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Electronic Supplementary Information

Unprecedented steric deformation of *ortho*-carborane

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1. Synthetic Procedures

Synthesis of **2a**: 2 g (13.9 mmol) *meta*-carborane was dissolved in 40 mL dry diethyl ether. 11.6 mL of 2.5 M solution of *n*-BuLi in hexanes (29.1 mmol) were added at 0^{o}C and the mixture allowed to warm to RT with stirring overnight. 4.5 mL (37.4 mmol) of freshly distilled 6,6-dimethyfulvene as an ether (5 mL) solution were added dropwise and the mixture heated to reflux for 4 h. The mixture was extracted into diethyl ether after aqueous work-up at 0^{o}C. Removal of solvent followed by recrystallisation in ethanol afforded colourless crystals. Yield 2.80 g (56%). Mass spectrometry: *m/z* envelope centred on 357 (M^{+}). Microanalysis: Theoretical C, 60.63 H, 9.05. Found C, 60.10 H, 9.11%.

Synthesis of **2b**: 2 g (13.9 mmol) *meta*-carborane was dissolved in 40 mL dry diethyl ether. 11.6 mL of 2.5 M solution of *n*-BuLi in hexanes (29.1 mmol) were added at 0^{o}C and the mixture allowed to warm to RT with stirring overnight. 5.13 g (35.1 mmol) of freshly distilled 6,6-pentamethylenefulvene as an ether (5 mL) solution were added dropwise and the mixture heated to reflux for 20 h. The mixture was extracted into diethyl ether after aqueous work-up at 0^{o}C. Removal of solvent followed by recrystallisation in ethanol afforded colourless crystals. Yield 3.20 g (53%). Mass spectrometry: *m/z* envelope centred on 437 (M^{+}). Microanalysis: Theoretical C, 66.01 H, 9.48. Found C, 66.18 H, 9.48%.

Synthesis of **3a**: 0.5 g (1.4 mmol) **2a** was dissolved in THF and deprotonated with 1.2 mL of 2.5 M solution of *n*-BuLi in hexanes (3.0 mmol) at 0^{o}C. 1.8 g (14.2 mmol) $FeCl_2$ then 7.5 mL of 2.0 M solution of NaCp in THF (15.0 mmol) were added to this solution which had previously been frozen at -196^{o}C (LN_2), allowed to warm to RT overnight then heated to reflux for 2 h. After removal of solvent the residue was taken up in DCM and filtered through silica to give a dark orange solution. This was evaporated and the solid was washed with cold petroleum ether to leave a yellow solid. Yield 209 mg (25%). Mass spectrometry: *m/z* envelope centred on 596 (M^{+}). Microanalysis: Theoretical C, 56.39 H, 6.76. Found C, 55.96 H, 6.73%.

Synthesis of **3b**: 0.5 g (1.15 mmol) **2b** was dissolved in THF and deprotonated with 0.96 mL of 2.5 M solution of *n*-BuLi in hexanes (2.4 mmol) at 0^{o}C. 1.46 g (11.5 mmol) $FeCl_2$ then 6.5 mL of 2.0 M solution of NaCp in THF (13.0 mmol) were added to this solution which had previously been frozen at -196^{o}C (LN_2), allowed to warm to RT overnight then heated to reflux for 2 h. After removal of solvent the residue was taken up in DCM and filtered through silica to give a dark orange solution. This was evaporated and the solid was washed with cold petroleum ether to leave an orange solid. Preparative TLC in 3:1 petroleum ether:DCM afforded the orange product. Yield 230 mg (29%). Mass spectrometry: *m/z* envelope centred on 676 (M^{+}). Microanalysis: Theoretical C, 60.36 H, 7.15. Found C, 61.07 H, 6.91%.

Synthesis of **4a**: 100 mg (0.167 mmol) **3a** was dissolved in dry degassed THF and added to this were 40 mg (1.74 mmol) Na metal and a few crystals of naphthalene. The solution was left stirring at room temperature for 36h. The excess Na was removed and the solution left open to the air for 20 mins. Preparative TLC in 3:1 petrol:DCM afforded a red compound. Yield 73 mg (73%). Mass spectrometry: *m/z* envelope centred on 597 (M^{+}). Microanalysis: Theoretical C, 56.39 H, 6.76. Found C, 56.12 H, 6.79%.

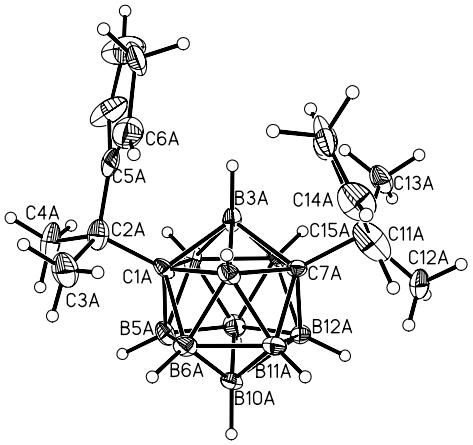
Synthesis of **4b**: 100 mg (0.147 mmol) **3b** was dissolved in dry degassed THF and added to this were 46 mg (2.0 mmol) Na metal and a few crystals of naphthalene. The solution was left stirring at room temperature for 36h. The excess Na was removed and the solution left open to the air for 20 mins. Preparative TLC in 2:1 petroleum ether:DCM afforded a deep purple compound. Yield 43 mg (43%). Mass spectrometry: *m/z* envelope centred on 677 (M^{+}). Microanalysis: Theoretical C, 60.63 H, 7.15. Found C, 59.52 H, 7.07%.

2. Additional Crystallographic Information

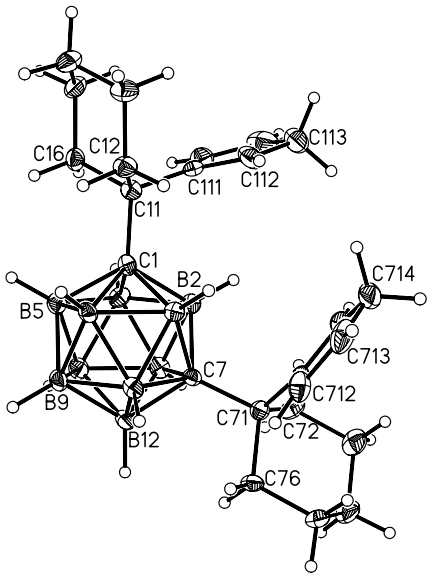
Intensity data were collected from single crystals on a Bruker X8 APEX2 diffractometer, with crystals mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Empirical absorption corrections were made using the program SADABS[15]. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL program suite.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystallographic experiments were routine except in the case of compound **2a**. Crystals of **2a** were poor quality and relatively weakly diffracting and the space group was ambiguous. Solution and refinement were also attempted in *P*2/*n* but anisotropic refinement in this space group gave many more non-positive definite atoms with R_1 = 0.1882 and R(int) = 0.158, where as the *P*2 model had R_1 = 0.0621 and R(int) = 0.140. Although the C−C bond esd's were slightly lower in the *P*2/*n* model (0.011 cf 0.014 Å) this reflects the fact that there were many more variables in *P*2. *P*2 was the final choice because of the greater stability of the anisotropic refinement.

15 SADABS, V2.05; G. M. Sheldrick, University of Göttingen, Germany, 2005.
16 SHELXTL, V6.10; Bruker-AXS, Madison, WI, USA, 2000.

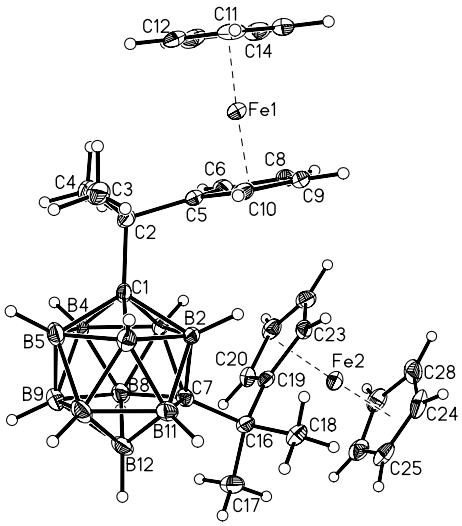
View of **2a**



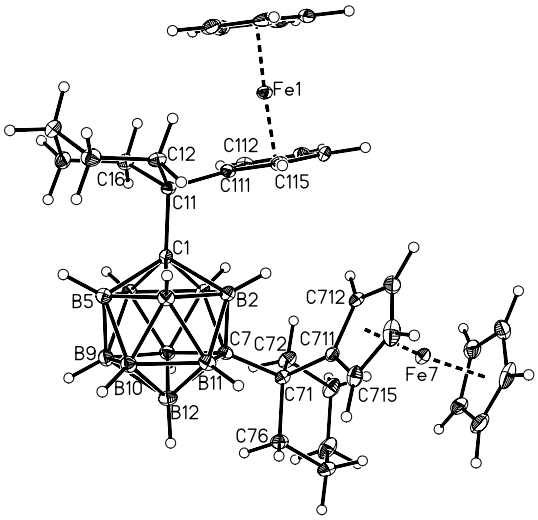
View of **2b**



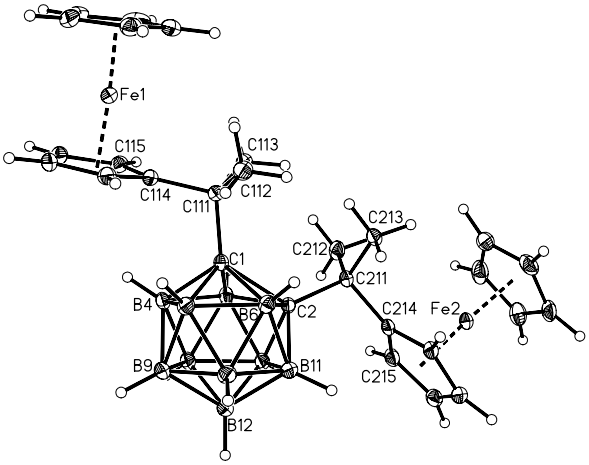
View of **3a**



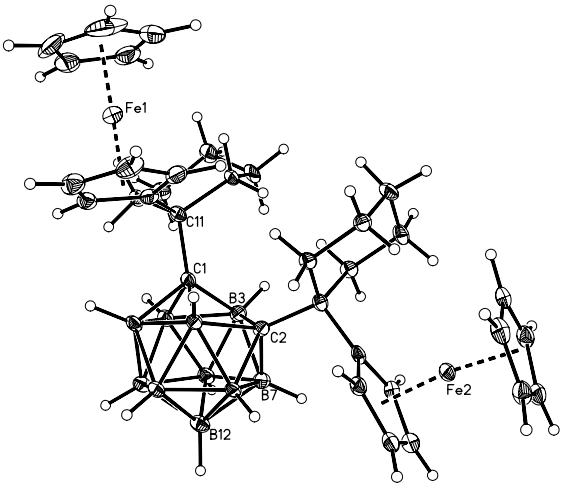
View of **3b**



View of **4a**



View of **4b**



3. Computational Details

Gaussian 03, Revision C.02[1] employing the BP86 functional.[2] 6-31G** basis sets were used for B, C and H atoms.[3] Geometries were optimised without constraints. Local minima and transition states were confirmed as such via analytical frequency calculations and transition states further characterised through IRC calculations[4] and shown to link to intermediates.

1 Gaussian 03, Revision C.02; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

2 (a) H. L. Schmider and A. D. Becke, *J. Chem. Phys.*, 1998, **108**, 9624; (b) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

3 (a) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (b) P. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

4 (a) C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.* 1990, **94**, 5523; (b) C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.* 1989, **90**, 2154.

1,7-*closo*-$C_2B_{10}H_{12}$			1,2-*closo*-$C_2B_{10}H_{12}$		
BP86 Energy =	-332.095017		BP86 Energy =	-332.070551	
Enthalpy 0K =	-331.921948		Enthalpy 0K =	-331.898064	
Enthalpy 298K =	-331.913073		Enthalpy 298K =	-331.889094	
Free Energy =	-331.952799		Free Energy =	-331.928965	
C	0.00005	-0.80480 1.30869	C	0.00000	-0.81751 -1.28029
B	-0.00003	0.90875 1.43683	B	-1.46144	-0.00006 -0.85692
B	0.89930	1.46605 0.00056	B	-1.45739	0.00007 0.91589
B	-0.89943	1.46597 0.00058	B	-0.89565	1.44519 0.02608
B	-1.45125	0.01761 0.88934	C	0.00000	0.81731 -1.28042
B	-1.45126	0.01831 -0.88930	B	0.89565	1.44519 0.02608
B	-0.00006	0.90987 -1.43612	B	-0.00000	0.89495 1.46911
B	1.45124	0.01844 -0.88932	B	0.00000	-0.89473 1.46925
B	0.89731	-1.41530 -0.00056	B	0.89566	-1.44519 0.02629
B	1.45126	0.01774 0.88931	B	-0.89565	-1.44519 0.02629
B	-0.89718	-1.41538 -0.00054	B	1.46144	-0.00006 -0.85692
C	0.00002	-0.80378 -1.30932	B	1.45739	0.00007 0.91589
H	-0.00004	1.40885 2.52012	H	-2.34529	-0.00013 -1.65542
H	-1.54083	2.47405 0.00098	H	-1.48905	2.46631 -0.14342
H	-2.40967	-0.08389 1.59194	H	0.00000	1.29804 -2.26041
H	1.54061	2.47419 0.00095	H	-2.49431	0.00012 1.50992
H	-2.40970	-0.08265 -1.59196	H	1.48904	2.46631 -0.14342
H	2.40971	-0.08367 1.59190	H	-1.48904	-2.46633 -0.14304
H	-0.00009	1.41082 -2.51902	H	-0.00000	1.54602 2.47166
H	0.00009	-1.39549 2.22727	H	0.00000	-1.29838 -2.26022
H	2.40968	-0.08243 -1.59201	H	0.00000	-1.54564 2.47190
H	1.43462	-2.47736 -0.00098	H	1.48905	-2.46633 -0.14304
H	-1.43440	-2.47749 -0.00096	H	2.34529	-0.00012 -1.65542
H	0.00004	-1.39374 -2.22836	H	2.49431	0.00012 1.50992

$[7,9\text{-}nido\text{-}C_2B_{10}H_{12}]^{2-}$			**INT**		
BP86 Energy =	-332.009356		BP86 Energy =	-332.001741	
Enthalpy 0K =	-331.845583		Enthalpy 0K =	-331.833448	
Enthalpy 298K =	-331.835395		Enthalpy 298K =	-331.822847	
Free Energy =	-331.877620		Free Energy =	-331.865992	
B	0.66249	0.09049 1.45877	B	-0.16102	-1.30342 0.90807
B	0.22478	-1.46738 0.80603	B	-1.04639	0.13749 1.34822
B	-1.09716	-0.13817 1.05423	B	0.92053	0.10875 1.28909
B	-0.08738	1.53010 0.77177	B	1.35916	-1.25198 -0.00000
B	1.49234	1.06268 0.16542	B	-0.16103	-1.30342 -0.90806
B	1.66884	-0.69319 0.16920	B	-1.63361	-0.93303 0.00000
B	0.22990	1.57871 -0.95146	B	0.92052	0.10875 -1.28910
B	-1.45310	1.23671 -0.42875	B	2.13899	0.22496 -0.00000
B	1.08607	0.12349 -1.36458	B	-1.04639	0.13748 -1.34822
C	0.50252	-1.35106 -0.85721	C	-1.73985	0.69784 0.00000
B	-1.09547	-1.45465 -0.48257	B	-0.48307	1.64752 -0.00000
C	-1.96468	-0.19774 -0.47320	C	1.04941	1.32234 -0.00000
H	0.37676	2.66843 -1.49342	H	1.32056	0.34031 -2.39283
H	-2.29129	2.13494 -0.35456	H	3.30001	0.49352 -0.00000
H	-3.05285	-0.36411 -0.36117	H	1.58003	2.28049 0.00000
H	-1.61918	-2.56408 -0.50107	H	-0.79152	2.80743 -0.00000
H	0.88692	-2.26898 -1.32979	H	-2.69694	1.22162 0.00000
H	1.88338	0.06459 -2.29427	H	-1.51162	0.38154 -2.41918
H	0.96890	0.10291 2.63373	H	-0.15784	-2.21027 1.69255
H	0.31822	-2.51135 1.41588	H	-1.51161	0.38155 2.41918
H	2.72769	-1.26705 0.33036	H	-2.63547	-1.58089 0.00000
H	2.49242	1.71835 0.40261	H	-0.15784	-2.21027 -1.69255
H	-1.80391	-0.24855 2.03673	H	1.32057	0.34031 2.39282
H	-0.27061	2.48378 1.50717	H	2.04589	-2.23199 -0.00000

TS1		**TS2**	
BP86 Energy =	-331.987041	BP86 Energy =	-331.975156
Enthalpy 0K =	-331.819946	Enthalpy 0K =	-331.808186
Enthalpy 298K =	-331.810092	Enthalpy 298K =	-331.798217
Free Energy =	-331.851693	Free Energy =	-331.839961
Neg. Frequency =	-170.4	Neg. Frequency =	-348.0
B	0.66454 1.52786 0.39581	B	-0.88913 1.47502 0.49095
B	1.38176 0.03211 1.10434	H	-0.81676 2.59471 0.91066
B	-0.30686 0.31932 1.43525	B	-1.43049 -0.07933 1.03298
B	-1.09871 1.38315 0.15220	H	-2.16336 -0.26244 1.96029
B	0.04958 1.05113 -1.19803	B	-0.26899 0.35484 -1.41561
B	1.76795 0.60046 -0.57582	H	-0.53833 0.68326 -2.53757
B	-1.36503 0.08841 -1.11027	B	0.84120 1.47567 -0.50228
B	-1.95708 -0.03082 0.59400	H	1.07266 2.59728 -0.83432
B	0.07038 -0.95990 -1.12806	C	-0.28240 -1.27643 0.71987
C	1.54967 -0.92199 -0.32392	H	-0.42857 -2.19701 1.29001
B	0.38118 -1.37317 0.69349	B	0.29764 -1.37958 -0.86389
C	-1.18781 -1.24310 0.02540	H	0.42381 -2.43740 -1.40242
H	-2.15605 -0.01445 -1.99913	B	0.26410 0.33816 1.42558
H	-3.05968 -0.04167 1.04622	H	0.47298 0.42690 2.60035
H	-1.66900 -2.22502 -0.05534	B	1.43234 -0.08266 -1.06859
H	0.48487 -2.43992 1.22476	H	2.32429 -0.10314 -1.86163
H	2.33164 -1.66302 -0.50744	B	-1.89411 0.68191 -0.51877
H	0.10779 -1.74101 -2.03553	H	-2.90099 0.98710 -1.08259
H	1.03285 2.62838 0.68891	B	-1.40137 -0.95503 -0.55190
H	2.19810 -0.07021 1.96957	H	-2.11532 -1.84105 -0.91769
H	2.76665 1.06637 -1.03438	B	1.36645 -0.96270 0.51665
H	0.18927 1.64980 -2.22687	H	2.13610 -1.72598 1.01431
H	-0.62801 0.24874 2.58921	C	1.66988 0.61513 0.48116
H	-1.70820 2.39976 0.31663	H	2.62041 0.91413 0.92884