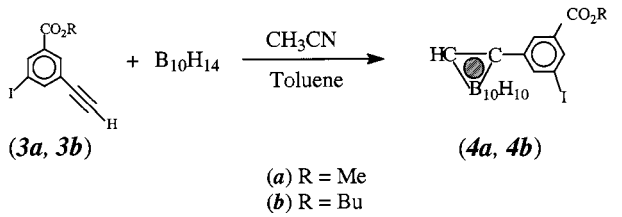
For this purpose, **1** is converted to the corresponding bis-trimethylsilylacetylene compound **5**. The reaction is conducted in a similar way as to produce the precursor of **1** [12,16], which is reacted with trimethylsilylacetylene in the presence of bis(dibenzylideneacetone)palladium(0), $Pd(dba)_2$ [17], cuprous iodide and triphenylphosphine in catalytic amounts. Scheme 4 shows the pathway to yield bis-trimethylsilylacetylene compounds. Triethylamine is used as a solvent. Due to the higher reactivity of the aryliodides, as compared with the arylbromides, the reaction proceeds in a relatively short time. Compound **5** is easily deprotected using potassium carbonate as a weak base in a catalytic amount to yield the methyl 3,5-bis(ethynyl)benzoate (**6**). The methyl 3,5-bis(trimethylsilyl-ethynyl)benzoate (**5**) shows a good solubility in methanol and, dichloromethane used as a co-solvent is not necessary.

2.4. Reaction of the acetylenic group of aryl compounds with decaborane (D)

It is reported [18] that decaborane reacts with acetylenic compounds in the presence of Lewis bases to produce 1-R-2-R′-1,2-$C_2B_{10}H_{10}$ derivatives with the accompanying elimination of a molecule of hydrogen. However, in the reaction of the protected acetylene (**1**) and the decaborane–acetonitrile complex, no carborane



Scheme 4. Coupling of acetylenic groups in the aromatic ring (C).



Scheme 5. Reaction of acetylenic group aryl compounds (**3a**, **3b**) with decaborane $B_{10}H_{14}$.

can be found. It was concluded that the trimethylsilyl group disturbed the cluster formation [19].

The reaction of **2** with the decaborane–acetonitrile complex also yields a complicated mixture of several products, which could not be isolated. In this case, it seems that the triazene group behaves as a degrading agent.

On the contrary the less sterically encumbered acetylene compounds **3a** and **3b** react with a decaborane–acetonitrile complex produced as earlier described [18], in toluene to the corresponding **4a** and **4b** carborane derivatives (Scheme 5). It has been found that for R=Bu, the reaction requires more time than for R=Me, but the reaction yield of the carborane **4b** is better too.

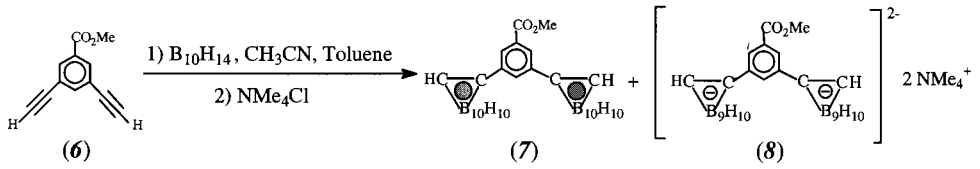
The two acetylenic groups of compound **6** then react with a decaborane–acetonitrile complex [18] to the methyl 3,5-bis(1′-(1′,2′-dicarba-*closo*-dodecaboranyl))-benzoate (**7**) (Scheme 6). The yield of the end product, however, is very low. One reason for this may be the competing partial degradation of **7** to yield **8**. Compound **8** has been separated by changing the polarity of the eluent from pure dichloromethane to a dichloromethane–methanol (1:1) mixture during the chromatographic purification of the reaction mixture. It was isolated with tetramethylammonium chloride as its bis-tetramethylammonium salt (**8**). The acetonitrile, which is used as a Lewis base in the complex with decaborane, may be the reason for the degradation.

This *nido* species **8** incorporates two anionic carborane cluster units with a pentagonal opened face linked by an aromatic ring with an ester group. The total charge of −2 may be delocalized in this pseudoaromatic system.

2.5. Characterisation of the compounds

2.5.1. Acetylene derivatives

The NMR spectra of the bis(ethynyl)benzoates **5** and **6** reflect the high symmetry of the molecules. Compound **5** displays two singlet signals in a ratio of 2:1 for the three aryl protons: at 8.01 ppm for the two protons in *o*-position to the carboxyl group and at 7.7 ppm for the one in *p*-position; a single signal whose relative area is 18 appears at 0.22 ppm, corresponding to the protons of the trimethylsilyl groups. Compound **6** also displays



Scheme 6. Reaction of acetylenic group aryl compound **6** with decaborane $B_{10}H_{14}$.

two singlet signals in a ratio of 2:1 at 8.07 ppm and at 7.72 ppm, corresponding to the protons in *o*-position and *p*-position to the carboxyl group, respectively, and at 3.12 ppm, a singlet for the protons of the trimethylsilyl group. In the $^{13}C\{^1H\}$-NMR spectra only four signals can be found at low field corresponding to the aromatic carbons (from 139 to 123 ppm).

2.5.2. Carborane derivatives

These compounds have been characterized by elemental analyses, IR, NMR and mass spectroscopies. The IR spectra show, for compounds **4a** and **4b**, the typical ν(B–H) absorption at frequencies near 2580 cm^{-1}, characteristic of *closo* 1-R-1,2-$C_2B_{10}H_{11}$ derivatives. The monosubstitution at CH is supported by the presence of a ν(C–H) carborane band at 3044 cm^{-1}. The ^{11}B-NMR spectra of compounds **4a** and **4b** present an spectral data pattern (1:1:2:4:2) for both compounds in the typical range (-1 and -13 ppm) for *closo* $C_2B_{10}H_{12}$ derivatives. The ^{1}H-NMR spectra of the mono *o*-carboranes **4a** and **4b** display, in addition to the aromatic proton signals at 8.3–7.9 ppm, a broad signal for the proton, connected with the carbon of the carborane at 4.0 ppm. In both compounds, the $^{13}C\{^1H\}$-NMR spectra display two resonances attributed to the cluster's carbon atoms, one at 59.7 ppm and the second at 74.0 ppm.

Due to the low reaction yield, purification and characterization of the bis-carborane cluster derivates **7** and **8** has been difficult. The infrared spectrum of the *closo* carborane **7** exhibited a B–H stretching absorption at 2599 cm^{-1}, whereas the corresponding absorption of the *nido* compound **8** appears at 2532 cm^{-1}. The ^{1}H-NMR spectrum of **7** displays a broad signal at 5.5 ppm for the proton, connected to the carbon of the cluster, and the $^{13}C\{^1H\}$ spectrum shows the two carbon atoms of the carborane substituent at 76.3 and 62.1 ppm. The ^{11}B-NMR patterns of both compounds **7** and **8** are consistent with the high symmetry of the molecule.

The ^{1}H-NMR spectrum of **8** displays the B–H–B resonance at -2.4 ppm, which unambiguously proves the *nido* character of the cluster [20]. This is supported by the ^{11}B-NMR spectrum, which shows nine equally weighted resonances in the range -8.4 to -35.4 ppm, typical for a *nido*-$C_2B_9H_{12}^-$ derivative carborane. Contrarily to the *closo* equivalent (**7**), the signals of the two cluster carbon atoms in the $^{13}C\{^1H\}$ spectrum are missing [21].

3. Conclusions

The procedure reported in this paper for the synthesis of adequately substituted ethynylbenzene derivatives seemed to be convenient to produce poly-*o*-carboranyl oligomers. The process is based on a series of controlled protection/deprotection steps aiming at producing the desired polyethynyl precursors. The carboxyl group bisecting the 3,5-positions of the aryl ring is adequately placed as a blocking agent and as a solubilizing group. Compound **6**, incorporating two ethynyl groups, is a representative example of the lower member of a series of polyethynylbenzene compounds. At this point two strategies could be followed: starting from the ethynyl compounds as a means to enlarge the number of ethynyl benzene units to finally incorporate the carborane cluster, or taking in consideration the somehow similar reactivity of ethyne and *o*-carborane to perform the protective/deprotective process on the cluster containing molecule, e.g. **4b**. To choose which of the two strategies was more suitable we succeeded in preparing the dicluster compound **7**. The yield, however, did not allow further studies on it. Yields of **4a** or **4b** were neither high enough. Thus it seems that if this procedure is applicable to produce polycarboranylbenzene oligomers it is more convenient first to produce the alkynylbenzene oligomers followed by cluster formation than the opposite.

4. Experimental

4.1. General

Microanalyses were performed using a Perkin–Elmer 240-B microanalyzer. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H-, $^{13}C\{^1H\}$- and ^{11}B-NMR spectra were recorded with a Bruker ARX 300 WB, operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C and 96.29 MHz for ^{11}B spectra. Chemical shift values for ^{1}H and ^{13}C spectra were referenced relative to tetramethylsilane, and to $BF_3{\cdot}OEt_2$ for ^{11}B spectra. Mass spectra were recorded on a Hewlett–Packard 5989 X.

All organic and inorganic salts were analytical reagent grade and used as received. Absolute MeOH was kept over 3 Å molecular sieves. Methyl iodide and trimethylsilylacetylene were obtained from Aldrich and also dried over 3 Å molecular sieves. The methyl 3-iodo-5-(trimethylsilyl-ethynyl)-benzoate (**1**), the butyl 3-(3,3-diethyltriazeno)-5-ethynyl-benzoate (**2**) [12] and $Pd(dba)_2$ [17] were prepared according to the literature. Triethylamine was freshly distilled over calcium hydride. Potassium carbonate, triphenylphosphine, copper iodide, magnesium sulfate and tetramethylammonium chloride were obtained from Fluka. The decaborane $B_{10}H_{14}$ was obtained from Dexsil Corporation and purified by sublimation at 0.01 mmHg before use.

All reactions were carried out under a dinitrogen atmosphere.

4.2. Synthesis of methyl 5-ethynyl-3-iodo-benzoate (*3a*)

Potassium carbonate (0.02 g, 0.13 mmol) was added to a solution of 0.461 g (1.29 mmol) of methyl 3-iodo-5-(trimethylsilyl-ethynyl)-benzoate (**1**) in 2.5 ml dichloromethane and 10 ml methanol. The reaction mixture was stirred at room temperature for 18 h. After the evaporation of the solvents, the residue was chromatographed on a silica gel column with dichloromethane as eluent ($R_f = 0.67$). Evaporation to dryness gave 0.341 g of (**3a**) (93%). Anal. Calc. for $C_{10}H_7IO_2$ (%): C, 41.99; H, 2.47. Found: C, 42.06; H, 2.27. EI-MS (m/z): 285.9 (100%, M^+). IR, ν (cm^{-1}): 3275, 3240 ($C_{ethynyl}$–H), 3064, 3008 (C_{aryl}–H), 2952 (C_{alkyl}–H), 1714 (C=O), 1560 (C–C)$_{aryl}$, 1285 (C–O). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.3 (m, 1H, C_{aryl}–H), 8.0 (m, 1H, C_{aryl}–H), 7.9 (m, 1H, C_{aryl}–H), 3.9 (s, 3H, CO_2CH_3), 3.2 (s, 1H, $C_{ethynyl}$–H). ^{13}C{^{1}H}-NMR ($CDCl_3$), δ (ppm): 164.6 (CO_2), 144.4, 138.5, 132.3, 131.7, 124.2 (C_{aryl}), 93.1 (C_{aryl}–I), 80.8, 79.6 ($C_{ethynyl}$), 52.5 (CO_2CH_3).

4.3. Synthesis of butyl 5-ethynyl-3-iodo-benzoate (*3b*)

In an autoclave (125 ml of volume) was placed 1.39 g (4.6 mmol) of butyl 3-(3,3-diethyltriazeno)-5-ethynyl-benzoate (**2**). After evacuation, 30 ml of methyl iodide was filled in, and the autoclave was saturated with nitrogen. The stirring solution was heated at 110°C, kept at this temperature for 17 h and cooled down. The methyl iodide was evaporated and the residue was chromatographed on a silica gel column with dichloromethane as eluent ($R_f = 0.73$). After the evaporation of the solvent, 1.32 g of **3b** could be obtained (88%). Anal. Calc. for $C_{13}H_{13}IO_2$ (%): C, 47.57; H, 3.99. Found: C, 46.37; H, 3.99. EI-MS (m/z): 327.9 (18%, M^+). IR, ν (cm^{-1}): 3254 ($C_{ethynyl}$–H), 3071 (C_{aryl}–H), 2959, 2931, 2868 (C_{alkyl}–H), 1721 (C=O), 1560 (C–C)$_{aryl}$, 1278 (C–O). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.3 (m, 1H, C_{aryl}–H), 8.1 (m, 1H, C_{aryl}–H), 8.0 (m, 1H, C_{aryl}–H), 4.3 (t, $^3J(H,H) = 6.6$ Hz, 2H, CO_2CH_2–), 3.2 (s, 1H, $C_{ethynyl}$–H), 1.7 (m, 2H, $CO_2CH_2CH_2$–), 1.4 (m, 2H, $CO_2(CH_2)_2CH_2$–), 1.0 (t, $^3J(H,H) = 7.3$ Hz, 3H, $CO_2(CH_2)_3CH_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$), δ (ppm): 164.4 (CO_2), 144.4, 138.6, 132.3, 129.0, 124.3 (C_{aryl}), 93.1 (C_{aryl}–I), 81.0, 79.4 ($C_{ethynyl}$), 65.5 (CO_2CH_2–), 30.7 ($CO_2CH_2CH_2$–), 19.2 ($CO_2(CH_2)_2CH_2$–), 13.7 ($CO_2(CH_2)_3CH_3$).

4.4. Synthesis of methyl 5-(1′-(1′,2′-dicarba-closo-dodecaboranyl))-3-iodo-benzoate (*4a*)

A total of 0.105 g (0.86 mmol) of decaborane was dissolved in 10 ml of acetonitrile and refluxed for 2 h under nitrogen. After cooling, 0.1 g (0.35 mmol) of **3a**, dissolved in 5 ml of toluene, was added and the reaction mixture was heated under reflux for 12 h more. The solvents were removed in vacuo, and the residue was treated with 5 ml of methanol for 30 min under stirring. Upon the evaporation of the solvent, the product was purified by chromatography on a silica gel column with dichloromethane:*n*-hexane (3:1) as eluent ($R_f = 0.67$). The solvent mixture was evaporated to dryness to afford 0.04 g of **4a** (29%). Anal. Calc. for $C_{10}H_{17}B_{10}IO_2$ (%): C, 29.71; H, 4.24. Found: C, 29.93; H, 4.14. EI-MS (m/z): 404.0 (100%, M^+). IR, ν (cm^{-1}): 3044 ($C_{cluster}$–H), 2959, 2931 (C_{alkyl}–H), 2615, 2573 (B–H), 1722 (C=O), 1567 (C–C)$_{aryl}$, 1300, 1237 (C–O). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.4 (t, $^4J(H,H) =$ 1.5 Hz, 1H, C_{aryl}–H), 8.0 (m, 1H, C_{aryl}–H), 7.9 (m, 1H, C_{aryl}–H), 4.0 (s, broad, 1H, $C_{cluster}$–H), 3.9 (s, 3H, CO_2CH_3), 3.2–0.8 (broad, 10H, B–H). ^{13}C{^{1}H}-NMR ($CDCl_3$), δ (ppm): 164.4 (CO_2), 140.4, 139.8, 135.8, 132.3, 127.5 (C_{aryl}), 94.1 (C_{aryl}–I), 73.9, 59.7 ($C_{cluster}$), 52.8 (CO_2CH_3). ^{11}B-NMR ($CDCl_3$), δ (ppm): −1.5 (d, $^1J(B,H) = 151$ Hz, 1B), −3.5 (d, $^1J(B,H) = 175$ Hz, 1B), −8.3 (d, $^1J(B,H) = 154$ Hz, 2B, B(8,10)), −10.7 (d, $^1J(B,H) = 175$ Hz, 4B, B(4,5,7,11)), −12.3 (d, $^1J(B,H) = 153$ Hz, 2B, B(3,6)).

4.5. Synthesis of butyl 5-(1′-(1′,2′-dicarba-closo-dodecaboranyl))-3-iodo-benzoate (*4b*)

A total of 0.155 g (1.24 mmol) of decaborane are dissolved in 10 ml of acetonitrile and refluxed for 2 h. After cooling, 0.37 g (1.13 mmol) of **3b**, dissolved in 5 ml toluene, was added and the reaction mixture was heated under reflux for 72 h. The solvents were removed in vacuo and the residue was treated with 5 ml of methanol for 30 min under stirring. The mixture was then extracted with *n*-hexane and the combined *n*-hexane phases were concentrated. For purification, it was chromatographed on a preparative silica thin layer with dichloromethane–*n*-hexane (1:1) as eluent ($R_f = 0.81$). The evaporation of the solvent gave 0.177 g of product

4b (35%). Anal. Calc. for $C_{13}H_{23}B_{10}IO_2$ (%): C, 34.98; H, 5.19. Found: C, 35.94; H, 5.09. EI-MS (m/z): 446.25 (4%, M^+). IR, ν (cm^{-1}): 3044 ($C_{cluster}$–H), 2959, 2931, 2875 (C_{alkyl}–H), 2580 (B–H), 1722, 1708 (C=O), 1567 (C–C)$_{aryl}$, 1293, 1237 (C–O). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.3 (t, ^4J(H,H) = 1.5 Hz, 1H, C_{aryl}–H), 8.0 (m, 1H, C_{aryl}–H), 7.9 (t, ^4J(H,H) = 1.9 Hz, 1H, C_{aryl}–H), 4.3 (t, ^3J(H,H) = 6.8 Hz, 2H, CO_2CH_2–), 4.0 (s, broad, 1H, $C_{cluster}$–H), 1.7 (m, 2H, $CO_2CH_2CH_2$–), 1.4 (m, 2H, $CO_2(CH_2)_2CH_2$–), 1.0 (t, ^3J(H,H) = 7.3 Hz, 3H, $CO_2(CH_2)_3CH_3$), 3.3–0.8 (broad, 10H, B–H). ^{13}C{^{1}H}-NMR ($CDCl_3$), δ (ppm): 163.9 (CO_2), 140.2, 139.7, 135.6, 132.6, 127.5 (C_{aryl}), 94.1 (C_{aryl}–I), 74.0 ($C_{cluster}$), 65.8 (CO_2CH_2–), 59.7 ($C_{cluster}$), 30.6 ($CO_2CH_2CH_2$–), 19.1 ($CO_2(CH_2)_2CH_2$–), 13.7 ($CO_2(CH_2)_3CH_3$). ^{11}B-NMR ($CDCl_3$), δ (ppm): −1.5 (d, ^1J(B,H) = 151 Hz, 1B), −3.5 (d, ^1J(B,H) = 172 Hz, 1B), −8.3 (d, ^1J(B,H) = 162 Hz, 2B, B(8,10)), −10.7 (d, ^1J(B,H) = 186 Hz, 4B, B(4,5,7,11)), −12.1 (d, ^1J(B,H) = 142 Hz, 2B, B(3,6)).

4.6. Synthesis of methyl 3,5-bis(trimethylsilyl-ethynyl)benzoate (5)

In a Schlenk was placed 0.002 g (0.004 mmol) of $Pd(dba)_2$, 0.006 g (0.024 mmol) of triphenylphosphine, 0.001 g (0.004 mmol) of cuprous iodide and 0.140 g (0.39 mmol) of **1**. The Schlenk was evacuated and filled with nitrogen. 0.077 g (0.78 mmol) of trimethylsilylacetylene, dissolved in 5 ml of freshly distilled dry triethylamine, was added. The suspension was stirred at 70°C for 15 h. After cooling, the suspension was filtered in order to remove the catalyst, which was washed carefully with diethylether. The washing solution and the filtrate were combined, washed with water and dried over magnesium sulfate. After removing the solvents in vacuum, the crude product was chromatographed in a silica gel column with dichloromethane–*n*-hexane (2:1) as eluent (R_f = 0.40). Evaporation to dryness afforded 0.092 g of **5** (72%). Anal. Calc. for $C_{18}H_{24}O_2Si_2$ (%): C, 65.80; H, 7.36. Found: C, 65.80; H, 7.17. EI-MS (m/z): 328.15 (27%, M^+). IR, ν (cm^{-1}): 3038 (C_{aryl}–H), 2994, 2949, 2898 (C_{alkyl}–H), 1732 (C=O), 1469 (C_{alkyl}–H), 1276 (C–O). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.0 (m, 2H, C_{aryl}–H), 7.7 (m, 1H, C_{aryl}–H), 3.9 (s, 3H, CO_2CH_3), 0.2 (s, 18H, $Si(CH_3)_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$), δ (ppm): 165.6 (CO_2), 139.0, 132.6, 130.5, 123.9 (C_{aryl}), 102.9, 96.1 ($C_{ethynyl}$), 52.4 (CO_2CH_3), −0.22 ($Si(CH_3)_3$).

4.7. Synthesis of methyl 3,5-bis(ethynyl)benzoate (6)

A solution of 0.085 g (0.26 mmol) of **5** and 0.004 g (0.026 mmol) of potassium carbonate in 10 ml of methanol was stirred for 18 h at room temperature. After evaporation to dryness, the residue was dissolved in 10 ml of dichloromethane and filtered through silica gel. The removing of the solvent afforded 0.038 g of **6** (79%). Anal. Calc. for $C_{12}H_8O_2$ (%): C, 29.71; H, 4.24. Found: C, 29.93; H, 4.14. EI-MS (m/z): 184.00 (70%, M^+). IR, ν (cm^{-1}): 3282 ($C_{ethynyl}$–H), 2958 (C_{alkyl}–H), 1728 (C=O), 1602, 1568 (C–C)$_{aryl}$, 1233 (C–O). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.1 (d, ^4J(H,H) = 1.5 Hz, 2H, C_{aryl}–H), 7.7 (t, ^4J(H,H) = 1.5 Hz, 1H, C_{aryl}–H), 3.9 (s, 3H, CO_2CH_3), 3.1 (s, 2H, $C_{ethynyl}$–H). ^{13}C{^{1}H}-NMR ($CDCl_3$), δ (ppm): 165.4 (CO_2), 139.2, 133.2, 130.8, 122.9 (C_{aryl}), 81.5, 78.9 ($C_{ethynyl}$), 52.4 (CO_2CH_3).

4.8. Synthesis of the methyl 3,5-bis(1′-(1′,2′-dicarba-closo-dodecaboranyl))benzoate (7) and the bis(tetramethylammonium) salt of 3,5-bis(7′-(7′,8′-dicarba-nido-undecaboranyl))methoxycarbonylphenyl (8)

A solution of 0.045 g (0.369 mmol) of decaborane in 5 ml of acetonitrile was refluxed for 2 h. After cooling, the solvent was evaporated and the residue dissolved in 10 ml of toluene. To the stirring solution was added 0.033 g (0.18 mmol) of **6** and the solution was heated at 110°C for 15 h. The cooled reaction mixture was evaporated to dryness and the residue dissolved in 5 ml of methanol. After stirring for 30 min, the solvent was removed under vacuo and the crude products were chromatographed on a silica gel column. The starting eluent was CH_2Cl_2–*n*-hexane 1:1, then CH_2Cl_2, with which 0.015 g of product **7** (20%) could be obtained ($R_{f(CH_2Cl_2)}$ = 0.48). Increasing the polarity of the eluent to CH_2Cl_2:methanol 1:1, a further fraction was collected and the solvent evaporated. The residue was treated with an aqueous solution of tetramethylammonium chloride, product **8** precipitated, was filtered and dried to give 0.01 g of the bis(tetramethylammonium) salt of 3,5-bis(7′-(7′,8′-dicarba-*nido*-undecaboranyl))-methoxycarbonylphenyl **8** (10%). Characterization of **7**: IR, ν (cm^{-1}): 3058 ($C_{cluster/aryl}$–H), 2953, 2924, 2853 (C_{alkyl}–H), 2599 (B–H), 1721 (C=O), 1598 (C–C)$_{aryl}$, 1248 (C–O). ^{1}H-NMR (CD_3COCD_3), δ (ppm): 8.3 (d, ^4J(H,H) = 1.9 Hz, 2H, C_{aryl}–H), 8.0 (t, ^4J(H,H) = 1.9 Hz, 1H, C_{aryl}–H), 5.5 (s, broad, 2H, $C_{cluster}$–H), 4.0 (s, 3H, CO_2CH_3), 2.9–0.2 (broad, 20H, B–H). ^{13}C{^{1}H}-NMR (CD_3COCD_3), δ (ppm): 165.6 (CO_2), 136.4, 133.3, 131.4, 130.8 (C_{aryl}), 76.3, 62.1 ($C_{cluster}$), 53.7 (CO_2CH_3). ^{11}B-NMR (CD_3COCD_3), δ (ppm): −2.4 (d, ^1J(B,H) = 144 Hz, 1B), −3.9 (d, ^1J(B,H) = 150 Hz, 1B), −8.6 (d, ^1J(B,H) = 169 Hz, 2B, B(8,10)), −10.6 (d, ^1J(B,H) = 187 Hz, 4B, B(4,5,7,11)), −12.3 (d, ^1J(B,H) = 156 Hz, 2B(3,6)). Characterization of **8**: Anal. Calc. for $C_{20}H_{52}B_{18}N_2O_2 \cdot 2CH_3COCH_3$ (%): C, 47.10; H, 9.66; N, 4.22. Found: C, 47.54; H, 8.86; N, 3.74. EI-MS (m/z): 414 (2%, M −132,-cluster). IR, ν (cm^{-1}): 3030 ($C_{cluster/aryl}$–H), 2955 (C_{alkyl}–H), 2532 (B–H), 1715 (C=O), 1445 (C–H)$_{alkyl}$, 1251 (C–O). ^{1}H-NMR (CD_3COCD_3), δ (ppm): 7.6 (m, 2H, C_{aryl}–H),

7.4 (m, 1H, C_{aryl}–H), 3.8 (s, 3H, CO_2CH_3), 3.4 (s, 24H, $N(CH_3)_4$), 3.0–0.2 (broad, 18H, B–H), −2,4 (broad, 2H, B–H–B). $^{13}C\{^1H\}$-NMR (CD_3COCD_3), δ (ppm): 168.3 (CO_2), 146.9, 131.1, 129.5, 125.2 (C_{aryl}), 56.3 ($N(CH_3)_4$), 52.2 (CO_2CH_3). ^{11}B-NMR (CD_3COCD_3), δ (ppm): −8.4 (d, $^1J(B,H) = 139$ Hz, 1B), −9.9 (d, $^1J(B,H) = 141$ Hz, 1B), −13.4 (d, $^1J(B,H) = 161$ Hz, 1B), −16.2 (d, $^1J(B,H) = 148$ Hz, 1B), −17.6 (d, $^1J(B,H) = 143$ Hz, 1B), −19.4 (d, $^1J(B,H) = 153$ Hz, 1B), −22.5 (d, $^1J(B,H) = 147$ Hz, 1B), −32.4 (dd, $^1J(B,H) = 135$ Hz, $^1J(B,H) = 36$ Hz, 1B), −35.4 (d, $^1J(B,H) = 138$ Hz, 1B).

Acknowledgements

This work was supported by the CIRIT (Project QFN95-4721) and the DGICYT (Project PB94-0226). B.F. thanks the EU for a Postdoctoral Fellowship in the HCM-programme (ERBCHBGCT930345). J.B. thanks the Generalitat de Catalunya for a Predoctoral Grant (1996-FI-98469 APQF).

References

[1] (a) X. Yang, C.B. Knobler, M.F. Hawthorne, Angew. Chem. 103 (1991) 1519. (b) X. Yang, C.B. Knobler, M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 30 (1991) 1507. (c) W. Clegg, W.R. Gill, J.A.H. MacBride, K. Wade, Angew. Chem. 105 (1993) 1402. (d) W. Clegg, W.R. Gill, J.A.H. MacBride, K. Wade, Angew. Chem. Int. Ed. Engl. 32 (1993) 1328. (e) X. Yang, W. Jiang, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 114 (1992) 979. (f) J. Müller, K. Base, T.F. Magnera, J. Michel, J. Am. Chem. Soc. 114 (1992) 972.

[2] L.G. Sneddon, M.G.L. Mirabelli, A.T. Lynch, P.J. Fazen, K. Su, J.S. Beck, Pure Appl. Chem. 63 (1991) 407. (b) T.D. Getman, P.M. Garrett, C.B. Knobler, M.F. Hawthorne, K. Thorne, J.D. Mackenzie, Organometallics 11 (1992) 2723.

[3] (a) R.F. Barth, A.H. Soloway, R.G. Fairchild, Cancer Res. 50 (1990) 1061. (b) H. Nemoto, J.G. Wilson, H. Nakamura, Y. Yamamoto, J. Org. Chem. 57 (1992) 435. (c) M.F. Hawthorne, Angew. Chem. 105 (1993) 997. (d) M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 32 (1993) 950.

[4] (a) H.M. Colquhoun, J.A. Daniels, I.R. Stephenson, K. Wade, Polym. Commun. 32 (1991) 272. (b) D.A. Brown, H.M. Colquhoun, J.A. Daniels, J.A.H. MacBride, I.R. Stephenson, K. Wade, J. Mater. Chem. 2 (1992) 793.

[5] J. Plešek, Chem. Rev. 92 (1992) 269.

[6] (a) D.M. Murphy, D.M.P. Mingos, J.M. Forward, J. Mater. Chem. 3 (1993) 67. (b) D.M. Murphy, D.M.P. Mingos, J.L. Hagitt, H.R. Powell, S.A. Westcott, T.B. Marder, N.J. Taylor, D.R. Kanis, J. Mater. Chem. 3 (1993) 139.

[7] (a) F. Teixidor, M.A. Flores, C. Viñas, R. Kivekäs, R. Sillanpää, Angew. Chem. 108 (1996), 2388. (b) F. Teixidor, M.A. Flores, C. Viñas, R. Kivekäs, R. Sillanpää, Angew. Chem. Int. Ed. Engl. 35 (1996), 2251. (c) H.C. Hang, M.F. Hawthorne, Organometallics 9 (1990) 2327, and references therein. (d) M.F. Hawthorne, in: J.F. Liebman, A. Greenberg, R.E. Williams (Eds.), Advances in Boron and the Boranes, VCH, New York, 1988, Ch. 10, pp. 225. (e) A. Demonceau, E. Saive, Y. de Froidmont, A.F. Noels, A.J. Hubert, I.T. Chizhevsky, I.A. Lobanova, V.I. Bregadze, Tetrahedron Lett. 33 (1992) 2009. (f) A. Demonceau, F. Simal, A.F. Noels, C. Viñas, R. Núñez, F. Teixidor, Tetrahedron Lett. 38 (1997) 7879.

[8] (a) E. Makrlik, P. Vanura, Talanta 32 (1985) 423. (b) C. Viñas, S. Gomez, J. Bertran, F. Teixidor, J.F. Dozol, H. Rouquette, Chem. Commun. (1998) 191. (c) C. Viñas, S. Gomez, J. Bertran, F. Teixidor, J.F. Dozol, H. Rouquette, Inorg. Chem. 37 (1998) 3640. (d) C. Viñas, J. Bertran, S. Gomez, F. Teixidor, J.F. Dozol, H. Rouquette, R. Kivekäs, R. Sillanpää, J. Chem. Soc. Dalton Trans. (1998) 2849.

[9] (a) R.J. Paxton, B.G. Beatty, M.F. Hawthorne, A. Varadarajan, L.E. Williams, F.L. Curtis, C.B. Knobler, J.D. Beatty, J.E. Shively, Proc. Natl. Acad. Sci. USA 88 (1991) 3387. (b) R.N. Grimes, Angew. Chem. 105 (1993) 1350. (c) R.N. Grimes, Angew. Chem. Int. Ed. Engl. 32 (1993) 1289.

[10] (a) O.I. Painter, D.J. Simmonds, M.C. Whiting, J. Chem. Soc. Chem. Commun. (1982) 1165. (b) I. Bidd, M.C. Whiting, J. Chem. Soc. Chem. Commun. (1985) 543. (c) E. Igner, O.I. Paynter, D.J. Simmonds, M.C. Whiting, J. Chem. Soc. Perkin Trans. 1 (1987) 2447.

[11] C.D. Eisenbach, H. Hayen, H. Nefzger, Makromol. Chem. Rapid Commun. 10 (1989) 463.

[12] J. Zhang, D.J. Pesak, J.L. Ludwick, J.S. Moore, J. Am. Chem. Soc. 116 (1994) 4227.

[13] (a) J. Zhang, J.S. Moore, Z. Xu, R.A. Aguirre, J. Am. Chem. Soc. 114 (1992) 2273. (b) J.S. Moore, J. Zhang, Angew. Chem. 104 (1992) 873. (c) ibid, Angew. Chem. Int. Ed. Engl. 31 (1992) 922. (d) T.C. Bedard, J.S. Moore, J. Am. Chem. Soc. 117 (1995) 10662. (e) A.S. Shetty, J. Zhang, J.S. Moore, J. Am. Chem. Soc. 118 (1996) 1019.

[14] J.S. Moore, E.J. Weinstein, Z. Wu, Tetrahedron Lett. 32 (1991) 2465.

[15] R. Eastmond, D.R.M. Walton, Tetrahedron 28 (1972) 4591.

[16] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 50 (1975) 4467.

[17] M.F. Rettig, P.M. Maitlis, Inorg. Syn. 17 (1977) 134.

[18] T.L. Heying, J.W. Ager Jr., S.L. Clark, D.J. Mangold, H.L. Goldstein, M. Hillman, R.J. Polak, J.W. Szymanski, Inorg. Chem. 2 (1963) 1089.

[19] N.N. Schwartz, E.I. O'Brien, S.L. Karlan, M.M. Fein, Inorg. Chem. 4 (1965) 661.

[20] C.E. Housecroft, Boranes and Metalloboranes. Structure, Bonding and Reactivity, Ellis Horwood, Leicester, 1990.

[21] G.R. Eaton, W.N. Lipscomb, NMR Studies of Boron Hydrides and Related Compounds, Benjamin, New York, 1969.