Electronic Supplementary Material (ESI) for Dalton Transactions

Asymmetric 1,8/13,2,*x*-$M_2C_2B_{10}$ 14-vertex metallacarboranes by direct electrophilic insertion reactions; the VCD and BHD methods in critical analysis of cage C atom positions

Amelia McAnaw, Maria Elena Lopez, David Ellis, Georgina M. Rosair and Alan J. Welch

Electronic Supplementary Information

Table S1 Crystallographic data for compound **6** (original and redetermination)

	6 (original)	**6** (redetermination)
Formula	$C_{12}H_{22}B_{10}Co_2$	$C_{12}H_{22}B_{10}Co_2$
M	392.26	392.26
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbca*
a / Å	14.807(3)	14.8157(18)
b / Å	13.264(3)	13.3179(18)
c / Å	16.769(3)	16.818(2)
α (°)		
β (°)		
γ (°)		
U / Å^3	3293.4(12)	3318.4(8)
Z	8	8
F(000) /e	1584	1584
D_{calc} / Mg m^{-3}	1.582	1.570
μ(Mo-K$_\alpha$) / mm^{-1}	2.001	1.986
θ_{max} (°)	22.27	35.17
Data measured	29332	98827
Unique data	2036	7274
Data $\geq 2\sigma$(I)	1103	6076
R_{int}	0.2121	0.0424
R, wR_2 (obs. data)	0.0560, 0.1312	0.0323, 0.0791
S	1.048	1.024
Variables	253	253
E_{max}, E_{min} / e Å^{-3}	1.122, –1.202	0.906, –1.190

Table S2 Vertex-to-Centroid distances (Å) in compound **6** [a]

Vertex	**6** (original)		**6** (redetermination)	
1	2.035(5)	Co1	2.0307(8)	Co1
2	<u>1.776(15)</u>	C2	<u>1.8084(17)</u>	C2
3	1.867(15)	B7	1.9005(19)	B7
4	1.900(18)	B6	1.917(2)	B6
5	<u>1.764(17)</u>	C5	<u>1.797(3)</u>	C5
6	1.896(15)	B4	1.9021(18)	B4
7	1.914(14)	B3	1.9220(18)	B3
8	1.857(14)	B13	1.8809(18)	B13
9	1.819(16)	B12	1.859(2)	B12
10	1.822(18)	B11	1.900(2)	B11
11	1.842(15)	B10	1.877(2)	B10
12	1.893(16)	B9	1.909(2)	B9
13	2.359(6)	Co8	2.3723(8)	Co8
14	1.603(15)	B14	1.5851(18)	B14

[a] Vertex numbers (left column) refer to the model before the C atoms were assigned; <u>underlined</u> entries identify C vertices; atom labels to the right of each entry are the final atom identifiers, shown in Figs. 2-7.

Conclusion

Even for the original determination the two VCDs from C atoms are measurably shorter than all VCDs from B atoms. Taking the longer VCD(C), 1.776(15) Å, and the shortest VCD(B), 1.819(16) Å, the difference, 0.043 Å, is ca. 2σ (where $\sigma = [\sigma_1^2 + \sigma_2^2]^{0.5} = 0.022$ Å).

Table S3 Vertex−H distances (Å) in compound **6** [a]

Vertex	**6** (original)		**6** (redetermination)	
2	<u>0.47(12)</u>	0.78(10)	<u>0.30(3)</u>	0.99(2)
3	1.26(10)	1.18(10)	1.13(2)	1.11(2)
4	1.27(10)	1.30(10)	1.13(2)	1.11(2)
5	<u>0.53(13)</u>	1.05(12)	<u>0.17(3)</u>	1.03(2)
6	1.00(11)	0.99(11)	1.06(2)	1.06(2)
7	1.17(10)	1.13(10)	1.12(2)	1.12(2)
8	1.07(10)	1.04(10)	1.07(2)	1.07(2)
9	1.23(11)	1.21(11)	1.07(2)	1.08(2)
10	0.90(13)	0.96(12)	1.08(3)	1.07(2)
11	1.07(11)	1.05(11)	1.07(2)	1.08(2)
12	1.16(10)	1.17(10)	1.10(2)	1.12(2)
14	0.79(11)	0.80(10)	1.08(2)	1.08(2)

[a] For each structure the left hand entry is the vertex−H distance for the "all-B" model (where all non-metal vertices are assigned as B atoms); <u>underlined</u> entries identify C vertices. The right hand entry is the vertex−H distance following assignment of the cage C atoms.

Conclusion

Even for the original determination the two BHDs from C atoms are measurably shorter than all BHDs from B atoms. Taking the longer BHD(C), 0.53(13) Å, and the shortest VCD(B) excluding vertex 14 (which is exceedingly unlikely to be a C atom because it is of degree-6, see manuscript), 0.90(13) Å, the difference, 0.37 Å, is ca. 2σ (where $\sigma = [\sigma_1^2 + \sigma_2^2]^{0.5} = 0.18$ Å).

Table S4 U_{eq} values (Å^2) for non-metal vertices refined as B in compound **6** [a]

Vertex	**6** (original)	**6** (redetermination)
2	0.019(4)	0.0096(3)
3	*0.041(4)*	*0.0166(3)*
4	0.050(4)	0.0206(3)
5	0.042(5)	0.0185(3)
6	0.048(4)	0.0192(3)
7	*0.033(3)*	*0.0151(3)*
8	*0.032(3)*	*0.0155(3)*
9	0.050(4)	0.0200(3)
10	0.070(5)	0.0241(4)
11	0.051(4)	0.0223(3)
12	0.045(4)	0.0188(3)
14	*0.042(4)*	*0.0169(3)*

[a] Vertex numbers (left column) refer to the model before the C atoms were assigned; underlined entries indicate C vertices identified by the VCD and BHD methods. *Italicised* entries show U_{eq} values for genuine B atoms that are ≤ those of atoms which are actually C.

Conclusion

Even though the U_{eq} values for the same vertex atom are all reduced and the e.s.d.s on these values are an order of magnitude smaller in the redetermination, the basic conclusion from analysis of the U_{eq} values is exactly the same for the original determination as for the redetermination – whilst the lowest U_{eq} is for vertex 2 (which is a C atom) the second lowest U_{eq} is not for vertex 5 (the other C atom). U_{eq} values for vertices 3, 7, 8 and 14 are all at least as small as that for vertex 5.

Overall Conclusion from Tables S2-S4

The VCD and BHD methods work perfectly well in identifying cage C atoms even if the overall crystallographic data is relatively imprecise. Equally, the U_{eq} method is as poor a method for identifying cage C atoms using very precise crystallographic data as it is when the data is less precise.

Table S5 Intermolecular contact distances (Å) of potential significance in compounds **1-6**

Compound	Atom A	Atom B	Symmetry operation B	Distance	Type of contact
1	H2	H10	1+x, +y, +z	2.165	dihydrogen
3	H2C	H14C	½–x, –½+y, z	2.181	dihydrogen
4	C84	C85	2–x, 1–y, 1–z	3.172	Cp π stacking
4	H2	H11	1+x, +y, +z	2.218	dihydrogen
5	H2	H10	1+x, +y, +z	2.165	dihydrogen
5	H4	H6	–x, –½+y, –z	2.289	dihydrogen
6	H2	H14	½–x, –½+y, z	2.217	dihydrogen
6	H14A	C83	½–x, –y, –½+z	2.589	H(Cp)…C(Cp)

Although in the crystal structure of compound **2** the CH unit at 1½-x, –½+y, ½–z appears to be directed towards O31 the O…H distance is 2.857 Å, greater than the sum of the van der Waals radii for these atoms.