DALTON
FULL PAPER

Synthesis, structure and reactivity of 1-(α-*C*,α′-halo-*o*-xylyl)-2-trialkylsilyl-1,2-dicarbaboranes †

Andrei S. Batsanov, Charlotte K. Broder, Andrés E. Goeta, Judith A. K. Howard, Andrew K. Hughes * and John M. Malget

Department of Chemistry, University Science Laboratories, South Road, Durham, UK DH1 3LE. E-mail: a.k.hughes@durham.ac.uk

Received 13th August 2001, Accepted 23rd October 2001
First published as an Advance Article on the web 3rd December 2001

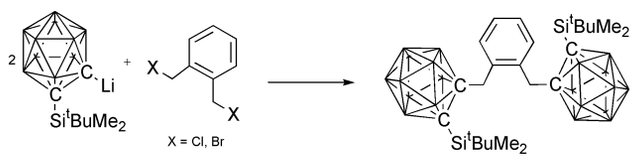
Treating Li[^{t}BuMe$_2$Si-1,2-$C_2B_{10}H_{10}$] with excess α,α′-dihalo-*o*-xylenes, 1,2-$C_6H_4(CH_2X)_2$ (X = Br, Cl), generates only 1-(α-*C*,α′-halo-*o*-xylyl)-2-(*tert*-butyldimethylsilyl)-1,2-dicarba-*closo*-dodecaboranes, 1-{*o*-($XCH_2C_6H_4CH_2$)}-2-^{t}BuMe$_2$Si-1,2-$C_2B_{10}H_{10}$ (X = Cl **1a**, Br **1b**). The structures of both **1a** and **1b** were determined by single crystal X-ray diffraction. Reaction of either **1a** or **1b** with ^{n}BuLi or MeLi affords the substituted ethane, (2-^{t}BuMe$_2$Si-1,2-$C_2B_{10}H_{10}$-1-*o*-$CH_2C_6H_4)_2C_2H_4$ **2** whereas reaction with ^{t}BuHNLi affords the substituted ethene (2-^{t}BuMe$_2$Si-1,2-$C_2B_{10}H_{10}$-1-*o*-$CH_2C_6H_4)_2C_2H_2$ **3**; both structures were confirmed by X-ray diffraction. Cleavage of the carborane–silicon bond in **1a** or **1b** by Bu_4NF gives dihydronaphthocarborane, **4**, which has been structurally characterised.

Introduction

Functionalised cyclopentadienyl ligands have made a significant impact on the chemistry of the early transition metals in recent years through the high activity of constrained geometry cyclopentadienyl amide ligands in alkene polymerisation.[1] Pendant arm donor ligand cyclopentadienyls have also been of significant interest in the chemistry of main group and other transition metals.[2,3] Given the relationship between cyclopentadienyl ligands and the *nido*-$C_2B_9H_{11}$ ligand,[4] we[5] and others[6,7] have been exploring the synthesis of ligands containing *nido*-carboranes attached to cyclopentadienyl,[8] amine and other donor atoms through carbon chains of various types and lengths. The development of bio-compatible amine-functionalised carboranes for a variety of other purposes, including use in boron neutron capture therapy (BNCT) remains an active area of research.[9]

We[5] have recently reported the synthesis of *closo*- and *nido*-carboranylamines *via* modifications to known procedures, and were interested to explore other syntheses. Thus the displacement of a tosyl or halide group by nucleophilic azide ion[10] and subsequent reduction to the amine[11] is a well-established procedure.[12] It has previously been reported however that this reaction fails for (halomethyl)carboranes, $XCH_2C_2B_{10}H_{11}$, X = Cl, Br, and only proceeds for the iodo derivatives.[13] Similar failures have been reported for a variety of reactions by other groups and were rationalised by the electronic influence of the carborane.[14]

The reactions of carborane nucleophiles with α,α′-dihalo-*o*-xylenes are well-established. The di-lithiation of *o*-carborane gives $Li_2C_2B_{10}H_{10}$, which reacts with α,α′-dibromo-*o*-xylene to give dihydronaphthocarborane, a precursor to naphthocarborane.[15] Mono-lithiation of *o*-carborane is not always a clean reaction, but the same effect is achieved by mono-silylation,[16–18] prior to metallation and Hawthorne reports that the reaction of two equivalents of Li(^{t}BuMe$_2$Si$C_2B_{10}H_{10}$) with α,α′-dihalo-*o*-xylenes gives substitution of both halides by the large carborane nucleophile (Scheme 1).[17]



Scheme 1 Product of the 2 : 1 reaction reported by Hawthorne.

We decided to explore the reaction of one equivalent of Li(^{t}BuMe$_2$Si$C_2B_{10}H_{10}$) with α,α′-dihalo-*o*-xylenes as a route to the synthesis of carborane–xylyl–amine ligands since we reasoned that carborane–xylyl–halide intermediates would be amenable to nucleophilic displacement. Here we report that these compounds also exhibit inactivity to nucleophilic substitution that in retrospect may be exploited to synthetic advantage to allow access to novel molecular architectures.

Results and discussion

The reaction of one equivalent of Li(^{t}BuMe$_2$Si$C_2B_{10}H_{10}$) with an excess of α,α′-dihalo-*o*-xylenes results in mono-substitution and affords 1-(α-*C*,α′-halo-*o*-xylyl)-2-(*tert*-butyldimethylsilyl)-1,2-dicarba-*closo*-dodecaboranes, 2-^{t}BuMe$_2$Si-1-{*o*-($XCH_2C_6H_4CH_2$)}-1,2-$C_2B_{10}H_{10}$ (X = Cl, **1a**; Br; **1b**) in excellent yield (Scheme 2). In keeping with the α,α′-dihalo-*o*-xylenes from which they are derived these compounds are potent irritants and lachrymators and as such skin contact should be avoided. Spectroscopic data for the Cl (**1a**) and Br (**1b**) derivatives are similar, so that only the chloro-derivative will be discussed. Considering the ^{1}H NMR data, the ^{t}BuMe$_2$Si substituent is clearly observed δ 0.46 (s, 6H, SiMe), 1.15 (s, 9H, Bu), and both methylene linkages are chemically distinct δ 3.70 (s, 2H, CH_2), 4.66 (s, 2H, CH_2). Due to the chemical inequivalence of the two methylene moieties the C_6H_4 unit is a complex multiplet between δ 7.18 and 7.39. The ^{11}B NMR spectrum confirms the retention of the *closo*-C_2B_{10} framework. Retention of the silyl protective group lends useful solubility and crystallinity which greatly aids separation and purification. Single crystal X-ray diffraction analysis for both **1a** and **1b** serves to further confirm the structural features with all parameters well within the expected range for compounds of this type. Fig. 1 shows the molecular structure of **1a**, that of **1b** is essentially identical.

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b107276e/

 DOI: 10.1039/b107276e

Table 1 Selected bond lengths (Å) and angles (°) for the structurally characterised compounds, where X represents the substituent on C(18). Atoms labelled with the suffix "A" are generated by the symmetry operation ($1 - x, -y, -z$)

	1a X = Cl(1)	**1b** X = Br(1)	**2** X = C(18A)	**3** X = C(18A)	**4** X = C(2)
C(1)–C(2)	1.699(2)	1.697(4)	1.694(2)	1.702(2)	1.649(2)
C(2)–Si(1)	1.9652(14)	1.961(3)	1.960(2)	1.9581(13)	
C(1)–C(11)	1.547(2)	1.540(4)	1.549(2)	1.542(2)	1.519(2)
C(11)–C(12)	1.521(2)	1.526(4)	1.517(2)	1.518(2)	1.518(2)
C(18)–X	1.825(2)	1.981(3)	1.549(3)	1.334(2)	1.528(2)
C(1)–C(2)–Si(1)	123.36(9)	123.6(2)	124.91(9)	124.01(8)	
C(18)–C(2)–C(1)					117.41(11)
C(2)–C(1)–C(11)	117.06(11)	116.8(2)	116.51(12)	117.63(9)	117.71(11)
C(1)–C(11)–C(12)	114.49(11)	114.8(2)	113.75(12)	114.47(10)	114.97(12)
C(17)–C(18)–X	110.14(10)	109.4(2)	111.3(2)	125.7(2)	114.96(12)

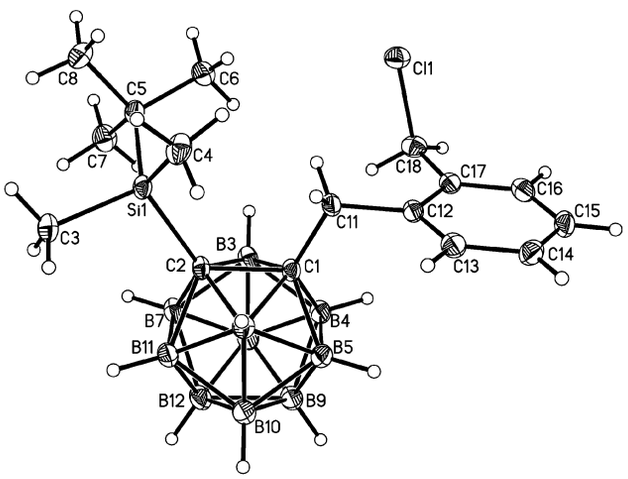


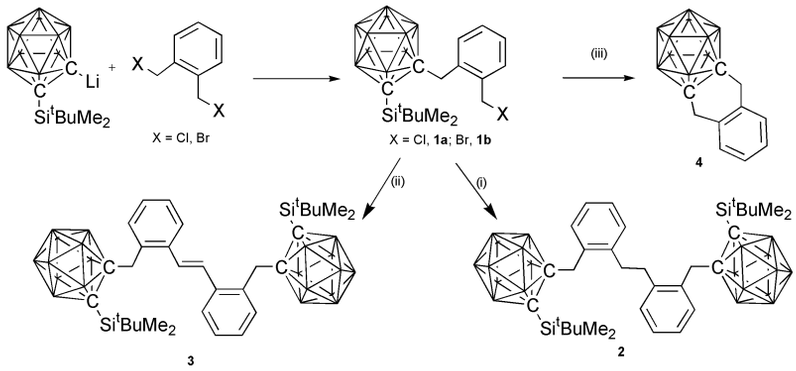
Fig. 1 A view of the molecular structure of **1a** showing 50% probability ellipsoids, hydrogen atoms as arbitrary sized spheres.

Selected bond lengths and angles appear in Table 1 and reveal C(1)–C(2) distances of 1.699(2) Å for **1a** and 1.697(4) Å for **1b**, which, although long for C–C single bonds, are within the normal range for polyhedral *closo*-carboranes, where the carbon atoms have large coordination numbers, here six. The other metric parameters are unremarkable.

In keeping with previous studies, we find these compounds are either inert to or are decomposed by reagents typically used to effect conversion of a halo group to an amine. Reagents investigated included NaN_3 and hexamethylenetetraamine (Delépine reaction).[19] No product of the desired formulation was obtained, as might be expected under such harsh conditions given that *o*-carborane is readily decapitated by amines.[20] Thus, whilst compounds **1a** and **1b** are potential precursors to functionalised *closo*- and *nido*-carboranes, they are not suitable for the synthesis of such carboranes carrying basic, or other, functions which are capable of deboronating **1a** and **1b** in competition with nucleophilic substitution of the chloride or bromide.

Given these limitations it is of interest to establish what transformations are possible for such systems. Carbarods[21] derived from carboranes are attracting attention as potential one-dimensional conductors and some of these materials exhibit liquid crystal behaviour.[22] For these reasons it was of interest to establish whether the halomethylene unit would undergo coupling reactions, as such a methodology could be applied to the rational stepwise construction of oligomeric materials.[23] Reaction of either **1a** or **1b** with ^{n}BuLi or MeLi results in a Wurtz type coupling reaction to afford the substituted ethane (2-^{t}BuMe$_2$Si-1,2-$C_2B_{10}H_{10}$-1-*o*-$CH_2C_6H_4$)$_2C_2H_4$ (**2**) in reasonable yield as a colourless highly crystalline air-stable solid. The formulation is entirely consistent with spectroscopic and analytical data and is firmly established by a single crystal X-ray diffraction study. Considering ^{1}H NMR data, a large change in chemical shift is observed for the methylene unit following loss of the electronegative halogen substituent and coupling to form the ethane (δ 4.66 for CH_2Cl in **1a**, δ 2.96 for CH_2CH_2 in **2**). In both ^{1}H and ^{13}C NMR data other characteristic resonances of both the aryl and BuMe$_2$Si units remain largely unaffected by the transformation. The ^{11}B NMR spectrum confirms retention of the *closo*-carborane fragment. The molecular structure determined by the single crystal X-ray study is shown in Fig. 2 and the structural parameters are reported in Table 1. The molecule sits on a crystallographic inversion centre at the mid-point of the C(18)–C(18A) bond, the length of which, 1.549(3) Å, is entirely consistent with a C–C single bond. The hybridisation of C(18) is sp^3 as evidenced by the C(17)–C(18)–C(18A) angle of 111.3(2)°. Other distances fall within normal ranges.

In the light of the alkyl lithium-promoted coupling reaction, we sought to discover if alternative bridge functionality could be generated. Treatment of either **1a** or **1b** with ^{t}BuHNLi results in bis-dehydrohalogenation to afford the alkene dimer *trans*-[2-^{t}BuMe$_2$Si-1,2-$C_2B_{10}H_{10}$-1-*o*-$CH_2C_6H_4$]$_2C_2H_2$ **3** in high



Scheme 2 Reactions discussed in this work. Reagents and conditions: (i) ^{n}BuLi, THF, room temp; (ii) ^{t}BuHNLi, THF, −100 °C; (iii) ^{n}Bu$_4$NF, THF, −78 °C.

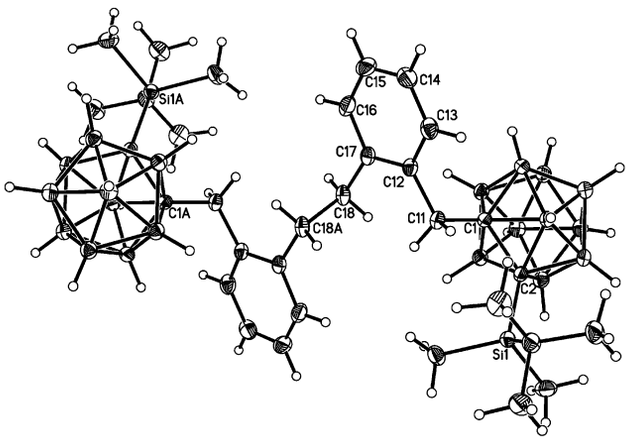


Fig. 2 Molecular structure of alkane **2** showing 50% probability ellipsoids, hydrogen atoms as arbitrary sized spheres. Atoms labelled with the suffix "A" are generated by the symmetry operation ($1 - x$, $-y$, $-z$).

yield as a colourless highly crystalline solid. Such a reaction is of particular synthetic utility as it provides a potential route to conjugated materials. Considering ^{1}H NMR data for **3**, the most notable feature is the resonance for the alkenic protons observed at δ 7.20. This assignment was further confirmed by both ^{1}H–^{1}H COSY and ^{1}H–^{13}C correlation experiments which also served to identify the alkenic carbons (δ 132.3). The product was further characterised by a structural study, the results of which appear in Fig. 3 with selected bond lengths and angles

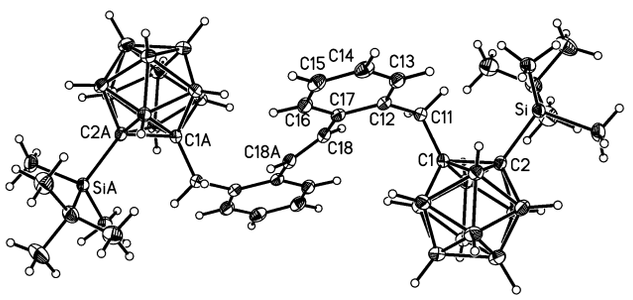


Fig. 3 Molecular structure of alkene **3** showing 50% probability ellipsoids, hydrogen atoms as arbitrary sized spheres. Atoms labelled with the suffix "A" are generated by the symmetry operation ($1 - x$, $-y$, $-z$).

in Table 1. The molecule again lies across a crystallographic inversion centre at the mid-point of the C(18)–C(18A) bond, the length of which, 1.334(2) Å, is consistent with a C=C double bond. The C(17)–C(18)–C(18A) angle of 125.7(2)° is consistent with sp^2 hybridisation for C(18), and the *trans*- or *E*-conformation of the double bond is confirmed by the requirement for a molecular inversion centre.

Careful removal of the SiMe$_2$^{t}Bu group from **1a** and **1b** using Bu$_4$NF at low temperature generates nascent (Bu$_4$F)[1-{*o*-(XCH$_2$C$_6$H$_4$CH$_2$)}-1,2-C$_2$B$_{10}$H$_{10}$], which has a nucleophilic site at the carborane 2-carbon atom, which can attack the free benzyl halide. Intramolecular attack results in cyclization to generate dihydronaphthocarborane, whilst it is also possible to envisage intermolecular attack and combinations of inter- and intra-molecular attack leading to polymers and cyclic oligomers respectively. High temperatures need to be avoided for this reaction, since wet Bu$_4$NF is a potent reagent for the deboronation of *closo*-carboranes under these conditions.[24] The spectroscopic properties of the single product of this reaction, **4**, are identical to those previously reported for dihydronaphthocarborane,[15] although NMR cannot uniquely discriminate between this and cyclic dimers or trimers of the same unit. These oligomers are expected to fragment readily under mass-spectrometry conditions, so that this technique is also not able to uniquely confirm the product formula. For this reason, the molecular structure of **4** was determined by X-ray diffraction and confirms that the product is indeed dihydronaphthocarborane; the structure is shown in Fig. 4 with selected bond lengths and

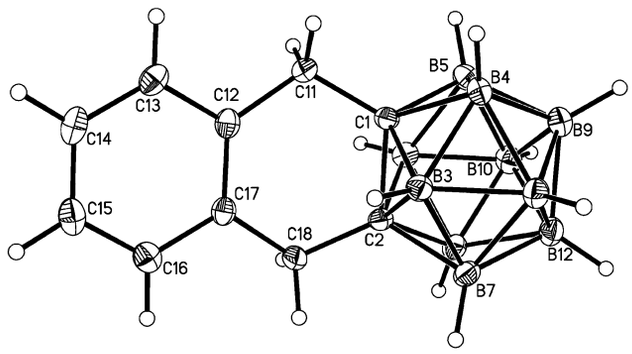


Fig. 4 Molecular structure of dihydronaphthocarborane **4** showing 50% probability ellipsoids, hydrogen atoms as arbitrary sized spheres.

angles in Table 1. The structure can be compared with that of "dihydrobenzocarborane".[25] The eight carbon atoms of the xylyl ring in **4** are essentially planar, with a maximum deviation from the least-square plane of 0.009 Å for C(14). One notable feature is a significant dishing of the molecule, as apparently required by the presence of sp^3 carbon atoms at C(11) and C(18), so that the C(1)–C(11)–C(12)–C(17)–C(18)–C(2) ring in **4** is far from planar, the largest deviation from a least-squares plane is 0.18 Å, whilst the analogous ring in dihydrobenzocarborane is planar, with a largest deviation of 0.033 Å.

In conclusion, we have demonstrated that (halo-*o*-xylyl)-*o*-carboranes are not suitable precursors to amine functionalised carborane ligands analogous to constrained geometry cyclopentadienyl ligands. Coupling reactions between the halo-*o*-xylyl units provide a means of preparing precursors to the rational stepwise construction of oligomeric carborane materials.

Experimental

All manipulations of air- and moisture-sensitive compounds were performed on a conventional vacuum/nitrogen line using standard Schlenk and cannula techniques or in a nitrogen filled glove box. When required, solvents were dried by prolonged reflux over the appropriate drying agent, prior to distillation and deoxygenation by freeze–pump–thaw processes where appropriate. NMR solvents were vacuum-distilled from suitable drying agents and stored under a dry nitrogen atmosphere. Elemental analysis was performed by the micro-analytical service within this department on an Exeter Instruments analyser. NMR spectra were recorded on the following instruments: Varian Unity-300 (^{1}H, ^{11}B, ^{13}C), Varian 500 (^{1}H, ^{13}C, HETCOR), ^{1}H and ^{11}B NMR were recorded on the Unity-300 unless otherwise stated. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^{1}H NMR spectra were referenced to residual protio impurity in the solvent ($CHCl_3$, 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm). ^{11}B NMR were referenced externally to $Et_2O{\cdot}BF_3$ δ = 0.0 ppm. Except where otherwise indicated, all spectra were recorded in $CDCl_3$ at ambient temperature.

CAUTION: α,α′-dihalo-*o*-xylenes and compounds **1a** and **1b** are potent irritants and lachrymators and as such skin contact should be avoided.

Syntheses

1-(-α-*C*,α′-Chloro-*o*-xylyl)-2-(*tert*-butyldimethylsilyl)-1,2-dicarba-*closo*-dodecaborane 1a. A solution of Li[^{t}BuMe$_2$Si-1,2-C$_2$B$_{10}$H$_{10}$] (5.00 g, 18.9 mmol) in 2 : 1 benzene–Et$_2$O (50 ml)

Table 2 Crystal data and structure refinement for compounds described in this paper

Compound	**1a**	**1b**	**2**	**3**	**4**
Empirical formula	$C_{16}H_{33}B_{10}ClSi$	$C_{16}H_{33}B_{10}BrSi$	$C_{32}H_{66}B_{20}Si_2$	$C_{32}H_{64}B_{20}Si_2$	$C_{10}H_{18}B_{10}$
Formula weight	397.06	441.52	723.23	721.21	246.34
Temperature/K	120(2)	120(2)	100(2)	120(2)	103(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	7.466(2)	7.4927(2)	9.329(1)	10.731(2)	7.215(1)
α/°	107.79(3)	72.0640(10)			
b/Å	10.056(2)	10.0475(3)	13.502(2)	16.232(2)	20.620(3)
β/°	91.10(3)	83.1420(10)	104.505(5)	110.64(2)	90.48(1)
c/Å	16.135(3)	16.2819(5)	18.097(2)	13.294(3)	9.268(1)
γ/°	99.24(3)	80.7340(10)			
Volume/Å^3	1135.5(4)	1147.78(6)	2206.8(5)	2167.0(7)	1378.8(2)
Z	2	2	2	2	4
μ/mm^{-1}	0.222	1.844	0.105	0.107	0.056
Reflections measured	14262	8297	24049	22108	11211
Unique reflections	6087	5791	5471	4965	3165
R_{int}	0.0985	0.0391	0.0538	0.0339	0.0493
Reflections $I > 2\sigma(I)$	5057	4153	4187	4135	2294
$R[F^2 > 2\sigma(F^2)]$	0.0458	0.0462	0.0453	0.0358	0.0459
$wR(F^2)$, all data	0.1321	0.1031	0.1209	0.0950	0.1225

was cooled to 0 °C and treated dropwise with α,α′-dichloro-*o*-xylene (7.00 g, 40 mmol) as a 2 : 1 benzene–Et_2O solution (50 ml). Following complete addition the mixture was allowed to warm to room temperature, and then brought to reflux for 12 h. The resulting pale yellow solution was evaporated to dryness *in vacuo* and the residue triturated with ethanol (*ca.* 30 ml). The mixture was cooled to −10 °C overnight to afford a colourless microcrystalline solid which was isolated by filtration, washed with an aliquot of chilled methanol (2 ml) and dried *in vacuo*. Yield 7.04 g, 94% (note: unreacted starting materials sublime *in vacuo*). (Found C 48.5; H 8.4; $C_{16}H_{33}B_{10}ClSi$ requires C 48.4; H 8.4%); δ_H 0.46 (s, 6H, $SiCH_3$), 1.15 (s, 9H, Bu), 3.70 (s, 2H, CH_2), 4.66 (s, 2H, CH_2), 7.18–7.39 (m, 4H, C_6H_4); δ_C 136.3, 134.6, 132.8, 130.8, 128.9, 128.8 (Ar), 80.6, 73.7 (cage C), 44.6 (CH_2), 39.3 (CH_2), 27.7 (CCH_3), 20.6 (CCH_3), −2.2 ($SiCH_3$); δ_B −1.3 (1B), −3.4 (1B), −7.8 (2B), −9.4 (3B), −10.4 (3B).

1-(α-*C*,α′-Bromo-*o*-xylyl)-2-(*tert*-butyldimethylsilyl)-1,2-dicarba-*closo*-dodecaborane 1b. An identical procedure was employed for the synthesis of **1b** from Li[^{t}BuMe$_2$Si-1,2-$C_2B_{10}H_{10}$] (5.00 g, 18.9 mmol) and α,α′-dibromo-*o*-xylene (10.6 g, 40 mmol). Yield 7.21 g, 86%. (Found C 43.0; H 7.4; $C_{16}H_{33}B_{10}BrSi$ requires C 43.5; H 7.5%); δ_H 0.51 (s, 6H, $SiCH_3$), 1.20 (s, 9H, Bu), 3.73 (s, 2H, CH_2), 4.61 (s, 2H, CH_2), 7.18–7.39 (m, 4H, C_6H_4); δ_C 136.6, 134.6, 132.9, 130.9, 128.9, 128.8 (Ar), 80.4, 73.7 (cage C), 39.6 (CH_2), 31.9 (CH_2), 27.9, 27.6 (CCH_3), 20.7 (CCH_3), −1.9, −2.3 ($SiCH_3$); δ_B −1.0 (1B), −5.6 (1B), −9.9 (3B), −11.8 (5B).

Alkane 2. A THF solution (25 ml) of **1a** (0.10 g, 0.25 mmol) was treated dropwise with a slight excess of ^{n}BuLi at room temperature and left to stir for 12 h. Volatiles were removed *in vacuo* and the residue triturated with ethanol (*ca.* 30 ml) to afford a bright white solid which was dried *in vacuo*. Yield 0.065 g, 72%. Crystalline samples were obtained by recrystallisation from CH_2Cl_2–ethanol solutions. Comparable yields were obtained using **1b**. (Found C 51.1; H 8.8; $C_{32}H_{66}B_{20}Si_2\cdot 0.5CH_2Cl_2$ requires C 51.0; H 8.8%); δ_H 0.42 (s, 6H, $SiCH_3$), 1.15 (s, 9H, Bu), 2.96 (s, 2H, CH_2), 3.38 (s, 2H, CH_2), 7.05–7.20 (m, 4H, C_6H_4); δ_C 139.9, 133.8, 132.0, 129.7, 128.4, 126.2 (Ar), 81.4, 74.0 (cage C), 39.5 (CH_2), 34.4 (CH_2), 27.9, 27.6 (CCH_3), 20.6 (CCH_3), −1.9, −2.3 ($SiCH_3$); δ_B −0.8 (1B), −5.5 (1B), −9.8 (2B), −11.4 (3B), −12.4 (3B).

Alkene 3. A THF solution (25 ml) of **1a** (0.10 g, 0.25 mmol) was treated dropwise with two equivalents of ^{t}BuHNLi (0.04 g, 0.5 mmol) as a THF solution (2 ml) at −100 °C (liquid N_2–toluene) and allowed to warm slowly to room temperature and left to stir for 12 h. The reaction was quenched by addition of propan-2-ol (1 ml), volatiles removed *in vacuo* and the residue triturated with ethanol (*ca.* 30 ml) to afford a bright white solid which was dried *in vacuo*. Yield 0.078 g, 86%. Crystalline samples were obtained by recrystallisation from CH_2Cl_2–ethanol solutions. Comparable yields were obtained using **1b**. (Found C 53.0; H 9.0; $C_{32}H_{64}B_{20}Si_2$ requires C 53.3; H 8.9%); δ_H 0.42 (s, 6H, $SiCH_3$), 1.11 (s, 9H, Bu), 3.65 (s, 2H, CH_2), 7.20 (s, 2H, CH), 7.22–7.62 (4H, C_6H_4); δ_C 137.2, 133.8, 129.2, 128.7, 127.8, 126.3 (Ar), 132.3 (CH), 81.0, 73.9 (cage C), 40.0 (CH_2), 27.7 (CCH_3), 20.6 (CCH_3), −2.1 ($SiCH_3$); δ_B 1.2 (1B), −3.5 (1B), −7.8 (3B), −9.6 (5B, vbr).

Dihydronaphthocarborane, 4. A stirred solution of **1a** (0.10 g, 0.25 mmol) in THF (25 ml) was cooled to −78 °C and treated slowly and dropwise with a solution of ^{n}Bu$_4$NF (0.065 g, 0.25 mmol) in THF (10 ml) and maintained at this temperature for 1 h. After slowly warming to room temperature, the volatiles were removed under reduced pressure and the residue was triturated with methanol (5 ml). The resulting solids were isolated by filtration and purified by recrystallisation from CH_2Cl_2–methanol to afford colourless crystals of pure **4**. Yield 0.044 g, 71%. Spectroscopic properties were identical to those reported by Matteson *et al.*[15]

X-Ray crystallography

Single crystal X-ray diffraction experiments were carried out with a SMART 1K CCD area detector, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The reflection intensities for **1b** were corrected by means of a ψ-scan, the reflections for the other compounds were not corrected for absorption. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL programs.[26] Crystal data and experimental details are listed in Table 2.

CCDC reference numbers 168850–168854.

See http://www.rsc.org/suppdata/dt/b1/b107276e/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We acknowledge the award of an EPSRC Senior Research Fellowship (J. A. K. H.), and support from the ERDF Centre for 21st Century Materials at the University of Durham (J. M. M.).

References

1 A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587; J. Chirinos, T. Rajmankina, A. Parada and F. Ciardelli, *Macromol. Chem. Phys.*, 2000, **201**, 2581; S. Park, W. J. Wang and S. P. Zhu, *Macromol. Chem. Phys.*, 2000, **201**, 2203; D. van Leusen, D. J. Beetstra, B. Hessen and J. H. Teuben, *Organometallics*, 2000, **19**, 4084; K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol and J. Okuda, *Organometallics*, 2000, **19**, 228; S. Tian, V. M. Arredondo, C. L. Stern and T. J. Marks, *Organometallics*, 1999, **18**, 2568.

2 J. Okuda, *Comments Inorg. Chem.*, 1994, **16**, 185; P. Jutzi and U. Siemeling, *J. Organomet. Chem.*, 1995, **500**, 175; C. S. Slone, D. A. Weinberger and C. A. Mirkin, *Prog. Inorg. Chem.*, 1999, **48**, 233; C. Müller, D. Vos and P. Jutzi, *J. Organomet. Chem.*, 2000, **600**, 127; P. Jutzi and T. Redeker, *Eur. J. Inorg. Chem.*, 1998, 663; H. Butenschon, *Chem. Rev.*, 2000, **100**, 1527; U. Siemeling, *Chem. Rev.*, 2000, **100**, 1495.

3 A. K. Hughes, A. Meetsma and J. H. Teuben, *Organometallics*, 1993, **12**, 1936; A. K. Hughes, S. M. B. Marsh, J. A. K. Howard and P. S. Ford, *J. Organomet. Chem.*, 1997, **527**, 195; A. K. Hughes and A. J. Kingsley, *J. Chem. Soc., Dalton Trans.*, 1997, 4139.

4 R. N. Grimes, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, vol 1, ch. 9; M. F. Hawthorne, *Acc. Chem. Res.*, 1968, **1**, 281; A. K. Saxena and N. S. Hosmane, *Chem. Rev.*, 1993, **93**, 1081.

5 A. S. Batsanov, A. E. Goeta, J. A. K. Howard, A. K. Hughes and J. M. Malget, *J. Chem. Soc., Dalton Trans.*, 2001, 1820.

6 K. Vyakaranam, S. Li, C. Zheng and N. S. Hosmane, *Inorg. Chem. Commun.*, 2001, **4**, 180.

7 S. Gomez, C. Viñas, M. Lamrani, F. Teixidor, R. Kivekäs and R. Sillanpää, *Inorg. Chem.*, 1997, **36**, 3565; F. Teixidor, S. Gomez, M. Lamrani, C. Viñas, R. Sillanpää and R. Kivekäs, *Organometallics*, 1997, **16**, 1278.

8 G. F. Zi, Q. C. Yang, T. C. W. Mak and Z. W. Xie, *Organometallics*, 2001, **20**, 2359; K. L. Chui, Q. C. Yang, T. C. W. Mak and Z. W. Xie, *Organometallics*, 2000, **19**, 1391; S. W. Wang, Q. C. Yang, T. C. W. Mak and Z. W. Xie, *Organometallics*, 2000, **19**, 334.

9 W. Tjarks, *J. Organomet. Chem.*, 2000, **614**, 37; A. H. Soloway, W. Tjarks, B. A. Barnum, F. G. Rong, R. F. Barth, I. M. Codogni and J. G. Wilson, *Chem. Rev.*, 1998, **98**, 1515.

10 J. March, *Advanced Organic Chemistry*, 3rd edn., Wiley, Chichester, 1985, p. 380.

11 J. March, *Advanced Organic Chemistry*, 3rd edn., Wiley, Chichester, 1985, p. 1106.

12 A. K. M. Annisuzzaman and R. L. Whistler, *J. Org. Chem.*, 1972, **37**, 1201; A. K. M. Annisuzzaman and R. L. Whistler, *Carbohydr. Chem.*, 1980, **8**, 297.

13 J. G. Wilson, A. K. M. Anisuzzaman, F. Alam and A. H. Solway, *Inorg. Chem.*, 1992, **31**, 1955.

14 A. Varadarajan, R. M. Sharkey, D. M. Doldgenberg and M. F. Hawthorne, *Bioconjugate Chem.*, 1991, **2**, 102.

15 D. S. Matteson and R. A. Davis, *Inorg. Chem.*, 1974, **13**, 859; D. S. Matteson and R. A. Davis, *J. Chem. Soc. D*, 1970, 669; see also A. Z. Bradley, A. J. Link, K. Biswas, D. Kahne, J. Schwartz, M. Jones Jr., Z. Zhu and M. S. Platz, *Tetrahedron Lett.*, 2000, **41**, 8691.

16 F. A Gomez, S. E. Johnson and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1991, **113**, 5915.

17 F. A. Gomez and M. F. Hawthorne, *J. Org. Chem.*, 1992, **57**, 1384.

18 W. Jiang, I. T. Chizhevsky, M. D. Mortimer, W. Chen, C. B. Knobler, S. E. Johnson, F. A. Gomez and M. F. Hawthorne, *Inorg. Chem.*, 1996, **35**, 5417.

19 N. Blažević, D. Kolbah, V. Šunjić and F. Kajfež, *Synthesis*, 1979, 161.

20 L. I. Zakharkin and A. V. Grebenikov, *Izv. Akad. Nauk SSSR, Ser. Chim.*, 1966, 2019; M. F. Hawthorne, D. C. Young, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen and M. M. Fein, *Inorg. Chem.*, 1963, **2**, 1120.

21 X. Yang, W. Jiang, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1992, **114**, 9719; P. F. H. Schwab, M. D. Levin and J. Michl, *Chem. Rev.*, 1999, **99**, 1863.

22 For a recent review of this area see P. Kaszynski, *Collect. Czech. Chem. Commun.*, 1999, **64**, 895.

23 H. M. Colquhoun, P. L. Herbertson, K. Wade, I. Baxter and D. J. Williams, *Macromolecules*, 1999, **31**, 1694.

24 H. Tomita, H. Luu and T. Onak, *Inorg. Chem.*, 1991, **30**, 812; M. A. Fox, J. A. H. MacBride and K. Wade, *Polyhedron*, 1997, **16**, 2499; M. A. Fox and K. Wade, *J. Organomet. Chem.*, 1999, **573**, 279; J. Yoo, J.-W. Huang and Y. Do, *Inorg. Chem.*, 2001, **40**, 568.

25 R. C. B. Copley, M. A. Fox, W. R. Gill, J. A. K. Howard, J. A. H. MacBride, R. J. Peace, G. P. Rivers and K. Wade, *Chem. Commun.*, 1996, 2033.

26 SHELXTL-NT, Version 5.1, Bruker Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA, 1998.