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5 Synthesis and characterisation of the *exo-nido* molybdacarborane
6 complex $\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10})$.
7 Strong B–H–Mo 3-centre bonding

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13 Dedicated to Professor Pascual Royo on the occasion of his 65th birthday in recognition of his many significant contributions to transition metal
14 chemistry.
15

16 **Abstract**

17 Reaction of $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^-$ and $\text{MoBr}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_2$ in THF affords the zwitterionic *exo-nido*
18 molybdacarborane complex $\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10})$, characterised by ¹H- and ¹¹B-NMR spectro-
19 scopy and by a crystallographic study. The complex is fluxional (having mirror symmetry on the NMR timescale) in solution at
20 room temperature although asymmetric in the solid state. Data are presented which suggest a significant 3c–2e B3–H3–Mo bond.
21 Deprotonation of $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^-$ with Li^nPr_2 followed by reaction with $\text{MoBr}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_2$
22 affords $\text{Li}[1,2\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-3-(}\eta\text{-C}_3\text{H}_5\text{)-3,3-(CO)}_2\text{-3,1,2-closo-MoC}_2\text{B}_9\text{H}_9]$ for which ¹H- and ¹¹B-NMR data are reported. © 2002
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25 **Keywords:** Deprotonation; Molybdacarborane; ¹H- and ¹¹B-NMR spectroscopy

26 **1. Introduction**

27 The interaction of transition metal fragments with
28 heteroborane cages continues to be an area of significant
29 research activity [1] and within this field studies of
30 metallacarboranes are pre-eminent. Metallacarboranes
31 are important compounds for a whole variety of
32 reasons, from their involvement with fundamental
33 studies of heteroborane shape [2] and isomerisation [3]
34 to applications in fields as diverse as catalysis [4] and
35 radionuclide extraction [5].

36 Carboranes which carry donor atoms attached to the
37 cage as substituents have a particularly rich coordina-
38 tion metal chemistry. If open (e.g. *nido* or *arachno*) they
39 could in principle co-ordinate to a transition metal
40 fragment in η -fashion (*endo* metal forming a cluster

41 vertex) as well as co-ordinating an *exo*-bound metal
42 through the donor atoms(s) or B–H–M bonds [6] or
43 both.

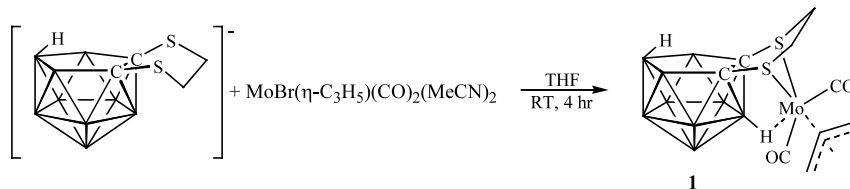
44 As part of our interest in *nido*-C₂B₉ carboranes
45 containing sulfur substituents [7] we are developing the
46 transition metal chemistry of $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}$
47 *nido*-C₂B₉H<sub>10}]^-. In this paper we report the reaction
48 of this anion with the $\{\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\}^+$ fragment
49 both with and without prior deprotonation of the *nido*
50 carborane. In the former case this leads to an anionic
51 *closo* species and in the latter case to an overall neutral,
52 zwitterionic, *exo-nido* species with both Mo–S bonds
53 and a strong B–H–Mo bond.</sub>

54 **2. Results and discussion**

55 The reaction between $[\text{NMe}_4][7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}$
56 *nido*-C₂B₉H_{10}] and $\text{MoBr}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_2$ in}

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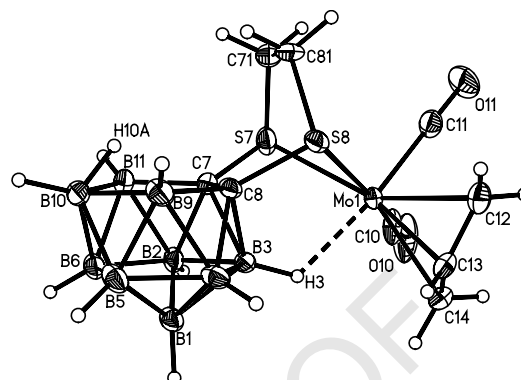
4 E-mail address: clara@icmab.es (C. Viñas).

Scheme 1. Synthesis of the *exo-nido* compound $\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10})$, **1**.

57 THF affords (Scheme 1) the *exo-nido* molybdacborane
58 compound $\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-}$
59 $7,8\text{-nido-C}_2\text{B}_9\text{H}_{10})$, **1**, in high yield after work-up involv-
60 ing column chromatography.

61 Compound **1** was characterised by microanalysis and
62 by IR and NMR spectroscopy. The IR spectrum
63 (CH_2Cl_2 solution) is dominated by a strong broad
64 absorption centred around 2530 cm^{-1} due to BH stretch
65 and by two strong, sharper, absorptions at 1939 and
66 1855 cm^{-1} due to CO stretches. By both ^{11}B - and ^1H -
67 NMR spectroscopy (CDCl_3 solution) the compound has
68 time-averaged C_s symmetry at room temperature. Thus
69 the $^{11}\text{B}\text{-}\{^1\text{H}\}$ -NMR spectrum reveals six resonances
70 (2:2:2:1:1:1, high frequency to low frequency) between
71 0 and -35 ppm , typical of a *nido* C_2B_9 residue. On
72 retention of proton coupling all become doublets ($^1J_{\text{BH}}$
73 $120\text{--}155\text{ Hz}$) due to *exo*-bound H atoms, with that at $-$
74 26 ppm additionally showing *endo*-H coupling of ca. 50
75 Hz. In the ^1H -NMR spectrum is the familiar pattern for
76 the $\eta\text{-C}_3\text{H}_5$ group (doublets for *syn* (ca. 7 Hz) and *anti*
77 (ca. 12 Hz) pairs of protons, doublet of triplets (near
78 heptet) for central proton) and a pair of multiplets for
79 the *endo* and *exo* protons of the $\text{SCH}_2\text{CH}_2\text{S}$ unit. Also
80 clearly visible are two broad resonances in the $^1\text{H}\{^{11}\text{B}\}$ -
81 NMR spectrum, presumably unresolved doublets, as-
82 signed to a $\{\text{BH}_2\}$ unit, the *exo* proton resonating at
83 0.55 ppm and the *endo* proton at -2.70 ppm , and a
84 signal integrating for 1 H atom at even lower frequency,
85 -5.55 ppm , assigned to the H atom bound to B3 and
86 involved in the $3c\text{-}2e^1\text{ B-H-Mo}$ bond.

87 A crystallographic study of **1** was undertaken. Fig. 1
88 presents a view of the compound and selected molecular
89 parameters are listed in Table 1. The overall structure of
90 the molecule is that of a zwitterionic *exo-nido* metalla-
91 carborane, with a formally cationic $\{\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\}^+$
92 unit bound to the side of a formally
93 anionic $\{\text{nido-C}_2\text{B}_9\text{H}_{10}\}^-$ unit via two S–Mo co-
94 ordinate bonds and one $3c\text{-}2e\text{ B3-H3-Mo}$ bond. In
95 the solid state the $\{\text{Mo}(\text{C11O11})\text{C}_2\text{B}_9\text{H}_{10}(\text{SCH}_2\text{CH}_2\text{S})\}$
96 unit has effective mirror symmetry, with the C_3H_5 ligand
97 lying to one side, and the C10O10 ligand to the other

Fig. 1. Perspective view of $\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10})$, compound **1**, showing the atomic numbering scheme. Atoms are drawn as 50% thermal ellipsoids, except for H atoms.Table 1
Selected interatomic distances (Å) and angles (°) for compound **1**

Interatomic distances			
B1–B2	1.768(5)	C8–B9	1.613(4)
B1–B3	1.748(5)	B9–B10	1.845(6)
B1–B4	1.781(5)	B10–B11	1.849(6)
B1–B5	1.794(5)	B11–C7	1.615(4)
B1–B6	1.811(5)	C7–S7	1.785(3)
B2–B3	1.756(5)	C8–S8	1.785(3)
B2–B6	1.749(5)	S7–C71	1.826(4)
B2–C7	1.720(4)	S8–C81	1.805(3)
B2–B11	1.828(5)	C71–C81	1.528(6)
B3–B4	1.765(5)	S7–Mo1	2.5170(10)
B3–C7	1.725(4)	S8–Mo1	2.5336(10)
B3–C8	1.732(4)	Mo1–C10	1.987(4)
B4–B5	1.767(5)	C10–O10	1.131(4)
B4–C8	1.725(4)	Mo1–C11	1.937(4)
B4–B9	1.809(5)	C11–O11	1.159(4)
B5–B6	1.820(6)	Mo1–C12	2.338(3)
B5–B9	1.764(5)	Mo1–C13	2.225(3)
B5–B10	1.776(6)	Mo1–C14	2.311(3)
B6–B10	1.774(5)	C12–C13	1.388(5)
B6–B11	1.778(5)	C13–C14	1.409(5)
C7–C8	1.581(4)	Mo1–H3	2.14(4)
Interatomic angles			
C7–S7–Mo1	95.17(10)	Mo1–C11–O11	177.1(3)
C7–S7–C71	99.08(16)	C10–Mo1–C11	79.80(16)
C71–S7–Mo1	102.51(12)	C12–C13–C14	116.3(3)
C8–S8–Mo1	94.55(10)	S7–Mo1–H3	77.9(10)
C8–S8–C81	98.55(15)	S8–Mo1–H3	80.1(10)
C81–S8–Mo1	104.14(13)	C11–Mo1–H3	170.9(10)
S7–Mo1–S8	73.57(4)	C10–Mo1–S8	165.40(10)
Mo1–C10–O10	174.8(3)		

¹ The idea of $3c\text{-}2e$ was introduced by Longuet–Higgins in *J. Chem. Phys.*, 1949, **46**, 275 to explain the bridged structure of diborane and in particular its hypercoordinated bridging hydrogen atom, then it was used extensively by Lipscomb in *Adv. Inorg. Chem. Radiochem.*, 1950, **1**, 117 to rationalize the structures of the series of higher boranes.

side, of this plane. Thus relatively little ligand motion is required to achieve the time-averaged C_s symmetry in solution which is evident from the NMR spectra.

Compound **1** is closely similar to $\text{RuCl}(\text{PPh}_3)_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10})$, [7]d one of several chloro- or hydrido- *exo-nido* ruthenium complexes of dithioether carboranes recently studied [7]f. The presence of B3–H3–M 3c–2e bonding is found to result, relative to equivalent values in the un-coordinated ligand, [8] in (i) a marked shift to low frequency of the ^{11}B -NMR resonance assigned to B3, (ii) a decrease in the $J_{\text{B3-H3}}$ coupling constant and (iii) the presence of a low frequency resonance in the ^1H -NMR spectrum assigned to H3. Fig. 2 compares the ^{11}B spectra of **1** (A) and $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^-$ (B) as stick diagrams, and confirms that $\delta(\text{B3})$ moves upfield by 11.5 ppm (from $\delta -10.4$ to -21.9) on complexation. At the same time $J_{\text{B3-H3}}$ is diminished from 175 to 127 Hz. Together with the low frequency chemical shift of H3 already noted these data are consistent with strong 3c–2e B3–H3–Mo bonding.

The Mo1–H3 distance is 2.14(3) Å, the Mo1...B3 distance is 2.834(3) Å, and the B3–H3–Mo1 angle is 121(3)°. As a consequence of the B3–H3–Mo bonding H3 is somewhat pulled out of a normal position radial to the carborane cage, lying only 0.30 Å below the least-squares plane through B2B3B4B5B6 (cf. H2–H6, 0.38–0.51 Å below this plane). Although clearly involved in a significant 3c–2e bond, the *trans* influence of the B–H unit on the metal is markedly less than that of a SR

ligand, since Mo1–C11 (*trans* to B3–H3) is 0.05 Å shorter than Mo1–C10 (*trans* to S8).

Attempts to deprotonate $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^-$ with NaH in THF [9] prior to metallation were unsuccessful, as established by ^{11}B -NMR spectroscopy. Equally, the anion was not deprotonated by ten equivalents of K^tBuO in refluxing DME. Presumably the presence of the dithioether substituent renders $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^-$ less acidic than alkyl or aryl analogues $[7\text{-R-8-R'-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^-$ [10]. However, the use of LiN^iPr_2 did remove the *endo*-proton from the open face of the carborane to afford the $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_9]^{2-}$ dianion, characterised as its Li salt by ^{11}B -NMR spectroscopy (Fig. 2C). In this ion are five resonances, 1:2:2:3:1 from high to low frequency, with the lowest frequency resonance, $\delta -46.1$, well separated from the rest. Further studies with *n*BuLi have also shown the capacity of this base to deprotonate the $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^-$. We do not have enough data to explain this deprotonation process, however, the influence of the Li cation can not be discarded.

The addition of $\text{MoBr}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_2$ to the solution of $\text{Li}_2[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_9]$ so produced affords a single product **2** tentatively formulated as $\text{Li}[1,2\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-3-(}\eta\text{-C}_3\text{H}_5\text{)-3,3-(CO)}_2\text{-3,1,2-closo-MoC}_2\text{B}_9\text{H}_9]$ (Scheme 2) on the basis of ^1H - and ^{11}B -NMR studies. The ^1H spectrum confirms retention of the $\text{SCH}_2\text{CH}_2\text{S}$ bridge and the presence of the $\eta\text{-C}_3\text{H}_5$ ligand. The ^{11}B spectrum (Fig. 2D) reveals five resonances between $\delta -2$ and -15 . The weighted

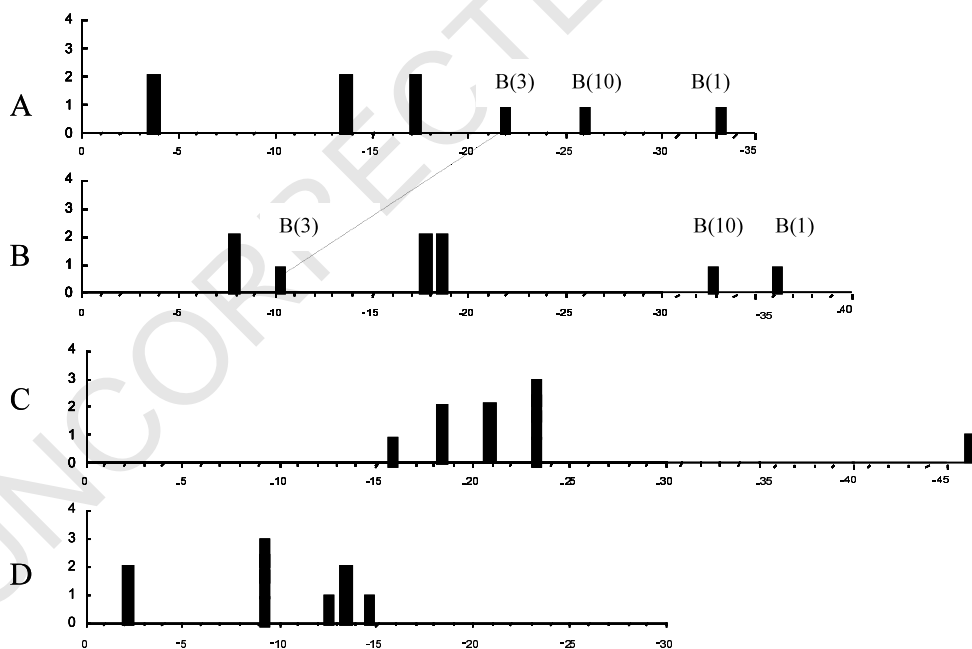
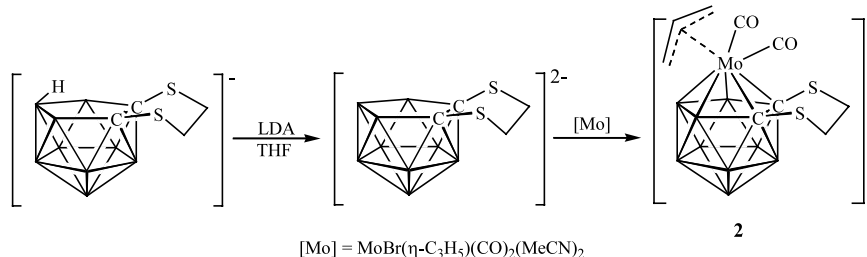


Fig. 2. Raw ^{11}B -NMR spectra with the peak assignments for the compounds: A, $\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10})$, **1**; B, $\text{NMe}_4[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]$; C, $\text{Li}_2[7,8\text{-}\mu\text{-(SCH}_2\text{CH}_2\text{S)-7,8-nido-C}_2\text{B}_9\text{H}_9]$; D, $\text{Li}[1,2\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-3-(}\eta\text{-C}_3\text{H}_5\text{)-3,3-(CO)}_2\text{-3,1,2-closo-MoC}_2\text{B}_9\text{H}_9]$, **2**.

Scheme 2. Synthesis of *closo* molybdacarborane complex **2**.

159 average ¹¹B chemical shift, ⟨δ¹¹B⟩, is −9.4 ppm, clearly
 160 signifying that metallacarborane **2** has a *closo* structure
 161 [2b–2d]. Moreover, the presence of only five resonances,
 162 with relative integrals 2:3:1:2:1 (high to low frequency),
 163 is indicative of a symmetric species. Thus we assume that
 164 **2** has a 3,1,2-MoC₂B₉ architecture, similar to 3-(η-
 165 C₃H₅)-3,3-(CO)₂-4-SMe₂-3,1,2-*closo*-MoC₂B₉H₁₀ and
 166 [1-Ph-3-(η-C₃H₅)-3,3-(CO)₂-3,1,2-*closo*-MoC₂B₉H₁₁][−]
 167 [3b].

168 3. Experimental

169 3.1. Synthesis-general

170 Experiments were performed under dry, oxygen-free
 171 N₂ using standard Schlenk techniques, with some
 172 subsequent manipulation in the open laboratory. Sol-
 173 vents were freshly distilled over CaH₂ (CH₂Cl₂) or Na
 174 wire (THF, 60–80 petroleum ether) and were degassed
 175 (3 × freeze–pump–thaw cycles) before use, or were
 176 stored over 4 Å molecular sieves (CDCl₃). IR spectra
 177 were recorded from CH₂Cl₂ solutions on a Nicolet
 178 Impact 400 spectrophotometer. NMR spectra at 400.1
 179 MHz (¹H) or 128.4 MHz (¹¹B) were recorded on a
 180 DPX400 spectrometer from CDCl₃ or (CD₃)₂CO solu-
 181 tions. Elemental analyses were determined by the
 182 departmental service (H-WU). The starting materials
 183 [NMe₄][7,8-μ-SCH₂CH₂S-7,8-*nido*-C₂B₉H₁₀] [8] and
 184 MoBr(η-C₃H₅)(CO)₂(MeCN)₂ [12] were prepared by
 185 literature methods or slight variants thereof. All other
 186 reagents and solvents were supplied commercially and
 187 were used as received.

188 3.2. Mo(η-C₃H₅)(CO)₂(7,8-μ-SCH₂CH₂S-7,8-*nido*- 189 C₂B₉H₁₀) (**1**)

190 To a stirring solution of MoBr(η-
 191 C₃H₅)(CO)₂(MeCN)₂ (0.12 g, 0.34 mmol) in 10 ml
 192 THF at 0 °C was added, dropwise, [NMe₄][7,8-μ-
 193 SCH₂CH₂S-7,8-*nido*-C₂B₉H₁₀] (0.10 g, 0.34 mmol) in
 194 the same solvent (30 ml). After further stirring for 4 h at
 195 room temperature (r.t.), solvent was removed in vacuo.
 196 The product was purified by flash chromatography on
 197 silica using CH₂Cl₂ as eluent, affording Mo(η-

C₃H₅)(CO)₂(7,8-μ-SCH₂CH₂S-7,8-*nido*-C₂B₉H₁₀) (**1**) as
 a yellow solid. Yield 0.12 g, 83%. Found: C, 25.82; H
 4.53; C₉H₁₉B₉MoO₂S₂ requires C 25.95, H 4.59%. IR:
 ν_{max} 2529 (BH), 1929, 1855 (CO) cm^{−1}. NMR (CDCl₃,
 291 K): ¹H, δ 4.5 (m, 1H, CH₂CHCH₂), 4.0 (d, ³J_{HH} 7.0
 Hz, 2H, CH₂CHCH₂[*syn*]), 3.5 (m, 2H, SCH₂), 3.3 (m,
 2H, SCH₂), 1.8 (d, ³J_{HH} 10.9 Hz, 2H,
 CH₂CHCH₂[*anti*]), 0.55 (br, 1H, BH10_{exo}), −2.7 (br,
 1H, BH10_{endo}) and −5.55 (s, 1H, H3). ¹H{¹¹B}, δ 4.5
 (m, 1H, CH₂CHCH₂), 4.0 (d, ³J_{HH} 7.0 Hz, 2H,
 CH₂CHCH₂[*syn*]), 3.5 (m, 2H, SCH₂), 3.3 (m, 2H,
 SCH₂), 2.38 (br s, 2H, BH_{exo}), 1.8 (d, ³J_{HH} 10.9 Hz,
 2H, CH₂CHCH₂[*anti*]), 1.48 (br s, 2H, BH_{exo}), 1.43 (br
 s, 2H, BH_{exo}), 0.55 (br s, 1H, BH10_{exo}), −2.7 (br s, 1H,
 BH10_{endo}) and −5.55 (s, 1H, H3). ¹¹B, δ −3.4 (d, ¹J_{BH}
 145.3 Hz, 2B), −13.6 (d, ¹J_{BH} 142.4 Hz, 2B), −17.3 (d,
¹J_{BH} 153.3 Hz, 2B), −21.9 (d, ¹J_{BH} 126.7 Hz, 1B, B3),
 −26.2 (d of d, ¹J_{BH} 119.5 Hz[*exo*], ¹J_{BH} 51 Hz[*endo*],
 1B, B10) and −33.64 (d, ¹J_{BH} 141.8 Hz, 1B, B1).

217 3.3. Li[1,2-μ-SCH₂CH₂S-3-(η-C₃H₅)-3,3-(CO)₂-3,1,2- 218 *closo*-MoC₂B₉H₉] (**2**)

219 To a stirring solution of [NMe₄][7,8-μ-SCH₂CH₂S-
 220 7,8-*nido*-C₂B₉H₁₀] (0.10 g, 0.34 mmol) in 10 ml THF at
 221 0 °C was added, dropwise, 0.34 ml of a 2M solution
 222 (0.68 mmol) of lithium di-isopropylamide in THF–
 223 heptane–ethylbenzol. ¹¹B{¹H}-NMR [(CD₃)₂CO, r.t.]
 224 of this Li₂[7,8-μ-SCH₂CH₂S-7,8-*nido*-C₂B₉H₉] inter-
 225 mediate, δ −15.4 (1B), −18.3 (2B), −21.1 (2B), −
 226 22.5 (3B) and −46.1 (1B). After 1 h MoBr(η-
 227 C₃H₅)(CO)₂(MeCN)₂ (0.14 g, 0.41 mmol) was added,
 228 and the reaction mixture stirred for a further 30 min.
 229 Solvent was removed in vacuo and the product was
 230 purified by recrystallisation from ethyl acetate:petro-
 231 leum ether (1:4) under nitrogen to afford Li[1,2-μ-
 232 SCH₂CH₂S-3-(η-C₃H₅)-3,3-(CO)₂-3,1,2-*closo*-
 233 MoC₂B₉H₉] (**2**) as a yellow solid. Yield 0.13 g, 79%.
 234 NMR (291 K): ¹H, CDCl₃, δ 5.8 (m, 1H, CH₂CHCH₂),
 235 5.2 (d, ³J_{HH} 8 Hz, 2H, CH₂CHCH₂[*syn*]), 5.0 (d, ³J_{HH}
 236 10 Hz, 2H, CH₂CHCH₂[*anti*]), 3.7–3.5 (m, 4H, SCH₂).
¹¹B{¹H}, (CD₃)₂CO, δ −2.1 (2B), −8.9 (3B), −12.3
 (1B), −13.3 (2B) and −14.5 (1B). 238

239 3.4. Crystallography

240 Crystals of **1** suitable for a crystallographic study were
 241 grown from diffusion of petroleum ether and a CDCl₃
 242 solution at –30 °C. Diffraction data were collected
 243 using a Bruker P4 diffractometer equipped with Mo–
 244 K_α X-radiation ($\lambda = 0.71073 \text{ \AA}$) by ω scans at 160(2) K.

245 3.4.1. Crystal data

246 Crystal size $0.6 \times 0.48 \times 0.12 \text{ mm}$, C₉H₁₉B₉MoO₂S₂,
 247 $M = 416.59$, monoclinic, $P2_1/n$, $\alpha = 6.966(3)$, $\beta =$
 248 $18.266(6)$, $\gamma = 13.729(6) \text{ \AA}$, $\beta = 96.90(3)^\circ$, $V =$
 249 $1734.3(11) \text{ \AA}^3$, $Z = 4$, $D_c = 1.596 \text{ Mg m}^{-3}$, $\mu = 0.993$
 250 mm^{-1} , $F(000) = 832$. θ Range for data collection 2.23 –
 251 25.02° , index range $-1 \leq h \leq 8$, $-21 \leq k \leq 1$, $-16 \leq$
 252 $l \leq 16$. About 4063 data collected, 3016 independent
 253 reflections ($R_{\text{int}} = 0.0308$), $R_1 = 0.0385$, $wR_2 = 0.1071$
 254 for all data, $S = 1.049$, largest peak 0.640 and deepest
 255 hole $-0.804 \text{ e \AA}^{-3}$.

256 Data were corrected for absorption by *psi* scans and
 257 the structure solved by direct and difference Fourier
 258 methods. Refinement [13] by was by full-matrix least-
 259 squares on F^2 for 238 parameters. All non-H atoms were
 260 refined with anisotropic displacement parameters. Ex-
 261 cept for H3, refined freely resulting in B3–H3 = 1.07(4)
 262 \AA , boron-bound H atoms were restrained to B–H =
 263 1.10(2) \AA , whilst carbon-bound H atoms were treated
 264 as riding on their respective C atom, C–H = 1.00 \AA
 265 (CH) and 0.99 \AA (CH₂). In all cases the (isotropic)
 266 displacement parameter of H atoms was set at $1.2 \times$
 267 that of the bound atom U_{eq} .

268 4. Supplementary material

269 Crystallographic data have been deposited with the
 270 Cambridge Crystallographic Data Centre as CCDC
 271 187076. Data can be obtained free of charge via
 272 www.ccdc.cam.ac.uk/conts/retrieving.html (or from the
 273 Cambridge Crystallographic Data Centre, 12 Union
 274 Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-
 275 336033; or deposit@ccdc.cam.ac.uk).

276 5. Uncited reference

277 [11].

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References

- 284
- [1] M. Davidson, in: M. Davidson, A.K. Hughes, T.B. Marder, K. Wade (Eds.), Contemporary Boron Chemistry, Royal Society of Chemistry, 2000, pp. 255–367. 285
286
- [2] E.g. in pseudocloso compounds; (a) Z.G. Lewis, A.J. Welch, J. Organometal Chem. 430 (1992) C45; 288
289
(b) P.T. Brain, M. Bühl, J. Cowie, Z.G. Lewis and A.J. Welch, J. Chem. Soc., Dalton Trans. (1996) 231; 290
291
(c) U. Grädler, A.S. Weller, A.J. Welch, D. Reed, J. Chem. Soc., Dalton Trans. (1996) 335; 292
293
(d) A.J. Welch, A.S. Weller, Inorg. Chem. 35 (1996) 4548; 294
(e) J.H. Kim, M. Lamrani, J.W. Hwang, Y. Do, Chem. Commun. (1997), 1761; 295
296
(f) F. Teixidor, M.A. Flores, C. Viñas, R. Sillanpää, R. Kivekäs, J. Am. Chem. Soc. 122 (2000) 1963. 297
298
- [3] E.g. (a) D.R. Baghurst, R.C.B. Copley, H. Fleischer, D.M.P. Mingos, G.O. Kyd, L.J. Yellowlees, A.J. Welch, T.R. Spalding, D. O'Connell, J. Organometal. Chem. 447 (1993) C14; 299
300
(b) S. Dunn, G.M. Rosair, R.L. Thomas, A.S. Weller, A.J. Welch, Angew. Chem. Int. Ed. Engl. 36 (1997) 645; 302
303
(c) A.J. Welch, A.S. Weller, J. Chem. Soc. Dalton Trans. (1997) 1205; 304
305
(d) S. Dunn, G.M. Rosair, A.S. Weller, A.J. Welch, Chem. Commun. (1998) 1065; 306
307
(e) R.M. Garrioch, P. Kuballa, K.S. Low, G.M. Rosair, A.J. Welch, J. Organometal. Chem. 585 (1999) 57; 308
309
(f) S. Dunn, R.M. Garrioch, G.M. Rosair, L. Smith, A.J. Welch, Collect. Czech. Chem. Commun. 64 (1999) 1013. 310
311
- [4] E.g. (a) T.E. Paxon, M.F. Hawthorne, J. Am. Chem. Soc. 96 (1974) 4674; 312
313
(b) J.A. Belmont, J. Soto, R.E. King, A.J. Donaldson, J.D. Hewes, and M.F. Hawthorne, J. Am. Chem. Soc. 111 (1989) 7475 and references therein; 314
315
(c) E. Hong, Y. Kim, Y. Do, Organometallics 17 (1998) 2933; 317
(d) F. Simal, S. Sebile, A. Demonceau, A.F. Noels, R. Nuñez, M. Abad, F. Teixidor, C. Viñas, Tet. Lett. 41 (2000) 5347. 318
319
- [5] E.g. (a) J. Plešek, Chem. Rev. 92 (1992) 269; 320
321
(b) J. Rais, P. Seluky, Nucleon 1 (1992) 17; 322
(c) C. Viñas, S. Gomez, J. Bertran, F. Teixidor, J.F. Dozol, H. Rouquette, Inorg. Chem. 37 (1998) 3640; 323
324
(d) C. Viñas, J. Bertran, S. Gomez, F. Teixidor, J.F. Dozol, H. Rouquette, R. Kivekäs and R. Sillanpää, J. Chem. Soc., Dalton Trans. (1998) 2849; 325
326
(e) C. Viñas, S. Gomez, J. Bertran, F. Teixidor, J.F. Dozol, H. Rouquette, Chem. Commun. (1998) 191; 327
328
(f) C. Viñas, S. Gomez, J. Bertran, J. Barron, F. Teixidor, J.F. Dozol, H. Rouquette, R. Kivekäs, R. Sillanpää, J. Organomet. Chem. 581 (1999) 188. 329
330
- [6] With respect to B–H–M bonding the carborane can act as either an η^1 -, η^2 - or η^3 ligand. Recent examples include (a) N.J. Patmore, M.F. Mahon, J.W. Steed, A.S. Weller, J. Chem. Soc., Dalton Trans. (2001) 277; 332
333
(b) D.D. Ellis, A. Franken, P.A. Jellis, J.A. Kautz, F.G.A. Stone, P.Y. Yu, J. Chem. Soc., Dalton Trans. (2000) 2509; 334
335
(c) C. Hague, N.J. Patmore, C.G. Frost, M.F. Mahon, A.S. Weller, Chem. Commun. (2001) 2238, respectively. 336
337
338
339
- [7] E.g. (a) F. Teixidor, J. Casabó, A.M. Romerosa, C. Viñas, J. Ruis, C. Miravittles, J. Am. Chem. Soc. 113 (1991) 9895; 340
341
(b) F. Teixidor, A. Romerosa, C. Viñas, J. Ruis, C. Miravittles, J. Casabó, J. Chem. Soc., Chem. Commun. (1992) 192; 342
343
(c) F. Teixidor, J.A. Ayllón, C. Viñas, J. Rius, C. Miravittles, J. Casabó, J. Chem. Soc., Chem. Commun. (1992) 1279; 344
345
(d) F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, R. Sillanpää, J. Casabó, J. Chem. Soc., Chem. Commun. (1992) 1281; 346
347
(e) F. Teixidor, C. Viñas, J. Casabó, A.M. Romerosa, J. Ruis, C. 348

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6

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- 349 Miravittles, *Organometallics* 13 (1994) 914;
- 350 (f) F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, R. Sillanpää, J.
- 351 Casabó, *Organometallics* 13 (1994) 2751;
- 352 (g) F. Teixidor, M.A. Flores, C. Viñas, R. Kivekäs, R. Sillanpää,
- 353 *Angew. Chem. Int. Ed. Engl.* 35 (1996) 2251;
- 354 (h) C. Viñas, M.A. Flores, R. Nuñez, F. Teixidor, R. Kivekäs, R.
- 355 Sillanpää, *Organometallics* 17 (1998) 2278;
- 356 (i) F. Teixidor, M.A. Flores, C. Viñas, R. Kivekäs, R. Sillanpää,
- 357 *Organometallics* 17 (1998) 4675. Reference [1f].
- 358 [8] F. Teixidor, R.W. Rudolph, *J. Organomet. Chem.* 241 (1983)
- 359 301.
- [9] M.F. Hawthorne, T.D. Andrews, P.M. Garret, F.P. Olsen, M. 360
Reintjes, F.N. Tebbe, L.F. Warren, P.A. Wegner, *Inorg. Synth.* 361
10 (1967) 91. 362
- [10] F. Teixidor, R. Nuñez, M.A. Flores, A. Demonceau, C. Viñas, J. 363
Organomet. Chem. 614–615 (2000) 48. 364
- [11] K. Johansen, G.M. Rosair, A.S. Weller, A.J. Welch, *Acta* 365
Crystallogr., Sect. C 54 (1998) 214. 366
- [12] (a) R.G. Hayter, *J. Organomet. Chem.* 13 (1968) 1; 367
(b) H. Tom-Dieck, H. Friedel, *J. Organomet. Chem.* 14 (1968) 368
375. 369
- [13] G.M. Sheldrick, *SHELXTL* Version 5.1, Bruker AXS, Madison, 370
WI, USA, 1999. 371

UNCORRECTED PROOF

Self-assembly of carborane molecules *via* C–H⋯I hydrogen bonding: the molecular and crystal structures of 3-I-1,2-*closo*-C₂B₁₀H₁₁

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The crystal structure of 3-I-1,2-*closo*-C₂B₁₀H₁₁ reveals that molecules are arranged as infinite head-to-tail zig-zag double chains held together by C–H⋯I hydrogen bonding.

The last two decades have witnessed the emergence of supramolecular chemistry¹ as an area of considerable interest, covering all aspects of the discipline from biochemistry to organic, organometallic, and physical chemistry and encompassing the thriving area of materials. The non-covalent interactions crucial in supramolecular chemistry are most effectively utilised when they are periodic, realising the field of molecular crystal engineering,² dependent on appropriate building-block molecules and suitable linking groups.

It has already been pointed out that boron-based clusters can play an important rôle in this field³ by virtue of their three-dimensional structures and well-developed derivative chemistries. In particular the three isomeric icosahedral carboranes, 1,2-, 1,7- and 1,12-*closo*-C₂B₁₀H₁₂ appear to have great potential as building blocks in supramolecular systems which is only now beginning to be explored.⁴ Moreover the CH protons of 1,2-carboranes are highly acidic⁵ (carrying a charge of +0.30 *cf.* 0.07–0.09 for the hydrogen atoms on boron⁶) and consequently have the potential for hydrogen bonding.⁷

Previously, self-assembly of carboranes *via* C–H⋯X hydrogen bonding has been limited to C–H⋯O interactions, both classical⁸ and bifurcated, C–H⋯(O)₂,⁹ C–H⋯π interactions¹⁰ and, recently, C–H⋯F interactions.¹¹ Self-assembly of carboranes by weaker C–H⋯I interactions is currently unreported, although intermolecular C–H⋯I–B interactions do exist in a few neutral iodo(hetero)boranes¹² where the source of the C–H unit is a co-crystallising molecule or ion. Crystal structures of four iodo dicarbadodecaboranes, C₂B₁₀H₁₁I, have previously been reported, namely 4-I-1,7-*closo*-C₂B₁₀H₁₂,¹³ 8-I-1,2-*closo*-C₂B₁₀H₁₂,¹⁴ 2-I-1,12-*closo*-C₂B₁₀H₁₂¹⁵ and 9-I-1,7-*closo*-C₂B₁₀H₁₂,¹⁶ but in none of these are there intermolecular C–H⋯I interactions.¹⁷ Here we report the first example of supramolecular self-assembly directed by carborane C–H⋯I interactions.

The carborane 3-I-1,2-*closo*-C₂B₁₀H₁₁ was synthesised according to the literature,¹⁸ through {BI} recapitulation of [7,8-*nido*-C₂B₉H₁₁]²⁻. The ¹H NMR spectrum of the product reveals a singlet at 3.84 ppm, assigned to the two C-bonded H atoms, *ca.* 0.3 ppm to high frequency relative to that in 1,2-*closo*-C₂B₁₀H₁₂, suggesting greater protonic character for these H atoms in the iodo species. Moreover, the solid-state IR spectrum of 3-I-1,2-*closo*-C₂B₁₀H₁₁ exhibits a C–H stretching frequency at 3052 cm⁻¹ measurably lower than that, 3070 cm⁻¹, in the unsubstituted parent. This lower energy stretching mode for C–H is fully consistent with the existence of H-bonding in the solid state, presumably of the C–H⋯I type. To establish the situation unequivocally, a single-crystal X-ray diffraction analysis[†] of 3-I-1,2-*closo*-C₂B₁₀H₁₁ was undertaken, colourless crystals having been grown by the slow evaporation of a hexane

solution of the compound.

A perspective view of a single molecule is shown in Fig. 1.

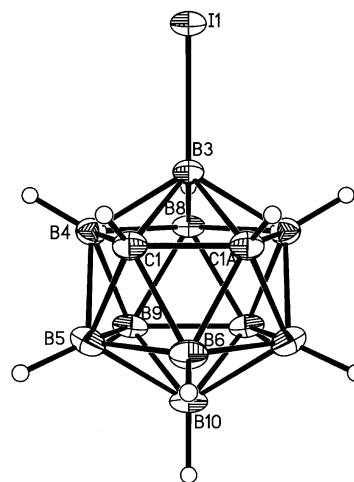


Fig. 1 Perspective view of a single molecule of 3-I-1,2-*closo*-C₂B₁₀H₁₁. The plane defined by I1B3B8B6B10 is a crystallographic mirror plane. Atoms reflected across this plane carry the letter A. Atoms are drawn as 50% thermal ellipsoids, except for H atoms. Interatomic distances (Å) and selected angles (°): C1–C1A 1.624(8), C1–B3 1.711(6), C1–B4 1.708(5), C1–B5 1.701(6), C1–B6 1.733(7), B3–I1 2.168(6), B3–B4 1.764(6), B3–B8 1.756(9), B4–B5 1.792(6), B4–B8 1.784(6), B4–B9 1.787(6), B5–B9 1.773(6), B5–B10 1.795(6), B9–B9A 1.789(9), B9–B10 1.791(7), I1–B3–C1 118.9(3), I1–B3–B4 123.1(2), I1–B3–B8 129.1(4).

The molecule has C_s symmetry which is crystallographically imposed. The cage has the expected near-icosahedral geometry with the lengths of the differing types of connectivity increasing in the expected sequence C–C < C–B < B–B, the magnitudes of these connectivities standing good comparison with those determined for 1,2-*closo*-C₂B₁₀H₁₂.⁸ Close inspection of the connectivities involving the substituted B atom, B3, and the otherwise equivalent atom, B6, reveals that iodide substitution has the effect of shrinking the cage connectivities somewhat, since B3–C1, B3–B4 and B3–B8 are all shorter than B6–C1, B6–B5 and B6–B10, respectively, by statistically significant amounts. The B3–I distance is 2.168(6) Å, in excellent agreement with other such distances in the literature.^{15,16,19}

The crystal structure of 3-I-1,2-*closo*-C₂B₁₀H₁₁ reveals two orientations of molecules (head-to-tail) arranged in infinite double zig-zag chains running parallel to the *b* crystallographic axis (Fig. 2). Both carborane C–H vertices participate in C–H⋯I interactions. The chains are held together by I⋯H1 hydrogen bonds, 3.215 Å, involving the protonic C-bound H atom, C(1)–H(1)⋯I 133.5°, and a bifurcated linkage at I, H⋯I–B3 114.6°; H⋯I⋯H 126.6°. Thus the environment at I in the crystal is quasi-planar—the sum of angles at I is 355.8°, and I is displaced only 0.33 Å out of the plane defined

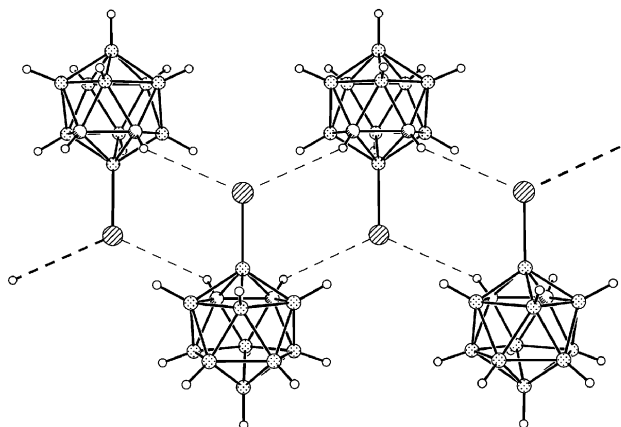


Fig. 2 Crystal structure of 3-I-1,2-closo-C₂B₁₀H₁₁ showing the C–H···I hydrogen bonding which results in a head-to-tail arrangement of molecules forming an infinite double zig-zag chain running parallel to the crystallographic *b* axis. I···H is 3.215 Å, C–H···I is 133.5°, and there is a bifurcated linkage at I, H···I–B 114.6° and H···I···H 126.6°.

by B3 and the two adjacent H1 atoms.

Individually these intermolecular C–H···I interactions are clearly weak, since the sum of the van der Waals radii of H and I is only 3.35 Å and CH···I distances between neutral molecules as small as 2.81 Å are known in the literature.²⁰ However, the adjacency of the acidic CH groups to the I-substituted boron atom obviously affords a molecule that can maximise its intermolecular C–H···I bonding in a very efficient fashion by adopting the double chain shown in Fig. 2. Certainly this is the first reported example of carborane self-assembly *via* C–H···I interactions.

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Notes and references

† Colourless single crystals of 3-I-1,2-closo-C₂B₁₀H₁₁ were grown from hexane. Crystal data for C₂H₁₁B₁₀I, 160(2) K, *M_r* = 270.11: crystal size 0.36 × 0.68 × 0.42 mm, orthorhombic, *Pnma*, *a* = 20.011(3), *b* = 8.0039(10), *c* = 6.4946(14) Å, *V* = 1040.2(3) Å³, *Z* = 4 (*C_s* symmetry imposed), *D_c* = 1.725 Mg m⁻³, *F*(000) = 504, *μ* = 3.009 mm⁻¹. Of 990 unique reflections from 1417 measured (*R_{int}* = 0.0480), 873 were

observed [*F_o* > 4σ(*F_o*)]. Refinement of 85 parameters converged at *R₁* = 0.0373, *wR₂* = 0.0801 (for all data), *R₁* = 0.0320, *wR₂* = 0.0773 (for observed data). *S* = 1.045, max. and min. residual electron density: 0.564 and –1.828 e Å⁻³ (near I1). Intensity data were collected on a Bruker P4 diffractometer, with Mo-Kα radiation (*λ* = 0.71073 Å) to 2θ_{max} = 50°, ω-scans, corrections for absorption (*φ*-scans), Lorentz and polarisation effects, and structures were solved by direct methods and refined (against *F²*) by full-matrix least-squares refinement.²¹ Cage C atoms were unambiguously identified by inspection of *U* values following isotropic refinement of all cage vertices as boron, and confirmed by C–C distances. H atoms treated as riding model. CCDC reference number 154905. See <http://www.rsc.org/suppdata/dt/b2/b206892n/> for crystallographic data in CIF or other electronic format.

- 1 J.-M. Lehn, *Supramolecular Chemistry: Concepts, Perspectives*, VCH, Weinheim, 1995.
- 2 D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, **33**, 601.
- 3 (a) R. N. Grimes, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1289 and references therein; (b) A. J. Welch, U. Venkatasubramanian, G. M. Rosair, D. Ellis and D. J. Donohoe, *Acta Crystallogr., Sect. C*, 2001, **57**, 1295.
- 4 P. C. Andrews, M. J. Hardie and C. L. Raston, *Coord. Chem. Rev.*, 1999, **189**, 169.
- 5 R. N. Grimes, *Carboranes*, Academic, New York, 1970.
- 6 R. J. Blanch, M. Williams, G. D. Fallon, M. G. Gardiner, R. Kadour and C. L. Raston, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 504.
- 7 (a) L. A. Leites, *Chem. Rev.*, 1992, **92**, 279; (b) G. Harakas, T. Vu, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1998, **120**, 6405 and references therein.
- 8 M. G. Davidson, T. G. Hibbert, J. A. K. Howard, A. Mackinnon and K. Wade, *Chem. Commun.*, 1996, 2285.
- 9 M. J. Hardie, P. D. Godfrey and C. L. Raston, *Chem. Eur. J.*, 1999, **5**, 1828.
- 10 M. J. Hardie and C. L. Raston, *Eur. J. Inorg. Chem.*, 1999, 195.
- 11 H. Lee, C. B. Knobler and M. F. Hawthorne, *Chem. Commun.*, 2000, **24**, 2485.
- 12 (a) J. R. Werner, O. Hollander, J. C. Huffman, J. A. K. Bauer, D. Dou, L.-H. Hsu, D. L. Leussing and S. G. Shore, *Inorg. Chem.*, 1995, **34**, 3065; (b) H. Yao, P. Lomme, C. Hu and P. Paetzold, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2477.
- 13 V. G. Andrianov, V. I. Stanko and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1967, **8**, 558.
- 14 V. G. Andrianov, V. I. Stanko, Yu. T. Struchkov and A. I. Klimova, *Zh. Strukt. Khim.*, 1967, **8**, 707.
- 15 W. Jiang, C. B. Knobler, C. E. Curtis, M. D. Mortimer and M. F. Hawthorne, *Inorg. Chem.*, 1995, **34**, 3491.
- 16 W. J. Marshall, R. J. Young, Jr. and V. V. Grushin, *Organometallics*, 2001, **20**, 523.
- 17 Established by interrogation of the Cambridge Structural Database.
- 18 J. Li, C. F. Logan, Jr. and M. Jones, *Inorg. Chem.*, 1991, **30**, 4866.
- 19 T. D. McGrath, M. A. Fox and A. J. Welch, *Acta Crystallogr., Sect. C*, 2000, **56**, 487.
- 20 E. L. Rimmer, R. D. Bailey, T. W. Hanks and W. T. Penninton, *Chem. Eur. J.*, 2000, **6**, 4071.
- 21 G. M. Sheldrick, SHELXTL Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1999.