

# Expected and unexpected outcomes of a heteroborane isomerisation

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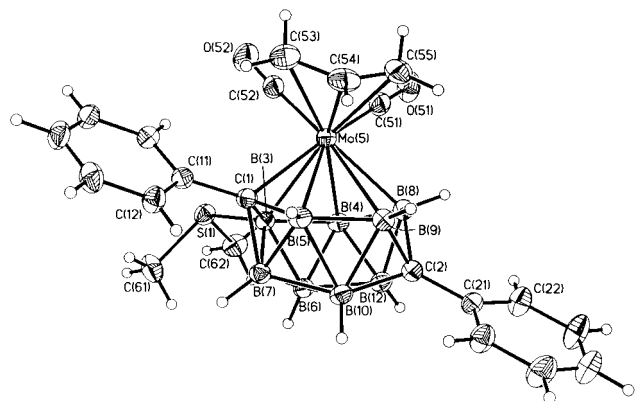
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Gentle thermolysis of compound **1**, an intermediate in the isomerisation of an overcrowded icosahedral carbametallaborane, surprisingly yields two rearranged products, compound **2** (expected from theory) and compound **3** (unexpected).

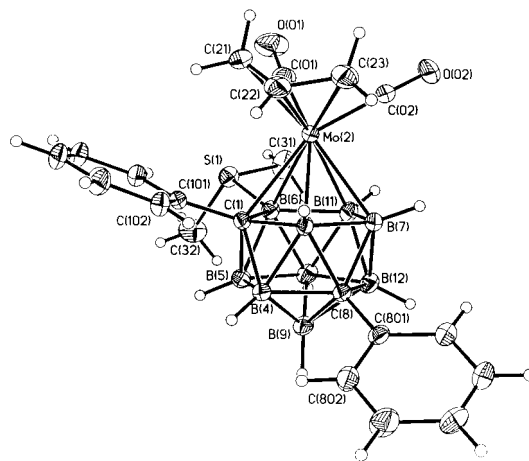
There is a substantial and continuing interest in the isomerisations of heteroboranes and the mechanisms by which such isomerisations occur.<sup>1</sup> Recently<sup>2</sup> we reported the first experimental isolation of an intermediate in the isomerisation of an overcrowded, notional  $C_{\text{cage}}$ -adjacent icosahedral metallacarborane. We showed that this species has a closed, non-icosahedral structure which previously had been recognised only theoretically,<sup>3</sup> and we demonstrated that it was a true intermediate by effecting its conversion to a  $C_{\text{cage}}$ -separated icosahedron on gentle warming.

We now report the results of initial experiments with a system where one boron vertex is tagged with an  $\text{SMe}_2$  group, which allows significant new insight into the precise isomerisation mechanism.

Deprotonation of the recently reported carbaborane 7,8- $\text{Ph}_2$ -9- $\text{SMe}_2$ -7,8-*nido*- $\text{C}_2\text{B}_9\text{H}_6$ <sup>4,5</sup> with NaH in thf, followed by reaction with  $[\text{MoBr}(\text{MeCN})_2(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2]$  at 0 °C, yields the neutral, charge-compensated species **1** in good yield.<sup>‡</sup> Compound **1** displays carbonyl stretching bands in the IR spectrum at relatively high frequency (1971 and 1917  $\text{cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ) which identify it as a potential non-icosahedron. This was confirmed by a crystallographic study<sup>§</sup> which revealed the structure shown in Fig. 1. Thus compound **1** constitutes only the second example of a derivative of Wales' hypothetical '1,2- $C_2$ ' intermediate<sup>3</sup> in the isomerisation of 1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$  to 1,7-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ . However, the presence of the  $\text{SMe}_2$  function attached to B(3) affords the possibility of mapping the movement of that boron atom when **1** is converted to the appropriate analogue of 1,7-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ , thus yielding valuable additional mechanistic information.

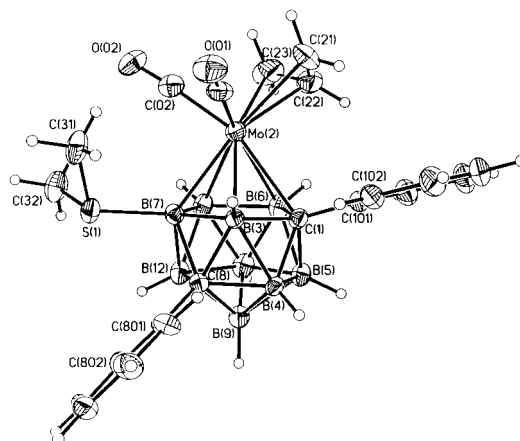


**Fig. 1** Perspective view of **1** (numbered as in ref. 3). Selected bond distances (Å) and angles (°): Mo(5)–C(51) 1.973(4), Mo(5)–C(52) 1.989(4), Mo(5)–C(53) 2.374(4), Mo(5)–C(54) 2.243(4), Mo(5)–C(55) 2.362(4), C(51)–O(51) 1.152(4), C(52)–O(52) 1.153(4), C(1)–C(11) 1.506(4), C(2)–C(21) 1.493(3), B(3)–S(1) 1.934(3); C(51)–Mo(5)–C(52) 76.57(14).

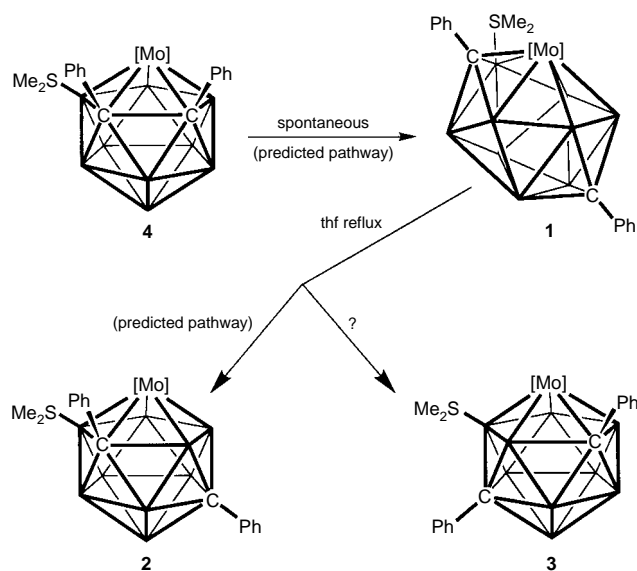


**Fig. 2** Perspective view of **2**. Selected bond distances (Å) and angles (°): Mo(2)–C(01) 1.947(3), Mo(2)–C(02) 1.931(3), Mo(2)–C(21) 2.360(3), Mo(2)–C(22) 2.236(3), Mo(2)–C(23) 2.355(3), C(01)–O(01) 1.159(4), C(02)–O(02) 1.155(3), C(1)–C(101) 1.521(3), C(8)–C(801) 1.512(4), B(6)–S(1) 1.937(3); C(01)–Mo(2)–C(02) 77.73(13).

To our considerable surprise, gentle thermolysis (thf reflux) of **1** affords two new carbametallaboranes, compounds **2** and **3**, isolated by thin layer chromatography in reasonable yields.<sup>‡</sup> Both display carbonyl stretching IR bands at low frequencies relative to those in **1** (1936 and 1853  $\text{cm}^{-1}$  in **2**; 1931 and 1840  $\text{cm}^{-1}$  in **3**) as expected for icosahedral compounds. Structural study of **2** and of **3**<sup>§</sup> confirmed this prediction. Compound **2** (Fig. 2) has a 1,8- $\text{Ph}_2$ -2-( $\eta^3\text{-C}_3\text{H}_5$ )-2,2-(CO)<sub>2</sub>-6- $\text{SMe}_2$ -2,1,8-*closo*- $\text{MoC}_2\text{B}_9\text{H}_8$  architecture whereas in compound **3** (Fig. 3) the  $\text{SMe}_2$  group is bound to B(7), *i.e.* **3** is 1,8- $\text{Ph}_2$ -2-( $\eta^3\text{-C}_3\text{H}_5$ )-2,2-(CO)<sub>2</sub>-7- $\text{SMe}_2$ -2,1,8-*closo*- $\text{MoC}_2\text{B}_9\text{H}_8$ . The overall reaction scheme is shown in Scheme 1, compound **4**



**Fig. 3** Perspective view of **3**. Selected bond distances (Å) and angles (°): Mo(2)–C(01) 1.974(8), Mo(2)–C(02) 1.929(9), Mo(2)–C(21) 2.368(9), Mo(2)–C(22) 2.201(9), Mo(2)–C(23) 2.370(9), C(01)–O(01) 1.152(10), C(02)–O(02) 1.170(10), C(1)–C(101) 1.513(9), C(8)–C(801) 1.509(9), B(7)–S(1) 1.936(7); C(01)–Mo(2)–C(02) 85.1(3).



**Scheme 1** Reaction scheme for formation of compound **1** from the notional overcrowded precursor **4**, and subsequent transformation of **1** into both **2** and **3**. The pathways identified as 'predicted' are those which are in agreement with the predictions of ref. 3. [Mo] = Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>.

representing the likely non-isolable (overcrowded) initial reaction product. To support the assumption that the B–S bond remains intact under the conditions of gentle thermolysis employed, a sample of 7,8-Ph<sub>2</sub>-9-SMe<sub>2</sub>-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub> was heated to reflux in thf for 1 h and was recovered unchanged (<sup>1</sup>H NMR spectroscopy).

As far as the relative positions of the cage carbon atoms is concerned both **2** and **3** are examples of '1,7-*I<sub>h</sub>*' species. According to Wales<sup>3</sup> 1,2-*I<sub>h</sub>* C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> is predicted to transform to the 1,2-*C<sub>2</sub>* C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> intermediate *via* a single route, whereas 1,2-*C<sub>2</sub>* C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> can rearrange to 1,7-*I<sub>h</sub>* C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> *via* two possible routes, all pathways involving low symmetry transition states. We have successfully tracked the transformation of **4** into the isolated intermediate **1**, and one pathway for the subsequent transformation of **1** into **2**, thus providing experimental support for these theoretical predictions. However, the conversion of **1** into the unexpected product **3** must occur *via* a pathway not currently articulated, and clearly demonstrates that further experimental and theoretical work in this fascinating area is warranted.

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## Notes and References

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‡ *Syntheses and selected data*: **1**: 7,8-Ph<sub>2</sub>-9-SMe<sub>2</sub>-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub><sup>4,5</sup> (1.73 mmol) in thf (30 ml) was deprotonated with an excess of NaH, then added to a stirring solution of [MoBr(MeCN)<sub>2</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>] (1.73 mmol) in thf (10 ml) at 0 °C. The solution was allowed to warm to room temp. and stirred for a total of 2 h. Removal of solvent *in vacuo* and work up by column chromatography [silica, CH<sub>2</sub>Cl<sub>2</sub>–light petroleum (7:3)] afforded a single orange band. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>–light petroleum at 4 °C afforded diffraction-quality crystals of compound **1** (65% yield). IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ /cm<sup>-1</sup>: 2554 (br, B–H), 1971 (vs, CO), 1917 (m, CO). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  7.85 (m, 2 H, Ph), 7.72 (m, 2 H, Ph), 7.38–7.19 (m,

6 H, Ph), 3.81 (m, 1 H, allyl<sub>centre</sub>), 2.68 (dd, 1 H, allyl<sub>syn</sub>), 2.55 (s, 3 H, SMe), 2.46 (dd, 1 H, allyl<sub>syn</sub>), 2.15 (s, 3 H, SMe), 1.90 (d, 1 H, allyl<sub>anti</sub>), 1.18 (d br, 1 H, allyl<sub>anti</sub>); <sup>11</sup>B{<sup>1</sup>H} NMR (124.8 MHz, CDCl<sub>3</sub>),  $\delta$  15.1 (1 B), 6.8 (2 B), 1.9 (2 B), –3.8 (1 B), –15.0 (1 B), –24.1 (2 B).

**2** and **3**: compound **1** (0.41 mmol) was dissolved in thf (15 ml) and heated to reflux for 1 h. Solvent was removed *in vacuo* and the residue applied as a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution to a TLC plate. Elution with CH<sub>2</sub>Cl<sub>2</sub>–light petroleum (2:3) (under a nitrogen atmosphere) afforded two mobile bands, compounds **2** (*R<sub>f</sub>* ca. 0.30) and **3** (*R<sub>f</sub>* ca. 0.35). Both bands were recovered and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>–light petroleum at 4 °C to afford diffraction-quality crystals in 54 and 31% yield, respectively. **2**: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ /cm<sup>-1</sup>: 2569 (br, B–H), 1936 (vs, CO), 1853 (s, CO). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  7.43 (m, 2 H, Ph), 7.29–7.10 (m, 8 H, Ph), 4.19 (m, 1 H, allyl<sub>centre</sub>), 3.32 (dd, 1 H, allyl<sub>syn</sub>), 2.93 (s, SMe), 2.21 (s, SMe), 2.39 (dd, 1 H, allyl<sub>syn</sub>), 1.42 (d, 1 H, allyl<sub>anti</sub>), 1.32 (d, 1 H, allyl<sub>anti</sub>); <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, CDCl<sub>3</sub>),  $\delta$  2.7 (1 B), –1.4 (1 B), –3.4 (1 B), –4.3 (1 B), –7.4 (2 B), –12.1 (2 B), –14.5 (1 B). **3**: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ /cm<sup>-1</sup>: 2559 (m br, B–H), 1931 (vs, CO), 1840 (vs, CO). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  7.57 (m, 2 H, Ph), 7.38–6.87 (m, 8 H, Ph), 3.71 (dd, 1 H, allyl<sub>syn</sub>), 3.18 (m, 1 H, allyl<sub>centre</sub>), 2.59 (apparent s, 6 H, 2 × SMe), 1.80 (d, 1 H, allyl<sub>syn</sub>), 1.62 (dd, 1 H, allyl<sub>anti</sub>), 1.22 (d, 1 H, allyl<sub>anti</sub>); <sup>11</sup>B{<sup>1</sup>H} NMR (128.4 MHz, CDCl<sub>3</sub>),  $\delta$  4.4 (1 B), 0.8 (1 B), –5.5 (3 B), –9.2 (1 B), –11.1 (sh, 1 B), –11.6 (1 B), –13.2 (1 B).

§ *Crystallographic data*: **1**: C<sub>21</sub>H<sub>29</sub>B<sub>9</sub>MoO<sub>2</sub>S, *M<sub>r</sub>* = 538.7, crystal size 0.4 × 0.4 × 0.8 mm, monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 13.4348(9), *b* = 10.7968(8), *c* = 19.0756(13) Å,  $\beta$  = 110.320(7)°, *U* = 2594.8(3) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.379 g cm<sup>-3</sup>, *F*(000) = 1096,  $\mu$  = 0.60 mm<sup>-1</sup>. Siemens P4 diffractometer, 293(2) K, Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å, 2 $\theta$ <sub>max</sub> = 50°, 4567 unique reflections, 3456 observed [*F<sub>o</sub>* > 4 $\sigma$ (*F<sub>o</sub>*)], corrections for absorption ( $\psi$ -scans), Lorentz and polarisation effects. Structure solved by direct methods and refined (on *F*<sup>2</sup>) by full-matrix least squares (339 variables) to *R*<sub>1</sub> = 0.0337, *wR*<sub>2</sub> = 0.0680 (for observed data), *S* = 1063. Max., min. residual electron density 0.25, –0.30 e Å<sup>-3</sup>.

**2**: C<sub>21</sub>H<sub>29</sub>B<sub>9</sub>MoO<sub>2</sub>S, *M<sub>r</sub>* = 538.7, crystal size 0.4 × 0.4 × 0.8 mm, monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 11.8254(10), *b* = 11.5468(7), *c* = 19.7695(11) Å,  $\beta$  = 107.277(5)°, *U* = 2577.6(3) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.388 g cm<sup>-3</sup>, *F*(000) = 1096,  $\mu$  = 0.61 mm<sup>-1</sup>. Siemens P4 diffractometer, 293(2) K, Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å, 2 $\theta$ <sub>max</sub> = 50°, 4539 unique reflections, 3639 observed [*F<sub>o</sub>* > 4 $\sigma$ (*F<sub>o</sub>*)], corrections for absorption ( $\psi$ -scans), Lorentz and polarisation effects. Structure solved by direct methods and refined (on *F*<sup>2</sup>) by full-matrix least squares (307 variables) to *R*<sub>1</sub> = 0.0298, *wR*<sub>2</sub> = 0.0666 (for observed data), *S* = 1094. Max., min. residual electron density 0.29, –0.40 e Å<sup>-3</sup>.

**3**: C<sub>21</sub>H<sub>29</sub>B<sub>9</sub>MoO<sub>2</sub>S, *M<sub>r</sub>* = 538.7, crystal size 0.1 × 0.3 × 0.4 mm, monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 12.8226(12), *b* = 13.840(2), *c* = 15.3573(14) Å,  $\beta$  = 109.733(7)°, *U* = 2565.4(5) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.395 g cm<sup>-3</sup>, *F*(000) = 1096,  $\mu$  = 0.61 mm<sup>-1</sup>. Siemens P4 diffractometer, 293(2) K, Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å, 2 $\theta$ <sub>max</sub> = 50°, 4475 unique reflections, 2881 observed [*F<sub>o</sub>* > 4 $\sigma$ (*F<sub>o</sub>*)], corrections for absorption ( $\psi$ -scans), Lorentz and polarisation effects. Structure solved by direct methods and refined (on *F*<sup>2</sup>) by full-matrix least squares (307 variables) to *R*<sub>1</sub> = 0.0622, *wR*<sub>2</sub> = 0.1420 (for observed data), *S* = 1.047. Max., min. residual electron density 1.78, –0.75 e Å<sup>-3</sup>. CCDC 182/819.

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