Supplementary Material (ESI) for Chemical Communications

Carborane Radical Anions: Spectroscopic and Electronic Properties of a Carborane Radical Anion with a 2n+3 Skeletal Electron Count

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Supplementary Information

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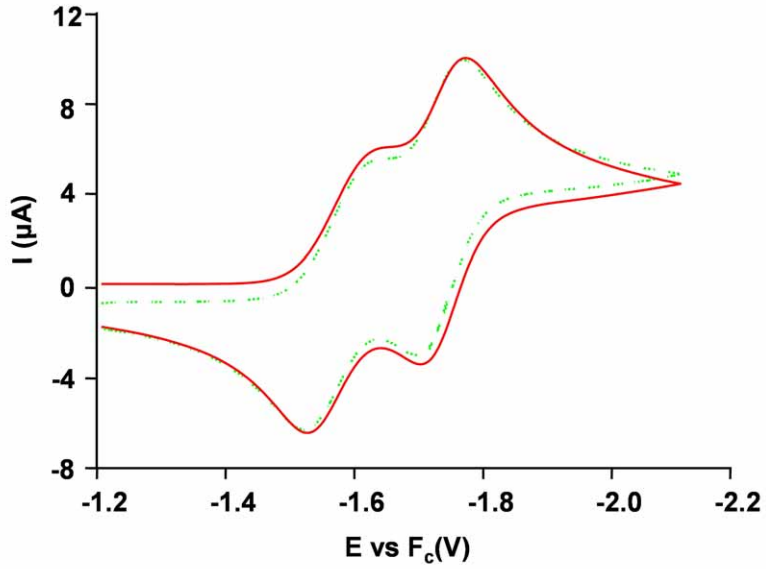


Figure S1. Experimental (green) and simulated (red) cyclic voltammograms (100 mV/s, 3M KCl calomel electrode, glassy carbon working electrode, Pt wire auxillary, Fc/Fc^+ = 0.395 V) of **1** in MeCN / 0.1M NBu_4PF_6.

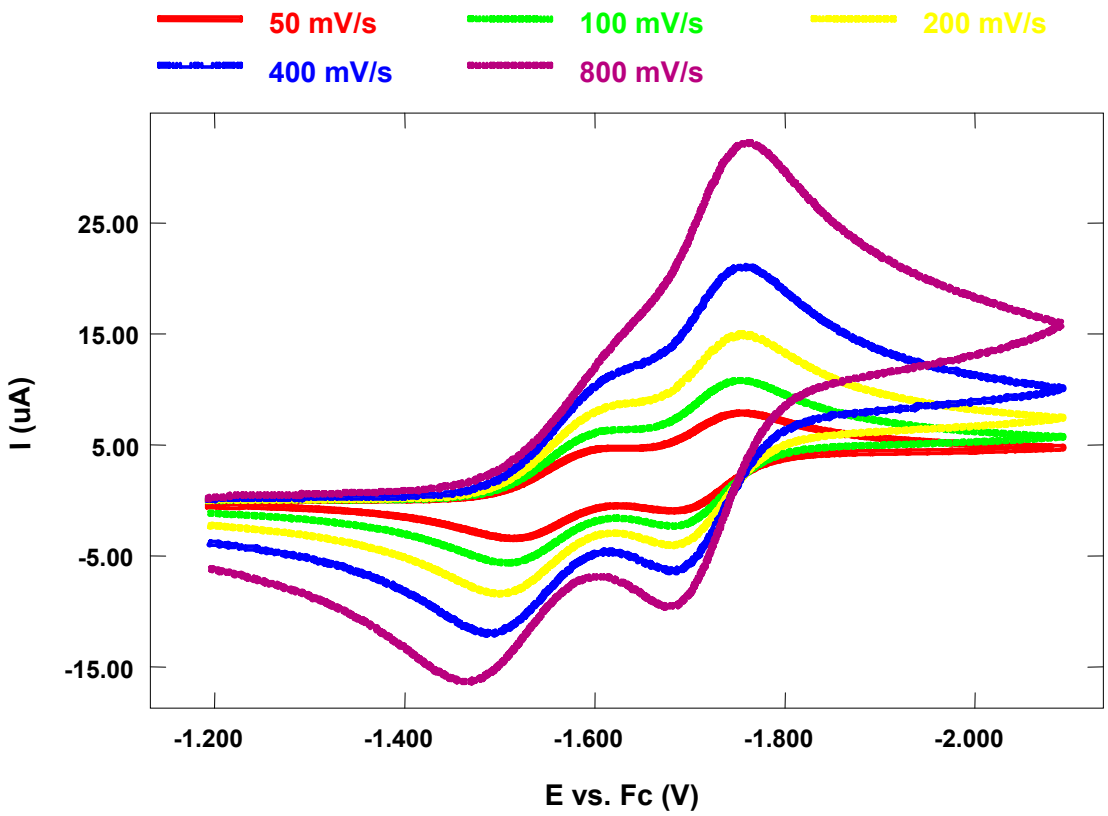
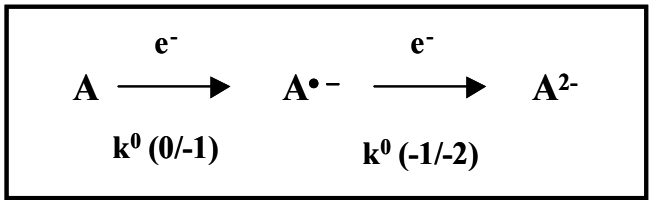


Figure S2. CV at scan rates of 0.05, 0.1, 0.2, 0.4 and 0.8 V/s of 1,2-diphenyl-*ortho*-carborane (**1**) in MeCN / 0.1M NBu_4PF_6 at a GC electrode.

Table S1. Cyclovoltammetry values, in MeCN at 0.2 V/s, for 1-(4-XC_6H_4)-2-Ph-1,2-$C_2B_{10}H_{10}$.

X	E_p^c (V)	E_p^a (V)	$E_{1/2}$ (V)	ΔE_p (mV)
H(**1**)	–1.63	–1.50	–1.56	123
	–1.76	–1.68	–1.73	75
F	–1.61	–1.48	–1.53	125
	–1.72	–1.65	–1.69	71
NMe_2	–1.70	–1.62	–1.66	84
	–1.82	–1.75	–1.79	72
NH_2	–1.71	–1.61	–1.65	95
	–1.82	–1.75	–1.79	74
OMe	–1.65	–1.55	–1.60	98
	–1.78	–1.71	–1.75	72
OH	–1.66	–1.57	–1.61	90
	–1.78	–1.71	–1.75	70

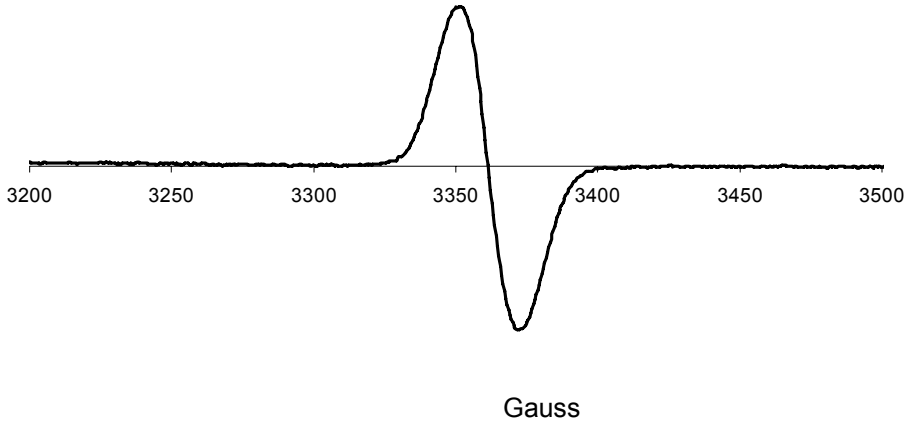
Table S2. Kinetic parameters for 1-(4-XC_6H_4)-2-Ph-1,2-$C_2B_{10}H_{10}$ based on the simulated simple EE mechanism



X	k^0(0/–1) (cm/s)	k^0(–1/–2) (cm/s)	α(0/–1)	α(–1/–2)
NMe_2	$2.0\cdot10^{-2}$	$1.0\cdot10^{-1}$	0.4	0.3
NH_2	$1.2\cdot10^{-2}$	$1.1\cdot10^{-1}$	0.4	0.4
OMe	$1.2\cdot10^{-2}$	$5.0\cdot10^{-2}$	0.4	0.4
OH	$2.2\cdot10^{-2}$	$1.6\cdot10^{-1}$	0.7	0.4
H	$4.0\cdot10^{-3}$	$3.8\cdot10^{-2}$	0.4	0.35
F	$6.0\cdot10^{-3}$	$4.0\cdot10^{-2}$	0.35	0.3

Figure S3 EPR spectrum of $\mathbf{1}^-$ as potassium salt in solid state**.**

Bruker ESP 300E instrument, microwave frequency 9.434 GHz, gain $5x10^4$, modulation amplitude 1.0 Gauss, modulation frequency 100 KHz, sweep time 21s, 64 scans.



NMR data for **1** in d_8-THF

^{11}B (128 MHz, ppm): -2.8 (d, 2B), -9.3 (d, 4B), -10.8 (d, 2B), -13.1 (d, 2B)

$^1H\{^{11}B\}$ (400 MHz, ppm): 7.55 (d, 4H), 7.28 (t, 2H), 7.20 (t, 4H), 3.36 (s, 2H, BH), 2.55 (s, 6H, BH), 2.37 (s, 2H, BH)

$^{13}C\{^1H\}$ (100 MHz, ppm): 130.9, 130.8, 130.4, 128.4, 85.8 (br, cage C)

NMR data for $\mathbf{1}^{2-}$ as sodium salt in d_8-THF

^{11}B (128 MHz, ppm): 3.74 (d, 2B), -11.2 (d, 2B), -17.7 (d, 4B), -30.3 (d, 2B)

$^1H\{^{11}B\}$ (400 MHz, ppm): 7.33 (d, 4H), 6.90 (t, 4H), 6.67 (t, 2H), 3.38 (s, 2H, BH), 2.42 (s, 2H, BH), 1.28 (s, 4H, BH), 0.38 (s, 2H, BH)

$^{13}C\{^1H\}$ (100 MHz, ppm): 154.7, 126.9, 126.0, 120.0, 81.2 (br, cage C)

Computational Details

All computations were carried out using the GAUSSIAN03 package.[1] The geometries of 1,2-Ph_2-1,2-$C_2B_{10}H_{10}$ (**1**) and [1,2-Ph_2-1,2-$C_2B_{10}H_{10}$]$^{-\cdot}$ ([**1**]$^-$) were optimised without symmetry constraints at the B3LYP/6-31G* level of theory. Frequency calculations on these geometries revealed no imaginary frequencies. The starting geometry used for **1** and [**1**]$^-$ was the X-ray crystal structure of **1**.[2] Other starting geometries of the radical anion [1,2-Ph_2-1,2-$C_2B_{10}H_{10}$]$^{-\cdot}$ based on open-face geometries gave minima with energies much higher than the optimised geometry of [**1**]$^-$ discussed here. TD-DFT computations were carried out at the B3LYP/6-31G* level of theory.

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, 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. Z.G. Lewis and A.J. Welch, *Acta Cryst. C*, 1993, **49**, 705.

Figure S4. Simulated IR spectra (upper) for neutral **1** and radical anion [**1**]$^{-}$ compared with experimental (lower i.e. Figure 1 in manuscript)

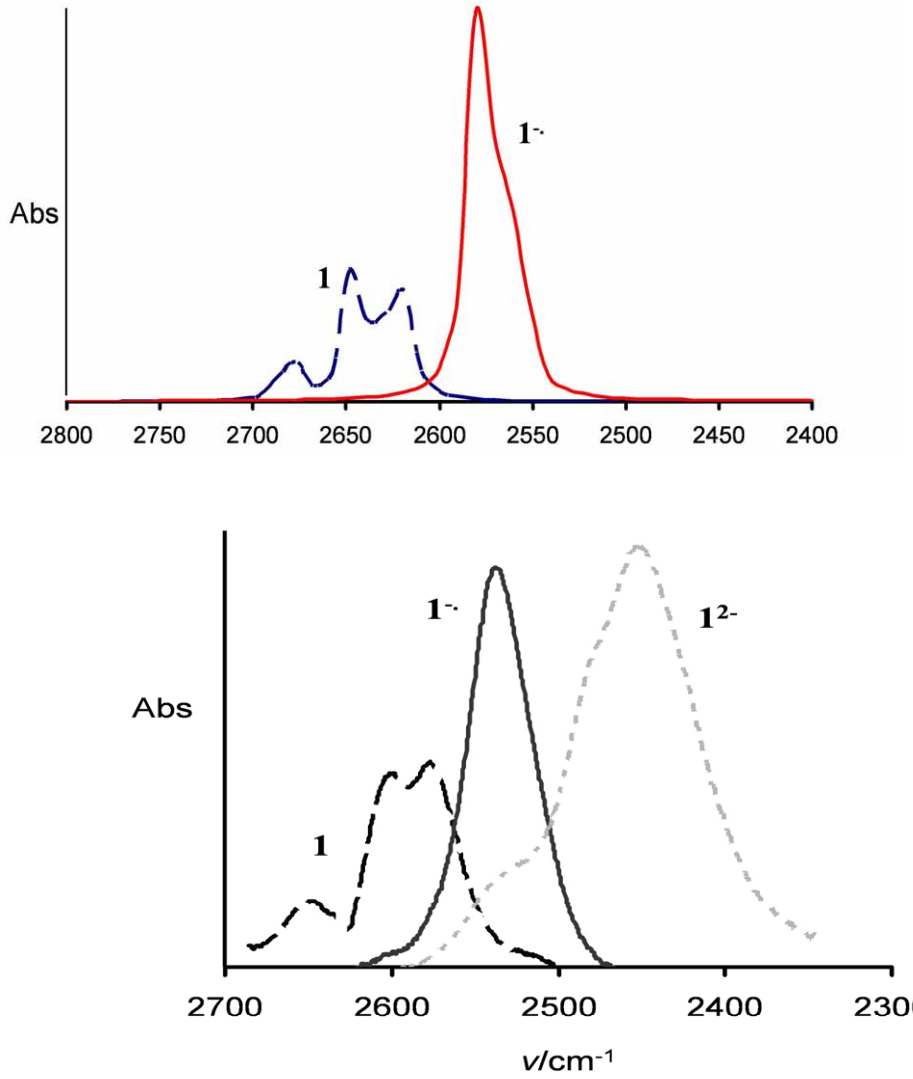


Figure S5. Observed and TD-DFT calculated (stick) UV spectra for radical anion [**1**]$^{-}$.

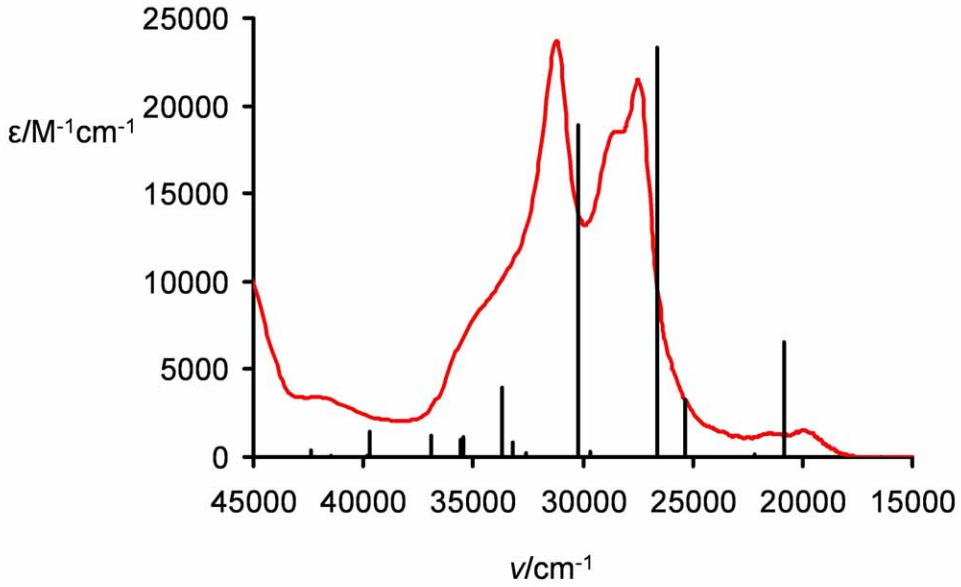
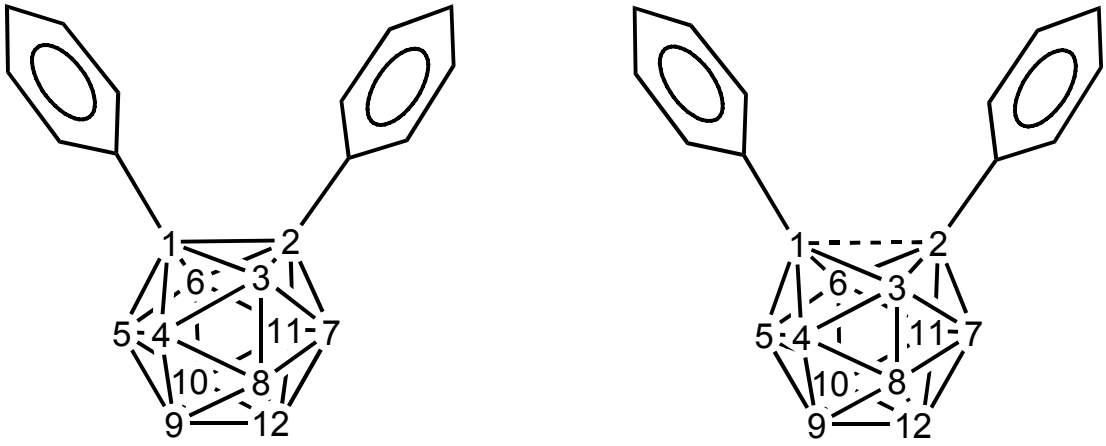


Figure S6. Cage numbering for **1** and [**1**]$^-$

The radical anion [**1**]$^-$ is numbered in the same way as the neutral carborane **1**. The *exo*-anions [1-X-2-Ph-1,2-$C_2B_{10}H_{10}$]$^-$ structurally related to [**1**]$^-$ are also numbered similarly (*Dalton Trans.* 2004, 2786).



1 **1**$^{-\cdot}$

Cartesian coordinates for **1** and [**1**]$^-$.

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44
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C 0.586446 1.624791 -0.055242
C -0.724485 -0.880734 0.039316
C -0.724523 0.880713 -0.039358
C 1.277495 -1.854648 1.254456
B -1.178564 -0.058265 -1.409015
B -2.071277 -1.478142 -0.823106
C 2.470694 2.575438 -1.261286
C 1.114330 -2.154635 -1.132559
B -2.073330 -1.405396 0.949709
B -1.178620 0.058228 1.408960
C 1.277759 1.854217 -1.254315
C 2.992359 -3.086633 0.073304
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B -2.944127 -0.060987 -1.442018
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B -3.509638 0.887585 -0.037656
C 2.306023 -2.877199 -1.122949
C 2.992239 3.086752 -0.073177
C 2.305577 2.877770 1.122968
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B 0.000133 2.774412 1.434332
B -0.880284 3.414771 0.000064
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