



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 663 (2002) 221–226

Journal
of Organo
metallic
Chemistrywww.elsevier.com/locate/jorgchem

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

Gemma Barberà^a, Clara Viñas^{a,*}, Francesc Teixidor^a, Georgina M. Rosair^b,
Alan J. Welch^b

^a Institut de Ciència de Materials, ICMAB-CSIC, Campus UAB, 08193 Bellaterra, Spain

^b Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK

Received 6 June 2002; accepted 18 July 2002

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

Abstract

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* 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 spectroscopy and by a crystallographic study. The complex is fluxional (having mirror symmetry on the NMR timescale) in solution at room temperature although asymmetric in the solid state. Data are presented which suggest a significant 3c–2e B3–H3–Mo bond. 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 $\text{MoBr}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_2$ 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 Elsevier Science B.V. All rights reserved.

Keywords: Deprotonation; Molybdacarborane; *nido*-carboranylthioethers; B–H–M agostic bond

1. Introduction

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

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

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

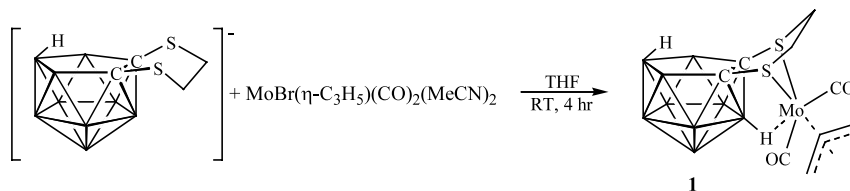
As part of our interest in *nido*-C₂B₉ carboranes containing sulfur substituents [7] we are developing the transition metal chemistry of $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^-$. In this paper we report the reaction of this anion with the $\{\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\}^+$ fragment both with and without prior deprotonation of the *nido* carborane. In the former case this leads to an anionic *closo* species and in the latter case to an overall neutral, zwitterionic, *exo-nido* species with both Mo–S bonds and a strong B–H–Mo bond.

2. Results and discussion

The reaction between $[\text{NMe}_4][7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10}]$ and $\text{MoBr}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_2$ in

* Corresponding author. Fax: +34-9-3-5805729

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**.

THF affords (Scheme 1) the *exo-nido* molybdacarborane 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**, in high yield after work-up involving column chromatography.

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

A crystallographic study of **1** was undertaken. Fig. 1 presents a view of the compound and selected molecular parameters are listed in Table 1. The overall structure of the molecule is that of a zwitterionic *exo-nido* metalla-carborane, with a formally cationic $\{\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\}^+$ unit bound to the side of a formally anionic $\{\text{nido-C}_2\text{B}_9\text{H}_{10}\}^-$ unit via two S–Mo coordinate bonds and one $3c\text{-}2e$ B3–H3–Mo bond. In the solid state the $\{\text{Mo}(\text{C}11\text{O}11)\text{C}_2\text{B}_9\text{H}_{10}(\text{SCH}_2\text{CH}_2\text{S})\}$ unit has effective mirror symmetry, with the C_3H_5 ligand lying to one side, and the $\text{C}10\text{O}10$ ligand to the other

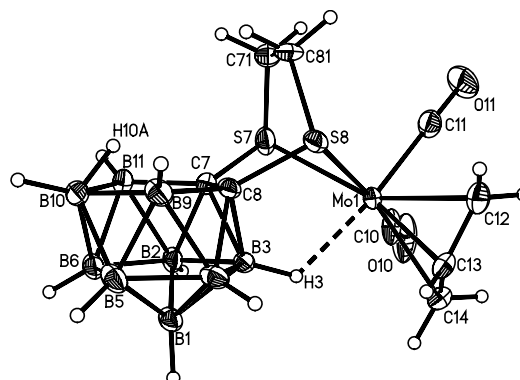


Fig. 1. Perspective view of $\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-nido-C}_2\text{B}_9\text{H}_{10})$, compound **1**, showing the atomic numbering scheme. Atoms are drawn as 50% thermal ellipsoids, except for H atoms.

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 $\text{RuCl}(\text{PPh}_3)_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_{10})$, [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 $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_{10}]^-$ (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 $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_{10}]^-$ 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 $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_{10}]^-$ less acidic than alkyl or aryl analogues $[7\text{-R-8-R}'\text{-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_{10}]^-$ [10]. However, the use of LiN^iPr_2 did remove the *endo*-proton from the open face of the carborane to afford the $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_9]^{2-}$ 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 $[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_{10}]^-$. 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 $\text{Li}_2[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_9]$ so produced affords a single product **2** tentatively formulated as $\text{Li}[1,2\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-3-}(\eta\text{-C}_3\text{H}_5)\text{-3,3-(CO)}_2\text{-3,1,2-}closo\text{-MoC}_2\text{B}_9\text{H}_9]$ (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

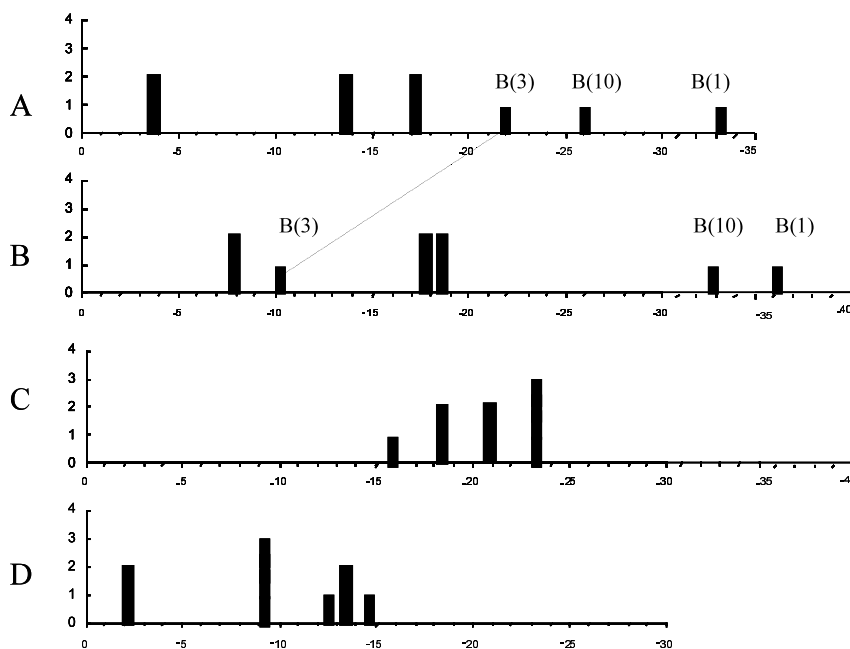
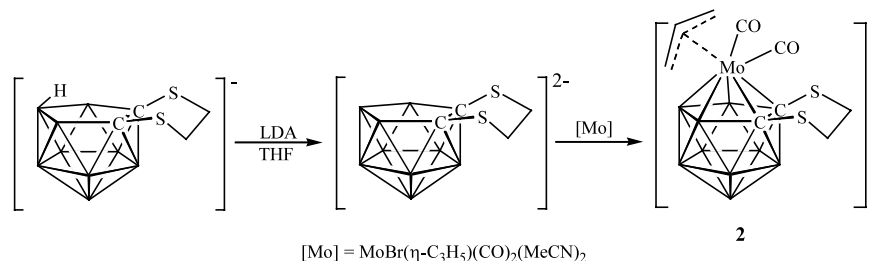


Fig. 2. Raw ^{11}B -NMR spectra with the peak assignments for the compounds: A, $\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_{10})$, **1**; B, $\text{NMe}_4[7,8\text{-}\mu\text{-SCH}_2\text{CH}_2\text{S-7,8-}n\text{-ido-C}_2\text{B}_9\text{H}_{10}]^-$;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

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

five resonances between δ -2 and -15 . The weighted average ^{11}B chemical shift, $\langle\delta^{11}\text{B}\rangle$, is -9.4 ppm, clearly signifying that metallacarborane **2** has a *closo* structure [2b–2d]. Moreover, the presence of only five resonances, with relative integrals 2:3:1:2:1 (high to low frequency), is indicative of a symmetric species. Thus we assume that **2** has a 3,1,2-MoC₂B₉ [11] architecture, similar to 3-(η -C₃H₅)-3,3-(CO)₂-4-SMe₂-3,1,2-*closo*-MoC₂B₉H₁₀ and [1-Ph-3-(η -C₃H₅)-3,3-(CO)₂-3,1,2-*closo*-MoC₂B₉H₁₁][−] [3b].

3. Experimental

3.1. Synthesis-general

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

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

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

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

To a stirring solution of [NMe₄][7,8- μ -SCH₂CH₂S-7,8-*nido*-C₂B₉H₁₀] (0.10 g, 0.34 mmol) in 10 ml THF at 0 °C was added, dropwise, 0.34 ml of a 2M solution (0.68 mmol) of lithium di-isopropylamide in THF–heptane–ethylbenzol. ¹¹B{¹H}-NMR [(CD₃)₂CO, r.t.] of this Li₂[7,8- μ -SCH₂CH₂S-7,8-*nido*-C₂B₉H₉] intermediate, δ -15.4 (1B), -18.3 (2B), -21.1 (2B), -22.5 (3B) and -46.1 (1B). After 1 h MoBr(η -C₃H₅)(CO)₂(MeCN)₂ (0.14 g, 0.41 mmol) was added, and the reaction mixture stirred for a further 30 min. Solvent was removed in vacuo and the product was purified by recrystallisation from ethyl acetate:petroleum ether (1:4) under nitrogen to afford Li[1,2- μ -SCH₂CH₂S-3-(η -C₃H₅)-3,3-(CO)₂-3,1,2-*closo*-MoC₂B₉H₉] (**2**) as a yellow solid. Yield 0.13 g, 79%. NMR (291 K): ¹H, CDCl₃, δ 5.8 (m, 1H, CH₂CHCH₂), 5.2 (d, ³J_{HH} 8 Hz, 2H, CH₂CHCH₂[*syn*]), 5.0 (d, ³J_{HH} 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).

3.4. Crystallography

Crystals of **1** suitable for a crystallographic study were grown from diffusion of petroleum ether and a CDCl_3 solution at $-30\text{ }^\circ\text{C}$. Diffraction data were collected using a Bruker *P4* diffractometer equipped with Mo-K_α X-radiation ($\lambda = 0.71073\text{ \AA}$) by ω scans at $160(2)\text{ K}$.

3.4.1. Crystal data

Crystal size $0.6 \times 0.48 \times 0.12\text{ mm}$, $\text{C}_9\text{H}_{19}\text{B}_9\text{MoO}_2\text{S}_2$, $M = 416.59$, monoclinic, $P2_1/n$, $\alpha = 6.966(3)$, $\beta = 18.266(6)$, $\gamma = 13.729(6)\text{ \AA}$, $\beta = 96.90(3)^\circ$, $V = 1734.3(11)\text{ \AA}^3$, $Z = 4$, $D_c = 1.596\text{ Mg m}^{-3}$, $\mu = 0.993\text{ mm}^{-1}$, $F(000) = 832$. θ Range for data collection $2.23\text{--}25.02^\circ$, index range $-1 \leq h \leq 8$, $-21 \leq k \leq 1$, $-16 \leq l \leq 16$. About 4063 data collected, 3016 independent reflections ($R_{\text{int}} = 0.0308$), $R_1 = 0.0385$, $wR_2 = 0.1071$ for all data, $S = 1.049$, largest peak 0.640 and deepest hole -0.804 e \AA^{-3} .

Data were corrected for absorption by *psi* scans and the structure solved by direct and difference Fourier methods. Refinement [13] by was by full-matrix least-squares on F^2 for 238 parameters. All non-H atoms were refined with anisotropic displacement parameters. Except for H3, refined freely resulting in $\text{B3-H3} = 1.07(4)\text{ \AA}$, boron-bound H atoms were restrained to $\text{B-H} = 1.10(2)\text{ \AA}$, whilst carbon-bound H atoms were treated as riding on their respective C atom, $\text{C-H} = 1.00\text{ \AA}$ (CH) and 0.99 \AA (CH_2). In all cases the (isotropic) displacement parameter of H atoms was set at $1.2 \times$ that of the bound atom U_{eq} .

4. Supplementary material

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

Acknowledgements

We acknowledge the award of NATO Collaborative Research Grant CRG 971636 which allowed G.B. to spend time at Heriot-Watt University. We also thank G. Evans for microanalysis and Dr. A.S.F. Boyd for NMR spectra. This work was supported by CICYT (Project MAT01-1575) and Generalitat de Catalunya (2001/SGR/00337).

References

- [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.
- [2] E.g. in *pseudocloso* compounds; (a) Z.G. Lewis, A.J. Welch, *J. Organometal Chem.* 430 (1992) C45; (b) P.T. Brain, M. Bühl, J. Cowie, Z.G. Lewis and A.J. Welch, *J. Chem. Soc., Dalton Trans.* (1996) 231; (c) U. Grädler, A.S. Weller, A.J. Welch, D. Reed, *J. Chem. Soc., Dalton Trans.* (1996) 335; (d) A.J. Welch, A.S. Weller, *Inorg. Chem.* 35 (1996) 4548; (e) J.H. Kim, M. Lamrani, J.W. Hwang, Y. Do, *Chem. Commun.* (1997), 1761; (f) F. Teixidor, M.A. Flores, C. Viñas, R. Sillanpää, R. Kivekäs, *J. Am. Chem. Soc.* 122 (2000) 1963.
- [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; (b) S. Dunn, G.M. Rosair, R.L. Thomas, A.S. Weller, A.J. Welch, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 645; (c) A.J. Welch, A.S. Weller, *J. Chem. Soc. Dalton Trans.* (1997) 1205; (d) S. Dunn, G.M. Rosair, A.S. Weller, A.J. Welch, *Chem. Commun.* (1998) 1065; (e) R.M. Garrioch, P. Kuballa, K.S. Low, G.M. Rosair, A.J. Welch, *J. Organometal. Chem.* 585 (1999) 57; (f) S. Dunn, R.M. Garrioch, G.M. Rosair, L. Smith, A.J. Welch, *Collect. Czech. Chem. Commun.* 64 (1999) 1013.
- [4] E.g. (a) T.E. Paxon, M.F. Hawthorne, *J. Am. Chem. Soc.* 96 (1974) 4674; (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; (c) E. Hong, Y. Kim, Y. Do, *Organometallics* 17 (1998) 2933; (d) F. Simal, S. Sebile, A. Demonceau, A.F. Noels, R. Nuñez, M. Abad, F. Teixidor, C. Viñas, *Tet. Lett.* 41 (2000) 5347.
- [5] E.g. (a) J. Plešek, *Chem. Rev.* 92 (1992) 269; (b) J. Rais, P. Seluky, *Nucleon* 1 (1992) 17; (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 and R. Sillanpää, *J. Chem. Soc., Dalton Trans.* (1998) 2849; (e) C. Viñas, S. Gomez, J. Bertran, F. Teixidor, J.F. Dozol, H. Rouquette, *Chem. Commun.* (1998) 191; (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.
- [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; (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; (c) C. Hague, N.J. Patmore, C.G. Frost, M.F. Mahon, A.S. Weller, *Chem. Commun.* (2001) 2238, respectively.
- [7] E.g. (a) F. Teixidor, J. Casabó, A.M. Romerosa, C. Viñas, J. Ruis, C. Miravittles, *J. Am. Chem. Soc.* 113 (1991) 9895; (b) F. Teixidor, A. Romerosa, C. Viñas, J. Ruis, C. Miravittles, J. Casabó, *J. Chem. Soc., Chem. Commun.* (1992) 192; (c) F. Teixidor, J.A. Ayllón, C. Viñas, J. Rius, C. Miravittles, J. Casabó, *J. Chem. Soc., Chem. Commun.* (1992) 1279; (d) F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, R. Sillanpää, J. Casabó, *J. Chem. Soc., Chem. Commun.* (1992) 1281;

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