

BUILDING A PICTURE OF HETEROBORANE ISOMERISATION: SYNTHESIS AND CHARACTERISATION OF THE 10-(DIALKYL-SULFANE)-7,8-DIPHENYL-7,8-DICARBA-*nido*-UNDECABORANES 7,8-Ph₂-10-L-7,8-*nido*-C₂B₉H₁₀ (L = SME₂, SMeEt, SEt₂) AND OF INTERMEDIATE AND ISOMERISED PRODUCTS ARISING FROM METALLATION OF THE FIRST OF THESE*

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Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday in recognition of his many outstanding contributions to boron cluster chemistry.

Three new, substituted, *nido* carboranes, 7,8-Ph₂-10-(SMe₂)-7,8-*nido*-C₂B₉H₁₀ (**1a**), 7,8-Ph₂-10-(SMeEt)-7,8-*nido*-C₂B₉H₁₀ (**1b**) and 7,8-Ph₂-10-(SEt₂)-7,8-*nido*-C₂B₉H₁₀ (**1c**) have been synthesised and characterised, including a crystallographic study of the first. Deprotonation of **1a** followed by treatment with (MeCN)₂(CO)₂MoBr(η-C₃H₅) at 0 °C affords the non-icosahedral 1,2-Ph₂-4-(SMe₂)-5-(η-C₃H₅)-5,5-(CO)₂-5,1,2-*closo*-MoC₂B₉H₈ (**2a**), which on subsequent warming transforms into icosahedral 2,8-Ph₂-5-(SMe₂)-1-(η-C₃H₅)-1,1-(CO)₂-1,2,8-*closo*-MoC₂B₉H₈ (**3a**). It is argued that under the conditions of these rearrangements the B-S bond is likely to remain intact, and consequently that the identity of the SMe₂-labelled boron atom in **3a** affords useful experimental information on the course of the isomerisation.

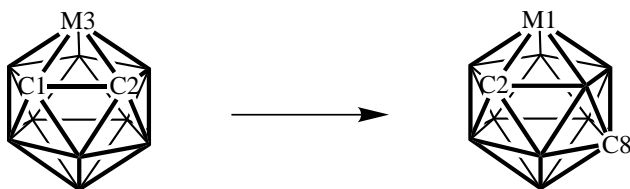
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The thermally-induced isomerisation of heteroboranes has been an area of considerable interest since the rearrangement of 1,2-*closo*-C₂B₁₀H₁₂ to 1,7-*closo*-C₂B₁₀H₁₂ was first reported 35 years ago¹. The mechanism of this 1,2 → 1,7 isomerisation, and the further 1,7 → 1,12 isomerisation², has been the subject of much speculation and theoretical analysis over many

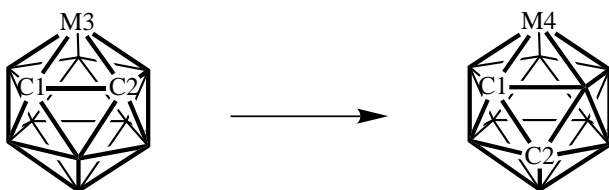
+ Part 23 in the Series Steric Effects in Heteroboranes; for Part 22 see ref.⁵

years³, but definitive experimental evidence has always been scarce. This is because (i) vertex-labelling experiments (*i.e.* following the movement of specific vertices tagged by attached substituents) have generally been unreliable because of the fragility of the vertex-substituent bond under the high temperatures usually required to effect the isomerisations, and (ii) no intermediate on the isomerisation pathway, the structural identity of which would have provided an important mechanistic signpost, had ever been isolated.

Recently, however, we have shown that organising for icosahedral metallocarboranes to be deliberately overcrowded leads to a dramatic reduction in the temperatures required for the 3,1,2-*closo*-MC₂B₉ → 1,2,8-*closo*-MC₂B₉ isomerisation⁴ (Scheme 1, net 1,2 → 1,7 cage C atom isomerisation) and the 3,1,2-*closo*-MC₂B₉ → 4,1,2-*closo*-MC₂B₉ isomerisation⁵ (Scheme 2, net 1,2 → 1,2 cage C atom isomerisation), opening up the possibility of valuable vertex-labelling work. Further, we have demonstrated that it is possible sometimes to isolate isomerisation intermediates of overcrowded metallocarboranes⁶. We therefore now have a potentially powerful



SCHEME 1

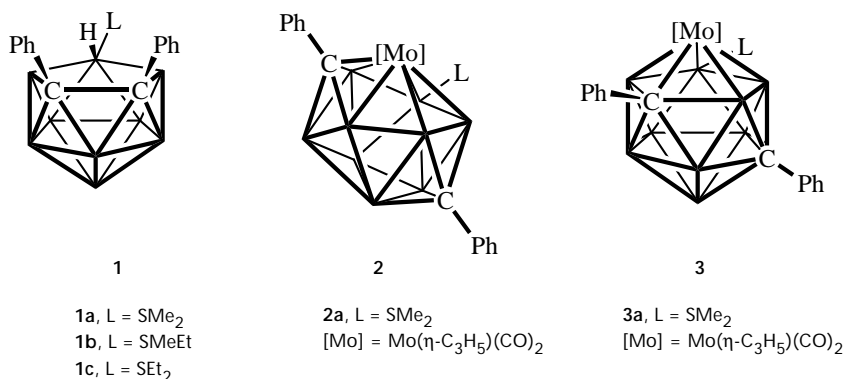


SCHEME 2

way of probing experimentally the isomerisation mechanism. Judicious use of vertex-labelling studies (allied, where appropriate, to the isolation of further intermediate species) should allow a complete and reliable picture of the rearrangement process to be built up.

In this paper we report the results of the low temperature 3,1,2-*closo*-MC₂B₉ → 1,2,8-*closo*-MC₂B₉ isomerisation of a molybdacarborane which carries an SR₂ substituent at the original position 5. We are able

to map the movement of the labelled boron atom from the first (transient) overcrowded icosahedral metallacarborane through to a non-icosahedral intermediate and on to the ultimate isomerised icosahedral product. The work depends, however, on the prior synthesis of new, specifically-substituted, carborane ligands, following procedures first reported by Plešek *et al.*⁷



EXPERIMENTAL

Synthesis and Spectroscopy

Unless otherwise stated, all reactions were carried out under an atmosphere of dry, oxygen free, N₂ using standard Schlenk techniques, with some subsequent manipulation in the open atmosphere. Toluene (Na), THF (Na wire), petroleum ether (Na wire) and dichloromethane (CaH₂) were dried and distilled under N₂ immediately prior to use. IR spectra were recorded from CH₂Cl₂ solutions on a Nicolet Impact 400 spectrophotometer. ¹H (Bruker AC200 spectrometer) and ¹¹B, ¹¹B-{¹H} and ¹¹B-{¹H}-¹¹B-{¹H} (COSY) (Bruker DPX400) NMR spectra were recorded from CDCl₃ solutions at room temperature. Chemical shifts are reported relative to external SiMe₄ (¹H) and BF₃·OEt₂ (¹¹B), with positive shifts to high frequency. Microanalyses were performed by the Departmental service. K[7,8-Ph₂-7,8-*nido*-C₂B₉H₁₀] (ref.⁸) and (MeCN)₂(CO)₂MoBr(η-C₃H₅) (ref.⁹) were prepared by standard literature methods or slight variants thereof. All other starting reagents were used as received from standard commercial sources.

Synthesis of 7,8-Ph₂-10-(SMe₂)-7,8-*nido*-C₂B₉H₉ (1a)

Following the method of Plešek *et al.*⁷, SMe₂ (3 ml, 40 mmol) in toluene (10 ml) and concentrated HCl (5 ml) were slowly added to a cooled, stirring solution of K[7,8-Ph₂-7,8-*nido*-C₂B₉H₁₀] (3.225 g, 10 mmol) in water (10 ml). After 5 min 16% aqueous CH₃CHO (*ca* 10 ml) was added following which the reaction mixture was stirred at room temperature for 18 h. The white solid formed was removed by filtration, dissolved in CHCl₃ (50 ml) and dried

over anhydrous MgSO_4 . Removal of solvent *in vacuo* afforded **1a** as a white solid. Yield 3.03 g (88%). Microanalysis, for $\text{C}_{16}\text{H}_{25}\text{B}_9\text{S}$ (346.7) calculated: 55.4% C, 7.27% H; found: 55.8% C, 7.92% H. ^1H NMR: 7.80–7.15 m, 10 H (C_6H_5); 2.06 s, 6 H (CH_3). ^{11}B - $\{^1\text{H}\}$ NMR: -6.4, 2 B (B9, B11); -11.6, 1 B (B3); -13.0, 2 B (B5, B6); -15.1, 2 B (B2, B4); -22.4, 1 B (B10); -32.6, 1 B (B1).

Synthesis of 7,8- Ph_2 -10-(SMeEt)-7,8-*nido*- $\text{C}_2\text{B}_9\text{H}_9$ (**1b**)

Similarly were reacted SMeEt (6 ml, 113 mmol) in toluene (20 ml), concentrated HCl (5 ml), $[\text{K}\{7,8\text{-Ph}_2\text{-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}\}]$ (4.230 g, 13 mmol) in water (15 ml), and 16% aqueous CH_3CHO (*ca* 10 ml). The white solid formed was isolated, dried over anhydrous MgSO_4 as a CH_2Cl_2 solution, then purified by column chromatography on silica, using CH_2Cl_2 -light petroleum (1 : 1) as eluent. Compound **1b** was obtained as a white solid. Yield 3.56 g (76%). Microanalysis, for $\text{C}_{17}\text{H}_{27}\text{B}_9\text{S}$ (360.8) calculated: 56.6% C, 7.54% H; found: 57.2% C, 6.72% H. ^1H NMR: 7.05–6.75 m, 10 H (C_6H_5); 3.12 d of q, 1 H, $J(\text{Ha-Hb}) \approx 13$, $J(\text{CH}_2\text{-CH}_3) \approx 7$ (CH_2); 2.85 d of q, 1 H, $J(\text{Ha-Hb}) \approx 13$, $J(\text{CH}_2\text{-CH}_3) \approx 7$ (CH_2); 2.45 s, 3 H (SCH_3); 1.50 m, 3 H (CH_2CH_3). ^{11}B - $\{^1\text{H}\}$ NMR: -6.8, 2 B (B9, B11); -10.9, 1 B (B3); -13.4, 2 B (B5, B6); -14.3, 2 B (B2, B4); -23.3, 1 B (B10); -32.2, 1 B (B1).

Synthesis of 7,8- Ph_2 -10-(SEt₂)-7,8-*nido*- $\text{C}_2\text{B}_9\text{H}_9$ (**1c**)

Similarly were reacted SEt_2 (6 ml, 57 mmol) in toluene (20 ml), concentrated HCl (10 ml), $[\text{K}\{7,8\text{-Ph}_2\text{-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}\}]$ (4.127 g, 12.7 mmol) in water (15 ml), and 16% aqueous CH_3CHO (*ca* 15 ml). The pale pink solid formed was isolated, dried over anhydrous MgSO_4 as a CH_2Cl_2 solution, then purified by column chromatography on silica, using CH_2Cl_2 -light petroleum (2 : 3) as eluent. Compound **1c** was obtained as a very pale pink solid. Yield 4.00 g (84%). Microanalysis, for $\text{C}_{18}\text{H}_{29}\text{B}_9\text{S}$ (374.8) calculated: 57.7% C, 7.80% H; found: 57.4% C, 7.16% H. ^1H NMR: 7.10–6.75 m, 10 H (C_6H_5); 3.05 d of q, 2 H, $J(\text{Ha-Hb}) \approx 13$, $J(\text{CH}_2\text{-CH}_3) \approx 7$ (CH_2); 2.95 d of q, 1 H, $J(\text{Ha-Hb}) \approx 13$, $J(\text{CH}_2\text{-CH}_3) \approx 7$ (CH_2); 1.50 m, 6 H (CH_3). ^{11}B - $\{^1\text{H}\}$ NMR: -6.7, 2 B (B9, B11); -10.8, 1 B (B3); -12.9, 2 B (B5, B6); -14.5, 2 B (B2, B4); -23.8, 1 B (B10); -32.3, 1 B (B1).

Synthesis of 1,2- Ph_2 -4-(SMe₂)-5-($\eta\text{-C}_3\text{H}_5$)-5,5-(CO)₂-5,1,2-*closo*- $\text{MoC}_2\text{B}_9\text{H}_8$ (**2a**)

Compound **1a** (0.501 g, 1.4 mmol) was deprotonated by reflux for 18 h in THF (40 ml) with NaH (0.141 g, 3.5 mmol). After cooling the excess NaH was allowed to settle and the supernatant solution was added by cannula to a stirring solution of $(\text{MeCN})_2(\text{CO})_2\text{MoBr}(\eta\text{-C}_3\text{H}_5)$ (0.494 g, 1.4 mmol) in THF (10 ml) at 0 °C. After *ca* 3 h solvent was removed *in vacuo* to reveal a brown oil, which yielded a single mobile orange band on column chromatography on silica (CH_2Cl_2 -light petroleum, 7 : 3). Removal of solvent afforded **2a** as an orange solid. Yield 0.317 g (42%). Microanalysis, for $\text{C}_{21}\text{H}_{29}\text{B}_9\text{MoO}_2\text{S}$ (538.8) calculated: 46.8% C, 5.43% H; found: 47.0% C, 5.58% H. IR: ν_{max} 1 967, 1 910 cm^{-1} (CO). ^1H NMR: 7.9–7.2 m, 10 H (C_6H_5); 4.20 m, 1 H, ($\text{CH}_{\text{centre}}$); 2.65 d of d, 1 H, $J(\text{H}_{\text{syn}}\text{-H}_{\text{centre}}) \approx 7$, $J(\text{H}_{\text{syn}}\text{-H}_{\text{syn}}) \approx 3$ (CH_{syn}); 2.60 s, 3 H (CH_3); 2.55 s, 3 H (CH_3); 2.30 d of d, 1 H, $J(\text{H}_{\text{syn}}\text{-H}_{\text{centre}}) \approx 7$, $J(\text{H}_{\text{syn}}\text{-H}_{\text{syn}}) \approx 4$ (CH_{syn}); 2.00 d, 1 H, $J(\text{H}_{\text{anti}}\text{-H}_{\text{centre}}) \approx 11$, (CH_{anti}); 1.10 d, 1 H, $J(\text{H}_{\text{anti}}\text{-H}_{\text{centre}}) \approx 10$ (CH_{anti}). ^{11}B - $\{^1\text{H}\}$ NMR: 13.8, 1 B; 9.2, 2 B; -0.1, 2 B; -3.7, 2 B; -22.2, 1 B; -24.0, 1 B.

Synthesis of 2,8-Ph₂-5-(SMe₂)-1-(η-C₃H₅)-1,1-(CO)₂-1,2,8-*closo*-MoC₂B₉H₈ (**3a**)

A small amount of compound **2a** (ca 0.1 g) was heated to reflux in THF (ca 20 ml) until IR spectroscopy showed conversion to be complete. Removal of solvent *in vacuo* and work up by column chromatography on silica (CH₂Cl₂-light petroleum, 7 : 3) afforded a single mobile band, yielding compound **3a** as an orange solid on removal of solvent. Microanalysis, for C₂₁H₂₉B₉MoO₂S (538.8) calculated: 46.8% C, 5.43% H; found: 46.4% C, 5.19% H. IR: ν_{\max} 1 936, 1 852 cm⁻¹ (CO). ¹H NMR: not available. ¹¹B-{¹H} NMR: 2.5, 1 B (B5); -2.4, 1 B; -4.7, 1 B; -6.2, 1 B; -7.6, 2 B; -10.5, 2 B; -14.2, 1 B.

Crystallographic Studies

Diffraction-quality crystals of compound **1a** were grown by the slow evaporation of a CHCl₃ solution, and of **2a** and **3a** by slow diffusion of a CH₂Cl₂ solution and light petroleum at -30 °C. Using a Siemens P4 diffractometer, diffraction data were collected (XSCANS, ref.¹⁰, ω scans) from single crystals of all three compounds, at room temperature for **1a**, but at 160 K for **2a** and **3a** (Oxford cryostream). Standard reflections were measured every 100 data, but in no case could significant crystal decomposition or movement be detected. Data were corrected for absorption effects by psi scans, and all three structures were solved by direct and difference Fourier methods and refined by full-matrix least-squares against F^2 . Non-hydrogen atoms were assigned anisotropic thermal vibration. Cage, phenyl and methyl H atoms were allowed to ride on their respective B or C atoms, with U_{iso} 1.2, 1.2 and 1.5 times the bound atom U_{eq} , respectively. Crystallographic computing utilised the SHELXTL system¹¹ on a Pentium 90 MHz PC. Table I gives pertinent crystallographic data. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-115171 (compound **1a**), CCDC-115172 (compound **2a**), CCDC-115173 (compound **3a**). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

Carboranes

The new carboranes 7,8-Ph₂-10-(SMe₂)-7,8-*nido*-C₂B₉H₉ (**1a**), 7,8-Ph₂-10-(SMeEt)-7,8-*nido*-C₂B₉H₉ (**1b**) and 7,8-Ph₂-10-(SEt₂)-7,8-*nido*-C₂B₉H₉ (**1c**) have been prepared in high yields as white or pale pink solids by the general reaction between K[7,8-Ph₂-7,8-*nido*-C₂B₉H₁₀] and SR₂ in the presence of acid and CH₃CHO, following the procedure first described for 10-(SMe₂)-7,8-*nido*-C₂B₉H₁₁ by Plešek *et al.*⁷.

The ¹H and ¹¹B-{¹H} NMR spectra of **1a** are fully consistent with C_s molecular symmetry. In the ¹¹B spectrum every resonance except that at -22.4 ppm appears as a doublet, $J(\text{B-H}) = 136\text{--}166$ Hz, identifying this resonance as due to the SMe₂-substituted B10. All the remaining resonances were unambiguously assigned by analysis of the results of a ¹¹B-{¹H}-¹¹B-{¹H} COSY experiment.

TABLE I
Crystallographic data for compounds **1a**, **2a** and **3a**

Parameter	1a	2a	3a
Crystal colour, habit	colourless needle	yellow block	yellow block
Crystal size, mm	0.63 × 0.12 × 0.10	0.63 × 0.38 × 0.34	0.35 × 0.32 × 0.16
Formula	C ₁₆ H ₂₄ B ₉ S · CHCl ₃	C ₂₁ H ₂₉ B ₉ MoO ₂ S	C ₂₁ H ₂₉ B ₉ MoO ₂ S
<i>M</i>	465.07	538.73	538.73
System	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> , Å	6.918(2)	9.2066(8)	10.655(3)
<i>b</i> , Å	12.834(6)	18.4739(13)	15.035(5)
<i>c</i> , Å	15.359(8)	29.439(2)	30.957(14)
α, °	65.42(3)	90	90
β, °	87.44(5)	90	90
γ, °	78.30(4)	90	90
<i>U</i> , Å ³	1 213.1(9)	5 007.1(7)	4 959(3)
<i>Z</i>	2	8	8
<i>D</i> _{calc}	1.273	1.429	1.443
μ(MoKα), mm ⁻¹	0.468	0.626	0.632
θ data collection, °	1.77–25.01	2.20–25.00	2.32–24.98
Data measured	5 206	5 487	5 380
Unique data	4 106	4 386	4 314
Observed data [<i>I</i> > 2σ(<i>I</i>)]	2 212	3 810	2 400
<i>R</i> , <i>wR</i> ₂ , all data	0.1725, 0.3011	0.0439, 0.0785	0.1404, 0.1741
<i>R</i> , <i>wR</i> ₂ , observed data	0.0931, 0.2298	0.0278, 0.0697	0.0594, 0.1218
Variables	304	331	307
<i>E</i> _{max} , <i>E</i> _{min} , e Å ⁻³	0.651, -0.539	0.293, -0.464	0.823, -0.774

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sigma_c^2(F_o)^2 + (aP)^2 + bP]$, where $P = [0.333\max\{F_o, 0\} + 0.667(F_o^2)]$, $\Sigma = [\sum [w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where *n* is the number of data and *p* is the number of parameters.

A crystallographic study of **1a** confirmed its structural identity. Figure 1 presents a perspective view of a single molecule, and Table II lists key interatomic distances and interbond angles. Compound **1a** was co-crystallised with one molecule of CHCl_3 solvate (which is partially disordered), but there are no significant molecule-solvate, intermolecular or inter-solvate interactions. In the crystal, **1a** effectively displays the C_s molecular symmetry it possesses in solution.

Interatomic distances are unexceptional. C7–C8, 1.609(8) Å, compares well with the corresponding distance in $[7,8\text{-Ph}_2\text{-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}]^-$ (ref.¹²) and the conformations of the two phenyl rings (defined by θ , the modulus of the average $C_{\text{cage}}\text{-}C_{\text{cage}}\text{-}C\text{-}C$ torsion angle¹³, 1.7(5) and 1.5(5)° in **1a**) are also similar. The B10–S10 distance, 1.901(7) Å, bears excellent comparison with that in 7-(SMe₂)-nido-B₁₁H₁₃ (ref.¹⁴). The SMe₂ unit is oriented about the B–S bond such that the sulfur lone pair of electrons lies *anti* to the carborane open face.

Compound **1b** was characterised by microanalysis and NMR spectroscopy. The CH₂ protons are magnetically inequivalent and show, in the ¹H spectrum, coupling to each other (13 Hz) and to the CH₂CH₃ protons (7 Hz), appearing as two doublets of quartets. The ¹¹B-¹H NMR spectrum is fully consistent with a 7,8-nido-C₂B₉ carborane, having two low-frequency resonances, *ca* –23 and –32 ppm, the former of which does not appear as a doublet on retention of proton coupling and therefore is due to B10. Unexpectedly, however, there are only six signals in the ¹¹B-¹H spectrum, 2 : 1 : 2 : 2 : 1 : 1 from high frequency to low frequency, suggestive of C_s molecular symmetry. Assuming no inversion at sulfur (which cannot in any

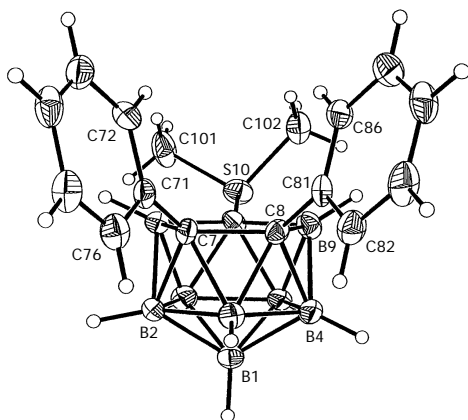


FIG. 1
Perspective view of 7,8-Ph₂-10-(SMe₂)-7,8-nido-C₂B₉H₉ (**1a**), demonstrating the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, except for H atoms

case occur since it would cause equivalence of the methylene protons) the overall molecule can never attain mirror symmetry, and so the signals of integral 2 in the boron spectrum of **1b** must arise from three 1+1 co-incidences. The ^{11}B chemical shifts are all within 1 ppm of those in **1a** and are assigned by analogy. Thus the replacement of SMe_2 by SMeEt has very little effect on the ^{11}B chemical shifts in these molecules, and it is therefore not unreasonable that there are, in **1b**, three co-incident ^{11}B resonances, *viz.* B2B4, B5B6 and B9B11.

Compound **1c** was also studied by microanalysis and NMR spectroscopy. Again, the protons on one methylene carbon atom are inequivalent, each appearing as a doublet (13.2 Hz) of quartets (7.4 and 7.5 Hz). Correspondingly, the methyl protons appear as a multiplet (strictly a doublet of dou-

TABLE II
Selected interatomic distances (Å) and angles (°) for **1a**

Atoms	Distances	Atoms	Distances	Atoms	Distances
B1-B4	1.762(10)	B1-B2	1.767(11)	B1-B3	1.769(11)
B1-B5	1.795(10)	B1-B6	1.814(11)	B2-B7	1.722(9)
B2-B6	1.761(11)	B2-B3	1.766(11)	B2-B11	1.791(10)
B3-C7	1.732(10)	B3-B8	1.737(10)	B3-B4	1.772(10)
B4-C8	1.739(10)	B4-B5	1.742(11)	B4-B9	1.778(11)
B5-B9	1.754(10)	B5-B10	1.780(11)	B5-B6	1.835(11)
B6-B10	1.773(10)	B6-B11	1.788(11)	B9-C8	1.605(10)
B9-B10	1.784(10)	S10-C101	1.778(8)	S10-C102	1.804(7)
S10-B10	1.901(7)	B10-B11	1.824(10)	B11-C7	1.615(10)
C7-C71	1.492(9)	C7-C8	1.609(8)	C8-C81	1.522(9)
Atoms	Angles	Atoms	Angles	Atoms	Angles
C101-S10-C102	102.7(4)	C101-S10-B10	103.4(4)	C102-S10-B10	106.3(3)
B6-B10-S10	114.6(5)	B5-B10-S10	113.1(5)	B9-B10-S10	124.5(5)
B11-B10-S10	127.5(5)	C71-C7-C8	119.2(5)	C71-C7-B11	118.4(5)
C71-C7-B2	120.7(5)	C81-C8-B3	118.2(5)	C71-C7-B3	117.1(5)
C81-C8-C7	117.6(5)	C81-C8-B4	120.8(5)	C81-C8-B9	117.3(5)

blets) at 1.5 ppm. The $^{11}\text{B}\{-^1\text{H}\}$ NMR spectrum is fully consistent with C_s molecular symmetry, and in the ^{11}B spectrum each resonance is split into a doublet, $J(\text{B-H}) = 129\text{--}145$ Hz, except that due to B10 at -23.8 ppm. The ^{11}B spectrum of **1c** was again fully assigned via $^{11}\text{B}\{-^1\text{H}\}\text{-}^{11}\text{B}\{-^1\text{H}\}$ correlated spectroscopy. Table III compares the ^{11}B chemical shifts of compounds **1a**, **1b** and **1c** and demonstrates a high degree of congruence as the SR_2 group is varied from SMe_2 (**1a**) to SMeEt (**1b**) to SEt_2 (**1c**).

Metallacarboranes

Deprotonation (NaH) of **1a** followed by reaction with $(\text{MeCN})_2(\text{CO})_2\text{MoBr}(\eta\text{-C}_3\text{H}_5)$ in THF at 0°C affords the neutral orange product **2a** in reasonable yield following work-up involving column chromatography. In the IR spectrum **2a** displays two carbonyl stretching modes, 1967 and 1910 cm^{-1} , very similar in frequency to those (1971 and 1917 cm^{-1}) of the product obtained by similar metallation of $[\text{7,8-Ph}_2\text{-9-SMe}_2\text{-7,8-nido-C}_2\text{B}_9\text{H}_8]^-$ (ref.^{6b}). The ^1H NMR spectrum of **2a** reveals resonances due to the phenyl groups, an η^3 -allyl ligand, and an SMe_2 moiety, signals for the last two clearly being indicative of overall molecular asymmetry. In the $^{11}\text{B}\{-^1\text{H}\}$ spectrum are only six resonances, of relative integral $1 : 2 : 2 : 2 : 1 : 1$ from highest (13.8 ppm) to lowest (-24.0 ppm) frequency. Although in isolation this might imply molecular symmetry, the asymmetry evident from the ^1H spectrum must mean that the three signals of integral two are $1+1$ co-incidences. The identity of the signal arising from the SMe_2 -bound B atom could not be determined unambiguously from an ^{11}B spectrum.

TABLE III
Comparison of ^{11}B NMR shifts^a (ppm) in compounds **1a**, **2a** and **3a**

Assignment	1a	2a	3a
B9, B11	-6.4	-6.8	-6.7
B3	-11.6	-10.9	-10.8
B5,B6	-13.0	-13.4	-12.9
B2,B4	-15.1	-14.3	-14.5
B10	-22.4	-23.3	-23.8
B1	-32.6	-32.2	-32.3

^a All ^{11}B spectra recorded from CDCl_3 solutions at 291 K .

The molecular structure of **2a** was established from a crystallographic study carried out at 160 K, and a perspective view of a single molecule is presented in Fig. 2. Table IV lists selected interatomic distances and interbond angles.

The $\{\text{MoC}_2\text{B}_9\}$ portion of **2a** is closed but not icosahedral. Vertices Mo5 and B10 each make six cage connectivities whilst the two cage carbon atoms, C1 and C2, each make four. Mo5–B distances average 2.45 Å and B10–B distances 1.94 Å, both being relatively long as a consequence of the high connectivity numbers of these atoms. The cage C atoms are separated by the B9–B10–B11 triangle, and the SMe_2 group is *exo*-bound to B4, B4–S4 = 1.921(3) Å. The overall shape of the cage of **2a** is identical to that which we have previously observed in products arising from the net addition of a $\{(\text{CO})_2\text{Mo}(\eta\text{-C}_3\text{H}_5)\}^+$ fragment to $[\text{7,8-Ph}_2\text{-7,8-nido-C}_2\text{B}_9\text{H}_9]^{2-}$ (ref.^{6a}) and to $[\text{7,8-Ph}_2\text{-9-(SMe}_2\text{)-7,8-nido-C}_2\text{B}_9\text{H}_8]^-$ (ref.^{6b}), and it is, moreover, the shape of the “1,2- C_2 ” intermediate predicted by Wales³ⁱ as a potential intermediate in the isomerisation of 1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ to 1,7-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$.

Mild heating (THF reflux) of **2a** results in its transformation into compound **3a**, a process conveniently followed by IR spectroscopy with the CO stretching bands of **2a** at 1 967 and 1 910 cm^{-1} giving way to new bands at 1 936 and 1 852 cm^{-1} after *ca* 1 h. We have previously shown^{6b} that such changes in $\nu(\text{CO})$ are consistent with the formation of an icosahedral molybdacarborane. The range of ^{11}B NMR chemical shifts observed in **3a**,

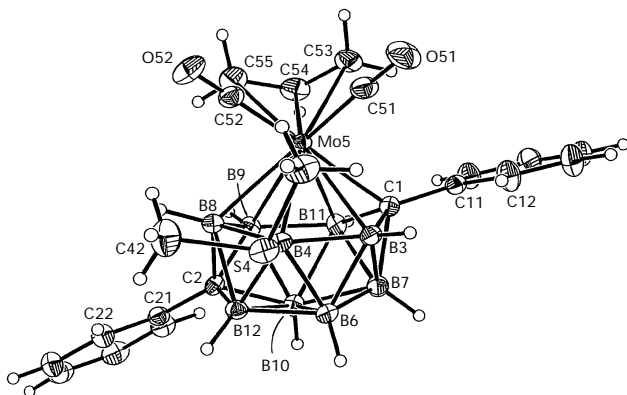


FIG. 2

Perspective view of 1,2- $\text{Ph}_2\text{-4-(SMe}_2\text{)-5-(}\eta\text{-C}_3\text{H}_5\text{)-5,5-(CO)}_2\text{-5,1,2-closo-MoC}_2\text{B}_9\text{H}_8$ (**2a**), demonstrating the (arbitrary) atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level, except for H atoms

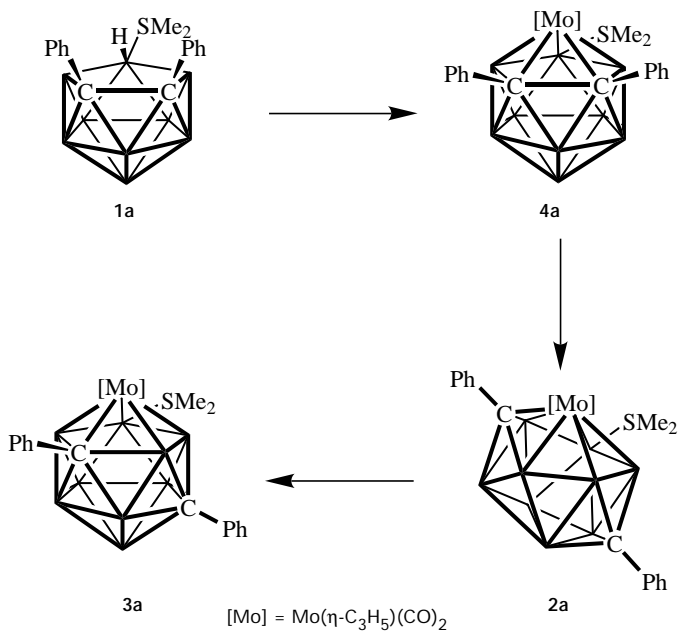
TABLE IV
Selected interatomic distances (Å) and angles (°) for **2a**

Atoms	Distances	Atoms	Distances	Atoms	Distances
Mo5-C52	1.982(3)	Mo5-C51	2.001(3)	Mo5-C54	2.257(2)
Mo5-C1	2.259(2)	Mo5-C55	2.367(2)	Mo5-C53	2.380(2)
Mo5-B8	2.402(3)	Mo5-B11	2.436(3)	Mo5-B4	2.438(3)
Mo5-B9	2.491(3)	Mo5-B3	2.508(3)	C1-C11	1.507(3)
C1-B11	1.574(4)	C1-B3	1.629(3)	C1-B7	1.662(3)
C2-C21	1.489(3)	C2-B9	1.559(3)	C2-B12	1.578(3)
C2-B8	1.682(3)	C2-B10	1.692(3)	B3-B6	1.786(4)
B3-B4	1.800(4)	B3-B7	1.823(4)	B4-B12	1.762(4)
B4-B8	1.774(4)	B4-B6	1.792(4)	B4-S4	1.921(3)
B6-B7	1.705(4)	B6-B12	1.767(4)	B6-B10	1.929(4)
B7-B10	1.847(4)	B7-B11	1.870(4)	B8-B12	1.829(4)
B8-B9	1.889(4)	B9-B11	1.795(4)	B9-B10	1.918(4)
B10-B11	1.985(4)	B10-B12	2.022(4)	S4-C41	1.797(3)
S4-C42	1.800(3)	C51-O51	1.141(3)	C52-O52	1.150(3)
C53-C54	1.404(4)	C54-C55	1.408(4)		
Atoms	Angles	Atoms	Angles	Atoms	Angles
C52-Mo5-C51	80.72(11)	C52-mO5-C1	156.34(9)	C51-Mo5-C1	86.44(9)
C11-C1-B11	122.6(2)	C11-C1-B3	122.6(2)	C11-C1-B7	115.1(2)
C11-C1-Mo5	127.7(2)	C21-C2-B8	128.3(2)	C21-C2-B9	121.9(2)
C21-C2-B12	120.8(2)	B8-B4-S4	120.3(2)	C21-C2-B10	124.9(2)
B12-B4-S4	106.7(2)	S4-B4-Mo5	128.31(13)	B6-B4-S4	110.7(2)
B3-B4-S4	110.8(2)	C42-S4-B4	105.85(12)	C41-S4-C42	101.28(14)
C41-S4-B4	107.95(12)	C53-C54-C55	119.1(3)	O51-C51-Mo5	179.1(2)
O52-C52-Mo5	178.0(2)				

2.5 to -14.2 ppm, further supports this conclusion. The observation of seven $^{11}\text{B}\{-^1\text{H}\}$ resonances implies an asymmetric cage (two 1+1 co-incidences) and in the ^{11}B spectrum the highest frequency resonance remains a singlet, identifying it as probably arising from an SMe_2 -bound boron atom.

Compound **3a** was also studied crystallographically. Figure 3 is a perspective view of a single molecule, and in Table V are selected molecular parameters determined. The molybdacarborane icosahedron has a 1,2,8-MoC₂B₉ heteroatom pattern and the SMe_2 group is bound to B5. B-S, Mo-C_{allyl}, Mo-CO and intrapolyhedral distances are all within the expected ranges⁶ and it is particularly noteworthy that the average Mo-B distance, 2.39 \AA , is substantially less than that in **2a** reflecting the change in polyhedral connectivity.

The structures of **1a**, **2a** and **3a** are represented together in Scheme 3. Metallation of deprotonated **1a** at 0°C presumably first affords the overcrowded icosahedral species **4a**, which undergoes sterically-driven isomerisation to the non-icosahedral **2a**. Relatively mild thermolysis of **2a** ultimately yields **3a**. Thus the **4a** to **3a** transformation is another example⁶ of a 3,1,2-*closo*-MC₂B₉ \rightarrow 1,2,8-*closo*-MC₂B₉ isomerisation (net 1,2 \rightarrow 1,7 cage C atom isomerisation) in which an intermediate on the isomerisation



SCHEME 3

TABLE V
Selected interatomic distances (Å) and angles (°) for **3a**

Atoms	Distances	Atoms	Distances	Atoms	Distances
Mo1-C11	1.909(8)	Mo1-C12	1.979(8)	Mo1-C14	2.240(7)
Mo1-C13	2.343(8)	Mo1-C15	2.355(8)	Mo1-B4	2.372(8)
Mo1-B5	2.374(8)	Mo1-B3	2.395(7)	Mo1-B6	2.436(8)
Mo1-C2	2.494(7)	C2-C21	1.497(10)	C2-B7	1.701(10)
C2-B3	1.724(10)	C2-B11	1.727(11)	C2-B6	1.730(11)
B3-C8	1.712(11)	B3-B4	1.777(11)	B3-B7	1.780(11)
B4-C8	1.735(10)	B4-B5	1.787(12)	B4-B9	1.816(12)
B5-B9	1.770(12)	B5-B6	1.788(12)	B5-B10	1.796(12)
B5-S5	1.921(8)	B6-B11	1.764(12)	B6-B10	1.781(11)
B7-C8	1.710(11)	B7-B12	1.736(12)	B7-B11	1.753(12)
C8-C81	1.520(9)	C8-B9	1.692(11)	C8-B12	1.7239(11)
B9-B12	1.758(13)	B9-B10	1.783(12)	B10-B11	1.762(12)
B10-B12	1.797(12)	B11-B12	1.789(12)	S5-C52	1.798(8)
S5-C51	1.804(7)	C11-O11	1.166(8)	C12-O12	1.142(9)
C13-C14	1.357(10)	C14-C15	1.378(11)		
Atoms	Angles	Atoms	Angles	Atoms	Angles
C11-Mo1-C12	80.0(3)	C11-Mo1-C2	157.2(3)	C12-Mo1-C2	115.2(3)
C21-C2-B7	116.7(6)	C21-C2-B3	122.3(6)	C21-C2-B11	115.2(6)
C21-C2-B6	121.2(6)	C21-C2-Mo1	107.9(5)	B9-B5-S5	114.8(5)
B4-B5-S5	123.4(5)	B6-B5-S5	123.7(5)	B10-B5-S5	113.1(5)
S5-B5-Mo1	110.0(4)	C81-C8-B9	117.6(6)	C81-C8-B7	119.9(6)
C81-C8-B3	120.5(6)	C81-C8-B12	117.0(6)	C81-C8-B4	117.0(6)
C52-S5-C51	100.1(4)	C52-S5-B5	103.1(4)	C51-S5-B5	107.5(4)
O11-C11-Mo1	179.1(7)	O12-C12-Mo1	174.2(8)	C13-C14-C15	121.9(7)

pathway (compound **2a**) has been isolated and structurally characterised. Under the relatively mild conditions employed we can be confident that the B-S exo bond remains intact throughout this rearrangement^{6b}, thus allowing us to trace the movement of vertex 10 of the original *nido* carborane **1a** through the intermediate **2a** to position 5 of the 1,2,8-MoC₂B₉ product **3a**.

Thus the experiments described herein contribute an important additional piece of information as we attempt to construct a complete experimental mapping of the isomerisation of heteroboranes. Future contributions will further develop the emerging picture.

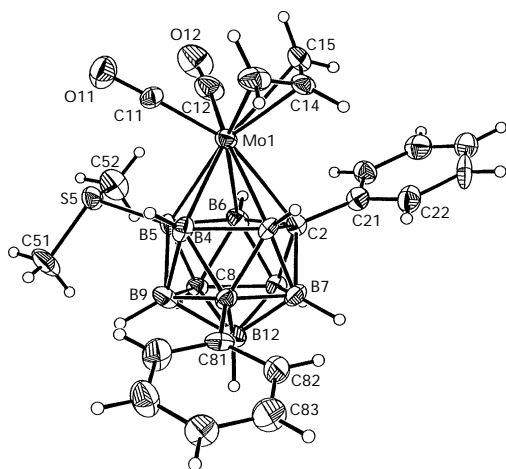


FIG. 3
Perspective view of 2,8-Ph₂-5-(SMe₂)-1-(η-C₃H₅)-1,1-(CO)₂-1,2,8-*closo*-MoC₂B₉H₈ (**3a**), demonstrating the atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level, except for H atoms

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