Unprecedented steric deformation of *ortho*-carborane†

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The reduction and subsequent oxidation of *meta*-carboranes containing bulky groups attached to the cage C atoms affords sterically-crowded *ortho*-carboranes with unprecedentedly long C–C connectivities.

Although it has been appreciated for more than 45 years that *ortho*-carborane, 1,2-*closo*-$C_2B_{10}H_{12}$, has a distorted icosahedral geometry,[1] its accurate structure has been determined only relatively recently. In 1996 Davidson, Wade *et al.*[2] used the acidic nature of the carborane CH units to form a supramolecular dimer with hexamethylphosphoramide, locking the CH units in C–H···O hydrogen bonds and so overcoming the disorder that had frustrated previous attempts to obtain an accurate structure crystallographically; the two independent C–C distances measured at 150 K were 1.629(6) and 1.630(6) Å. Later, Rankin and co-workers[3] redetermined the gas phase structure of *ortho*-carborane by electron diffraction, improving on the accuracy of previous determinations[4] and affording C1–C2 1.624(8) Å, in excellent agreement with the results of a parallel computational study, 1.621 Å.

The C–C distance in *ortho*-carborane can be lengthened to *ca.* 1.8 Å by attaching bulky substituents to the cage C atoms,[5] or to nearly 1.9 Å by incorporating the cage C atoms in suitable exopolyhedral cycles.[6] Alternatively, the C–C distance can be extended *electronically* by π-donor substituents at one cage C atom to distances >2 Å,[7] but such species can be argued to have formal skeletal electron counts in excess of the $(2n + 2)$ (n = no. of vertices) normally associated with *closo* species[8] and so bear closer comparison with $(2n + 3)$ carborane radical anions[9] or $(2n + 4)$ *nido* dianions.[8] The electronic causes for long C–C distances in neutral and anionic *ortho*-carboranes as a function of various substituents have been explored computationally.[10] Herein we report unprecedented lengthening of the C1–C2 connectivity of *ortho*-carborane, to 2.15 Å, and related deformation of the carborane icosahedron by intramolecular steric crowding alone.

When *ortho*-carborane is doubly deprotonated and allowed to react with two equivalents of the substituted fulvene **1** (**a**, R = Me) the known,[11] singly-substituted, product 1-$CMe_2(C_5H_5)$-1,2-*closo*-$C_2B_{10}H_{11}$ is afforded on aqueous work-up, implying that the $CMe_2(C_5H_5)$ substituent is already too bulky to 1,2-disubstitute by this approach. However, double deprotonation of *meta*-carborane, 1,7-*closo*-$C_2B_{10}H_{12}$ (**I**), followed by treatment with two equivalents of **1** readily yields the disubstituted species 1,7-$\{CR_2(C_5H_5)\}_2$-1,7-*closo*-$C_2B_{10}H_{10}$ (**2a**, R = Me; **2b**, R_2 = Pm) (Pm = pentamethylene) on work-up (Scheme 1).‡ In **2** there are two isomeric forms of the cyclopentadienyl ring, with the CH_2 function α or β; by ^1H NMR spectroscopy the ratio α : β is 1 : 2 for **2a** and 2 : 9 for **2b**. Compounds **2** are converted to the corresponding bis-ferrocenyl species 1,7-$(CR_2Fc)_2$-1,7-*closo*-$C_2B_{10}H_{10}$ **3a** and **3b** {Fc = (η-C_5H_4)Fe(η-C_5H_5)} by standard means.

It is well established that 2e reduction of *meta*-carborane followed by reoxidation affords *ortho*-carborane.[12] Similarly, reduction (Na, THF) then reoxidation of compounds **3** produces the crowded substituted *ortho*-carboranes **4a** and **4b**. By this (indirect) method may be prepared *ortho*-carborane derivatives with substantially sterically demanding groups attached to the two cage carbon atoms that are not possible starting from *ortho*-carborane directly.

Crystallographic study§ of **4a** and **4b** reveals the extent of the steric crowding within. Molecules of **4a** have effective C_2 symmetry about an axis from the mid-point of C1–C2 to the mid-point of B9–B12, with the Me groups of the CMe_2Fc substituents interdigitated about this axis and the Fc units oriented away from both the C1/C2 region and the BH cage vertices. The C1–C2 distance is 1.9378(16) Å. In **4b** (Fig. 1) the CPmFc substituent on C2 has an orientation that corresponds to the CMe_2Fc substituent in **4a**, but the other CPmFc substituent (on C1) has rotated so that its Pm group is side-on to the Pm group on C21 not face-on (which presumably would be untenable). Nevertheless, the C1–C2 distance in **4b** is 2.156(4) Å, easily the longest such distance experimentally recorded for a true $(2n + 2)$ *ortho*-carborane derivative. Further evidence for the severe intramolecular crowding in **4b** is the presence of two H···H distances of 2 Å (H12B···H26B 1.995 Å, H12B···H22A 1.997 Å) and distortion of the Fc group on C211 as a result of the forced orientation of the adjacent Pm group; the C211–C215 ring is tilted at C211 (the C21–C211 bond meets the plane at 11.38°) and the two Cp rings on Fe2 subtend a dihedral angle of 11.65°.

As the cage carbon atoms C1 and C2 are progressively forced apart by steric crowding, the boron atoms to which they are both connected, B3 and B6, are pulled together, the B3···B6 separation reducing from 2.886 Å (average) in *ortho*-carborane,[2] to 2.756 Å in **4a** to 2.663 Å in **4b**. Concomitantly, a smaller,

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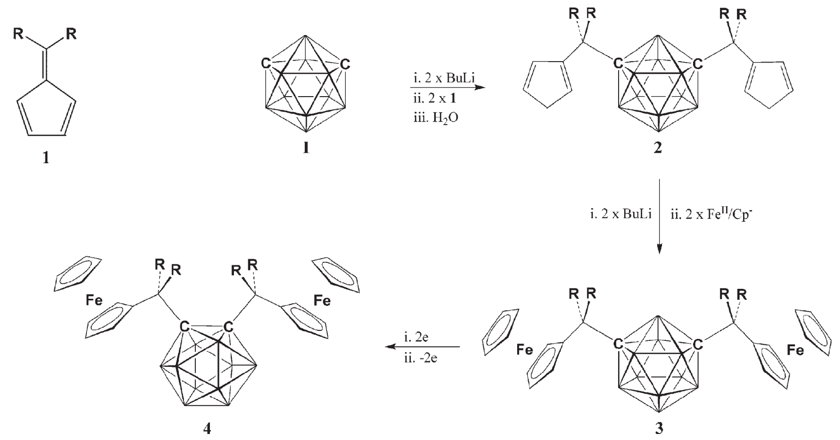

Scheme 1 Synthesis of compounds **2–4** (**a**, R = Me; **b**, R_2 = Pm). For **2** the β,β isomer of the C_5 ring is arbitrarily shown.

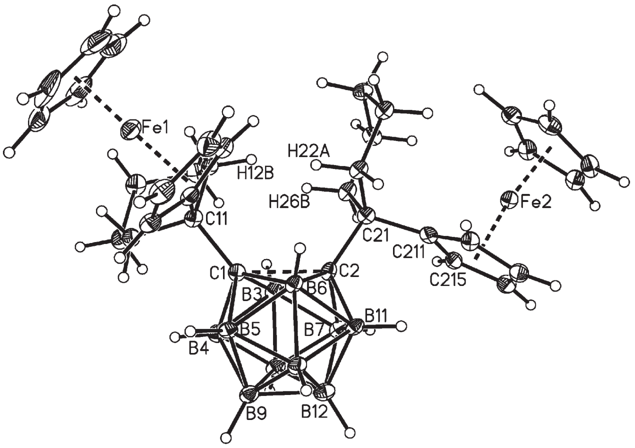

Fig. 1 Perspective view of compound **4b** (50% probability ellipsoids); C1–C2 2.156(4) Å.

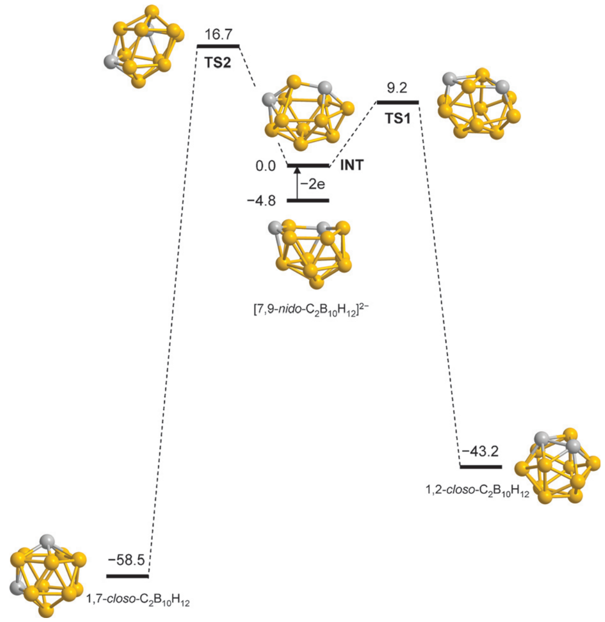

Fig. 2 Computational study of the 2e oxidation of [7,9-*nido*-$C_2B_{10}H_{12}$]^{2}. All energies in kcal mol^{-1}.

second-order, effect is a lengthening of the B3–B8 and B6–B10 connectivities, from (averages¶) 1.766(8) Å in *ortho*-carborane,[2] to 1.794(3) Å in **4a** to 1.818(7) Å in **4b**, to become the longest B–B distances in the last.

Why do the *meta*-carborane derivatives **3** convert to the crowded *ortho*-carborane derivatives **4** on reduction and reoxidation? Why do they not simply reclose on oxidation to the less crowded (and thermodynamically preferred) original *meta*-carborane species? In Fig. 2 are presented the results of a DFT study‖ on the reoxidation of [7,9-*nido*-$C_2B_{10}H_{12}$]$^{2-}$, the product of 2e reduction of *ortho*- (and *meta*-) carborane. Two-electron oxidation of [7,9-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ affords a basket-shaped intermediate 4.8 kcal mol^{-1} above the dianion. This intermediate (**INT**) isomerises to *ortho*-carborane *via* a transition state (**TS1**) with an activation energy of +9.2 kcal mol^{-1}, or, alternatively, isomerises to *meta*-carborane *via* an alternative transition state (**TS2**) with an activation energy of +16.7 kcal mol^{-1}. Clearly, therefore, oxidation of [7,9-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ will preferentially afford *ortho*-carborane over *meta*-carborane. **INT** and **TS2** have been previously characterised by Brown and McKee[13] (*o*-*m*-INT and *o*-*m*-TS2, respectively, in ref. 13) in their computational study of the isomerisation of *ortho*- to *meta*-carborane by a non-TFR (TFR = triangular face rotation) pathway, but **TS1** has not previously been reported. It is significant that **TS1** in this study is considerably more stable than *o*-*m*-TS1 in McKee's study, and thus that the profile from *ortho*- to *meta*-carborane in Fig. 2, with an overall activation energy of 59.9 kcal mol^{-1}, is computed to be more favourable than McKee's non-TFR pathway and comparable with his TFR route.

The deformation of the C1C2B3B6 diamond of *ortho*-carborane in the sterically crowded compounds **4** is reminiscent of that of the C1C2M3B6 unit in semi-pseudo-*closo*[14] and pseudo-*closo*[15] metallacarboranes which we and others first studied a decade or more ago, but this is the first time such a deformation has been described in carboranes. In pseudo-*closo* metallacarboranes there is a pronounced shift to high frequency of $\langle\delta(^{11}B)\rangle$, the weighted average ^{11}B chemical shift, compared to analogous undistorted species. A similar phenomenon is observed here. $\langle\delta(^{11}B)\rangle$ barely changes on metallation from **2a** to **3a** and **2b** to **3b**, lying between −11 and −12 ppm in all cases. However, as *meta* **3a** converts to *ortho* **4a** $\langle\delta(^{11}B)\rangle$ moves 4.3 ppm to high frequency, and as *meta* **3b** converts to the even more distorted *ortho* **4b** the average shift is even greater, 6.5 ppm.

In conclusion, by utilising the fact that *meta*-carboranes can be converted to *ortho*-carboranes by successive reduction and reoxidation, we have prepared unprecedented, sterically-crowded, $(2n + 2)$ skeletal electron *ortho*-carborane derivatives which relieve that crowding by severe structural deformation. We have previously proposed (derivatised) sterically crowded metallacarboranes as potential vehicles by which to study the mechanism(s) of isomerisation of carboranes experimentally, a possibility which relies on the ability of the crowded species to isomerise at relatively low temperatures. However, results so far[16] indicate only limited agreement between theoretical predictions (on carboranes) and experimental results (on metallacarboranes), possibly linked to the greater electronic complexity of metallacarboranes. It may be that our ability now to prepare severely crowded carboranes could revive interest in this area. In this context it is informative to note that *ortho*-carborane **4b** converts to *meta*-carborane **3b** in refluxing toluene.[17]

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Notes and references

‡ *Selected NMR spectroscopic data* ($CDCl_3$, 298 K): for **2a**: ^{1}H: Major (β) isomer; δ 6.42 (m, 1H, CH), 6.30 (m, 1H, CH), 6.23 (m, 1H, CH), 2.87 (m, 2H, CH_2), 1.31* (s, 6H, CH_3). Minor (α) isomer; δ 6.62, 1H, CH), 6.37 (m, 1H, CH), 6.05 (m, 1H, CH), 2.93 (m, 2H, CH_2), 1.31* (s, 6H, CH_3). Relative integrals given are internal and the ratio of α : β is 1 : 2. * = coincident resonance. ^{11}B{^{1}H}: δ −6.4 (2B), −12.0 (6B), −14.2 (2B), $\langle\delta(^{11}\mathrm{B})\rangle$ −11.34.

For **2b**: ^{1}H: Major (β) isomer; δ 6.38 (m, 2H, CH), 6.03 (m, 1H, CH), 2.98 (br m, 2H, CH_2 [C_5H_5]), 2.08 (br d, 2H, CH_2 [Pm]), 1.45 (br m, 8H, CH_2 [Pm]). Minor (α) isomer; δ 6.47 (m, 1H, CH), 6.32 (m, 1H, CH), 6.18 (m, 1H, CH), 2.83 (br m, 2H, CH_2 [C_5H_5]), 1.90 (br d, 2H, CH_2 [Pm]), 1.03 (br m, 8H, CH_2 [Pm]). Relative integrals given are internal and the ratio of α : β is 2 : 9. ^{11}B{^{1}H}: δ −6.6 (2B), −12.3 (6B), −14.7 (2B), $\langle\delta(^{11}\mathrm{B})\rangle$ −11.65.

For **3a**: ^{1}H: δ 4.15 (m, 4H, C_5H_4), 4.10 (s, 10H, Cp), 4.01 (m, 4H, C_5H_4), 1.38 (s, 12H, CH_3). ^{11}B{^{1}H}: δ −6.7 (2B), −12.2 (6B), −14.1 (2B), $\langle\delta(^{11}\mathrm{B})\rangle$ −11.50.

For **3b**: ^{1}H: δ 4.15 (m, 4H, C_5H_4), 4.07 (s, 10H, Cp), 3.98 (m, 4H, C_5H_4), 2.17 (m, 4H, CH_2), 1.90 (m, 8H, CH_2), 1.59 (m, 6H, CH_2), 1.37 (m, 2H, CH_2). ^{11}B{^{1}H}: δ −5.9 (2B), −12.4 (8B), $\langle\delta(^{11}\mathrm{B})\rangle$ −11.12.

For **4a**: ^{1}H: δ 4.24 (m, 4H, C_5H_4), 4.15 (m, 4H, C_5H_4), 4.12 (s, 10H, Cp), 1.87 (s, 12H, CH_3). ^{11}B{^{1}H}: δ −2.6 (2B), −6.6 (4B), −7.9 (2B), −12.6 (2B), $\langle\delta(^{11}\mathrm{B})\rangle$ −7.25.

For **4b**: ^{1}H: δ 4.23 (m, 4H, C_5H_4), 4.19 (m, 4H, C_5H_4), 4.11 (s, 10H, Cp), 2.63 (m, 4H, CH_2), 2.33 (m, 4H, CH_2), 2.24 (m, 4H, CH_2), 1.73 (m, 6H, CH_2), 1.52 (m, 2H, CH_2). ^{11}B{^{1}H}: δ −0.7 (4B), −3.7 (4B), −14.2 (2B), $\langle\delta(^{11}\mathrm{B})\rangle$ −4.61.

§ *Crystal data*: for **2a** (mixture of α,α; β,β and α,β isomers): $C_{18}H_{32}B_{10}$, $M = 356.54$, monoclinic, $P2$, $a = 14.804(3)$, $b = 10.428(3)$, $c = 27.942(6)$ Å, $\beta = 100.501(15)°$, $V = 4241.3(17)$ Å^3, $Z = 8$, $D_c = 1.117$ Mg m^{-3}, $\mu = 0.055$ mm^{-1}, $F(000) = 1520$. $\theta_{max} = 24.69°$. 7586/59 225 independent reflections ($R_{int} = 0.1145$), $R_1 = 0.0621$, $wR_2 = 0.1403$, $S = 1.016$ for data with $I > 2\sigma(I)$.

For **2b**: $C_{24}H_{40}B_{10}$ (β,β isomer), $M = 436.66$, monoclinic, Cc, $a = 21.315(4)$, $b = 8.1515(16)$, $c = 15.649(3)$ Å, $\beta = 112.03(3)°$, $V = 2520.6(9)$ Å^3, $Z = 4$, $D_c = 1.151$ Mg m^{-3}, $\mu = 0.058$ mm^{-1}, $F(000) = 936$, $\theta_{max} = 26.12°$. 2424/13998 reflections ($R_{int} = 0.0399$), $R_1 = 0.0582$, $wR_2 = 0.1515$, $S = 1.152$, $I > 2\sigma(I)$.

For **3a**: $C_{28}H_{40}B_{10}Fe_2$, $M = 596.40$, triclinic, $P - 1$, $a = 10.187(2)$, $b = 12.513(3)$, $c = 13.387(2)$ Å, $\alpha = 96.618(8)$, $\beta = 112.070(7)$, $\gamma = 112.308(8)°$, $V = 1395.2(5)$ Å^3, $Z = 2$, $D_c = 1.420$ Mg m^{-3}, $\mu = 1.060$ mm^{-1}, $F(000) = 620$, $\theta_{max} = 28.03°$. 6521/25611 reflections ($R_{int} = 0.0533$), $R_1 = 0.0411$, $wR_2 = 0.0893$, $S = 1.018$, $I > 2\sigma(I)$.

For **3b**: $C_{34}H_{48}B_{10}Fe_2$, $M = 676.52$, triclinic, $P - 1$, $a = 9.808(8)$, $b = 12.947(10)$, $c = 14.060(11)$ Å, $\alpha = 73.99(2)$, $\beta = 78.525(15)$, $\gamma = 70.027(18)°$, $V = 1601(2)$ Å^3, $Z = 2$, $D_c = 1.403$ Mg m^{-3}, $\mu = 0.933$ mm^{-1}, $F(000) = 708$, $\theta_{max} = 28.11°$. 7594/11459 reflections ($R_{int} = 0.0356$), $R_1 = 0.0471$, $wR_2 = 0.0984$, $S = 1.008$, $I > 2\sigma(I)$.

For **4a**: $C_{28}H_{40}B_{10}Fe_2$, $M = 596.40$, monoclinic, $P2_1/n$, $a = 8.7366(14)$, $b = 16.920(3)$, $c = 19.641(3)$ Å, $\beta = 100.783(7)°$, $V = 2852.1(8)$ Å^3, $Z = 4$, $D_c = 1.389$ Mg m^{-3}, $\mu = 1.037$ mm^{-1}, $F(000) = 1240$, $\theta_{max} = 32.63°$. 9673/71 682 reflections ($R_{int} = 0.0462$), $R_1 = 0.0323$, $wR_2 = 0.0760$, $S = 1.034$, $I > 2\sigma(I)$.

For **4b**: $C_{34}H_{48}B_{10}Fe_2$, $M = 676.52$, monoclinic, $P2_1/n$, $a = 15.1029(17)$, $b = 15.4587(19)$, $c = 15.6930(18)$ Å, $\beta = 118.556(6)°$, $V = 3218.2(7)$ Å^3, $Z = 4$, $D_c = 1.396$ Mg m^{-3}, $\mu = 0.928$ mm^{-1}, $F(000) = 1416$, $\theta_{max} = 25.14°$. 5648/47 044 reflections ($R_{int} = 0.0885$), $R_1 = 0.0492$, $wR_2 = 0.1275$, $S = 1.053$, $I > 2\sigma(I)$.

¶ E.s.d.'s of the mean of N independent observations given by the expression $\sigma^2 = (\sigma_1{}^2 + \sigma_2{}^2)$ if $N = 2$, or $\sigma^2 = \{\sum_{i=1}^{i=N}(\chi^i - \bar{\chi})^2\}/(N - 1)$ where χ^i is the ith and $\bar{\chi}$ the mean value if $N > 2$.

‖ Calculations run with Gaussian 03 with the BP86 functional and 6-31G** basis sets. See ESI† for full details.†

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