Electronic Supplementary Information for Dalton Transactions

Supplementary Data to

Salts of the 1-Cyanocarba-*closo*-dodecaborate Anions $[1\text{-NC-}closo\text{-}1\text{-}CB_{11}X_{11}]^-$ (X = H, F, Cl, Br, I)

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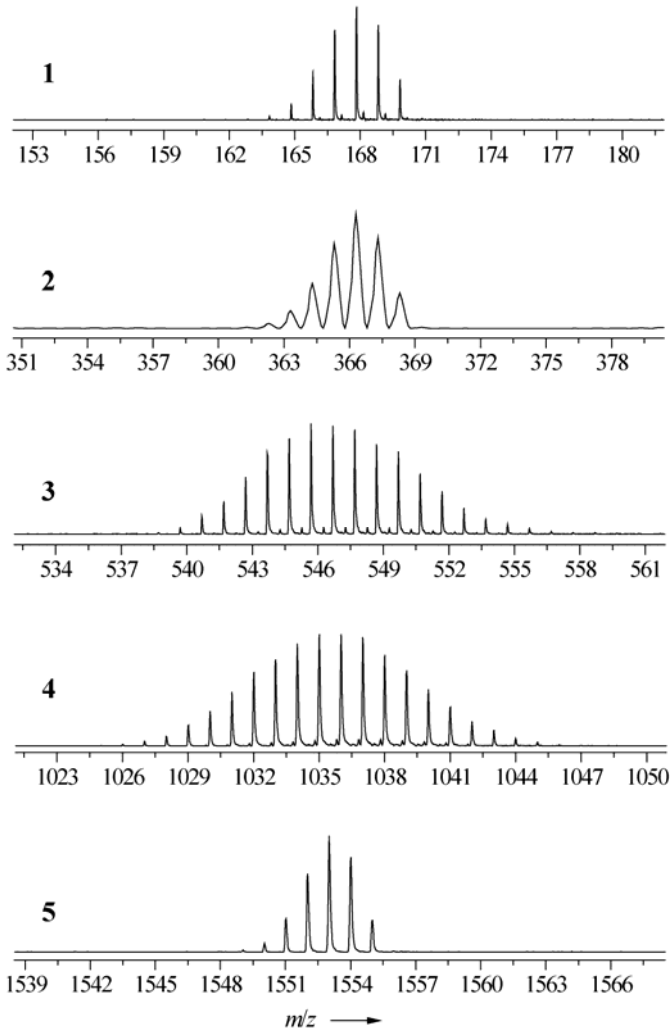

Fig. S1. MALDI-mass spectra of $[1\text{-NC-}closo\text{-}1\text{-}CB_{11}X_{11}]^-$ (X = H (**1**), Cl (**3**), Br (**4**), I (**5**)) and ESI-mass spectrum of $[1\text{-NC-}closo\text{-}1\text{-}CB_{11}F_{11}]^-$ (**2**).

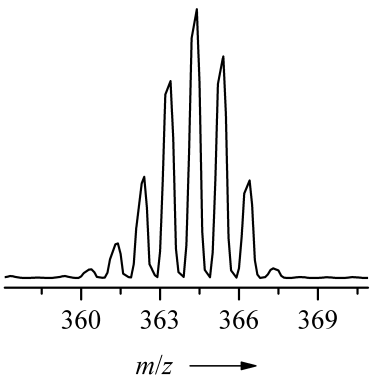

Fig. S2. (–)-ESI mass spectrum of $[1\text{-NC-6-HO-}closo\text{-}1\text{-}CB_{11}F_{10}]^-$ in CH_3CN containing a small amount of aqueous HCl (1 mol L^{-1}).

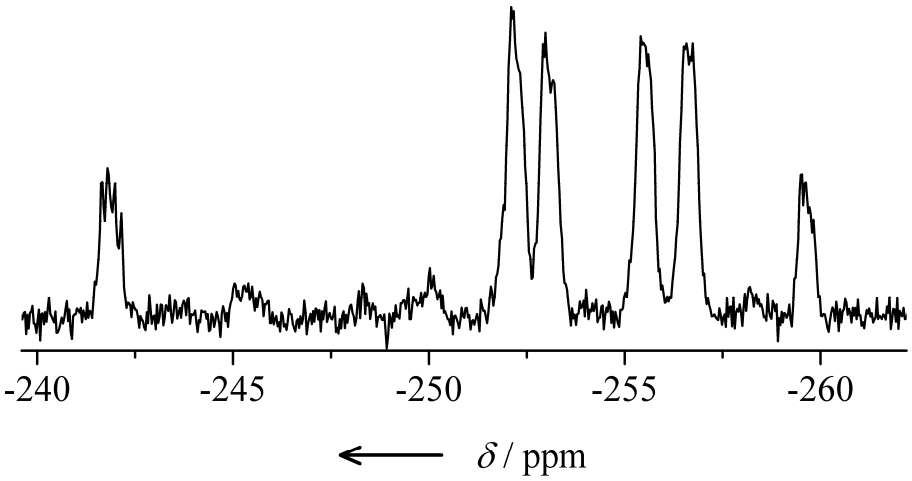

Fig. S3. ^{19}F NMR spectrum of [1-NC-6-HO-*closo*-1-$CB_{11}F_{10}$]$^-$ measured in CH_3CN containing a small amount of aqueous HCl (1 mol L^{-1}).

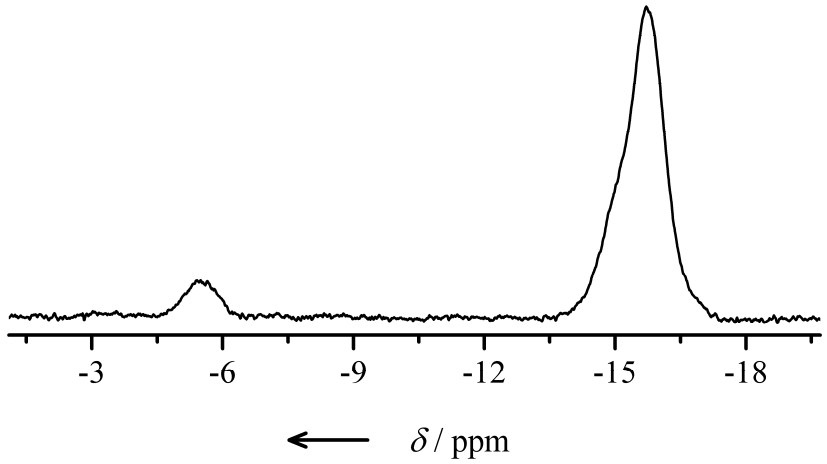

Fig. S4. ^{11}B NMR spectrum of [1-NC-6-HO-*closo*-1-$CB_{11}F_{10}$]$^-$ measured in CH_3CN containing a small amount of aqueous HCl (1 mol L^{-1}).

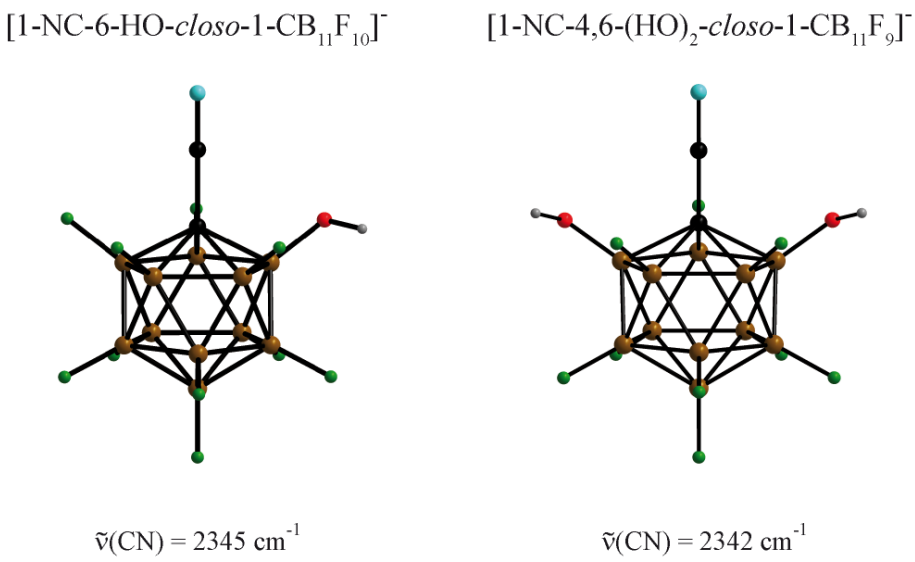

Fig. S5. Calculated structures and calculated $\tilde{\nu}$(CN) of [1-NC-6-HO-*closo*-1-$CB_{11}F_{10}$]$^-$ and [1-NC-4,6-$(HO)_2$-*closo*-1-$CB_{11}F_9$]$^-$ at the B3LYP/6-311++G(d,p) level of theory.

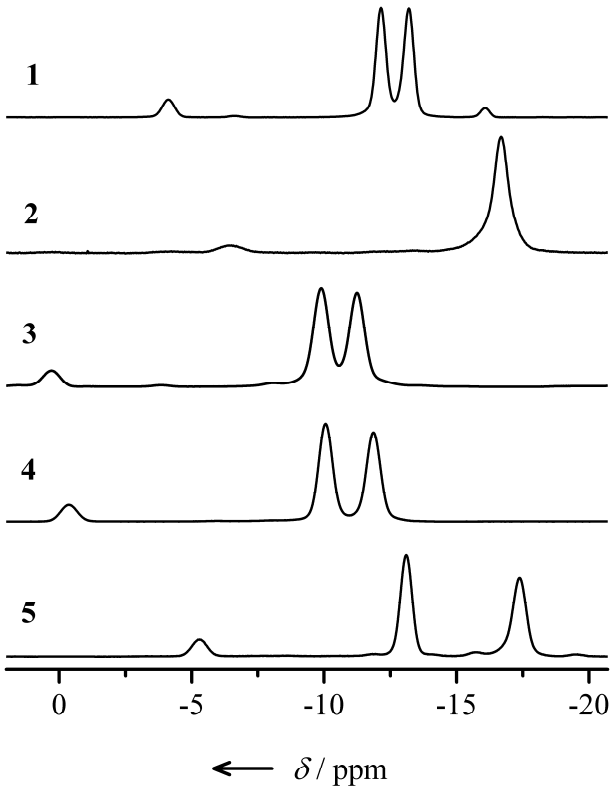

Fig. S6. $^{11}B\{^1H\}$ NMR spectra of [1-NC-*closo*-1-$CB_{11}X_{11}$]$^-$ (X = H (**1**), F (**2**), Cl (**3**), Br (**4**), I (**5**)).

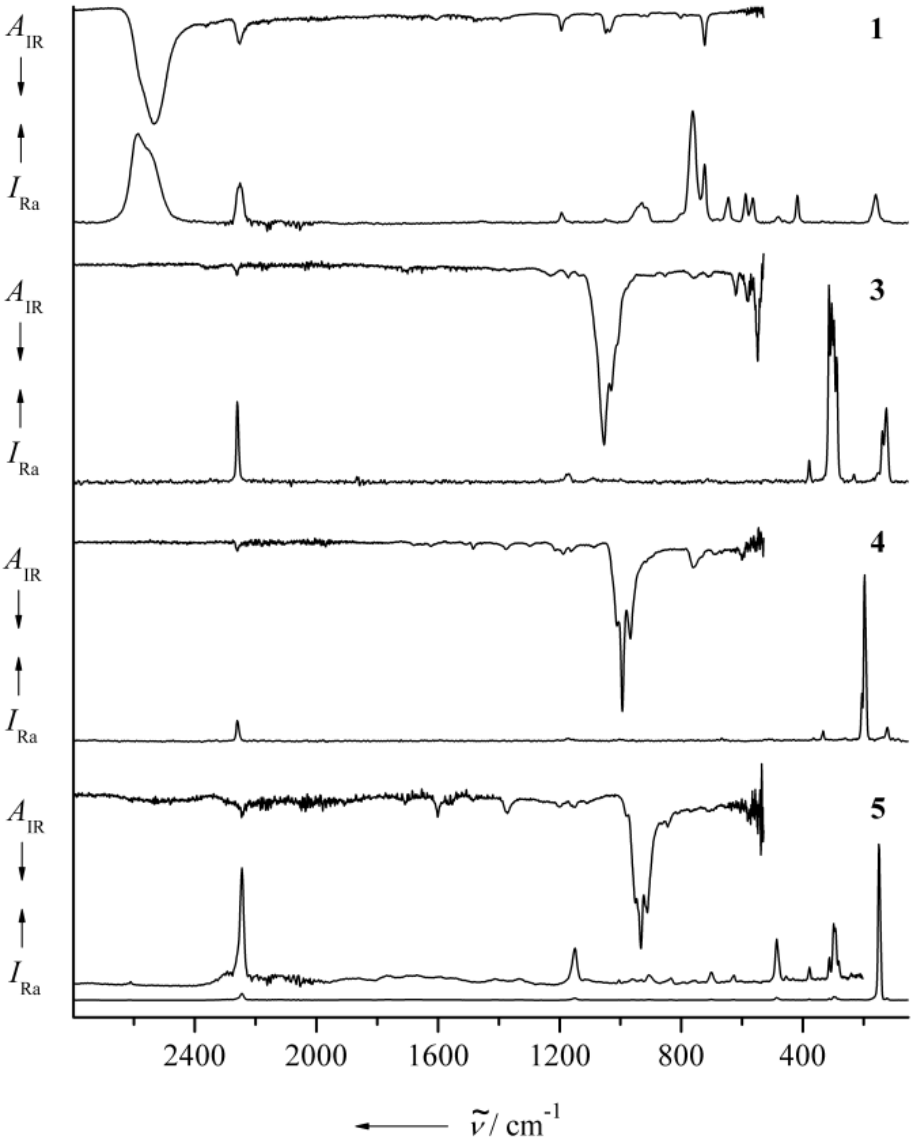

Fig. S7. $^{11}B\{^{1}H\}$ NMR spectra of [1-NC-*closo*-1-$CB_{11}X_{11}$]$^-$ (X = H (**1**), F (**2**), Cl (**3**), Br (**4**), I (**5**))]. (The vibrational spectra of Cs[1-NC-*closo*-1-$CB_{11}F_{11}$] (Cs[**2**]) are not depicted due to small amounts of impurities present in the salt.)

Table S1 Experimental and calculated[a] ^{19}F and ^{11}B chemical shifts [ppm][b]

Anion		F2–6	F7–11	F12	B2–6	B7–11	B12	Ref.
[1-NC-*closo*-1-$CB_{11}F_{11}$]$^-$ (**1**)	exp.	–252.9	–256.0	–241.3	–16.8	–16.8	–6.5	[c]
	calc.	–284.5	–287.8	–268.0	–17.8	–17.5	–7.0	[c]
[1-H-*closo*-1-$CB_{11}F_{11}$]$^-$	exp.	–257.2	–256.7	–253.1	–18.2	–16.6	–8.5	1, 2
	calc.	–291.6	–289.1	–282.0	–19.9	–17.7	–9.4	[c]
[1-H_2N-*closo*-1-$CB_{11}F_{11}$]$^-$	exp.	–255.9	–263.3	–252.7	–18.5	–17.3	–10.7	2
	calc.	–290.9	–295.9	–281.0	–20.0	–18.3	–11.8	2

		F2+5	F3+4	F7+9	F8	F10+11	F12	B2+5	B3+4	B6	B7+9	B8	B10+11	B12	
[1-NC-6-HO-*closo*-1-$CB_{11}F_{10}$]$^-$	exp.[d, e]	–253.0	–252.2	(–256.6)	–259.6	(–255.5)	–241.9	——	——	–14.8	— –16.2	——	——	–5.5	[c]
	calc.	–286.5	–284.1	–287.6	–288.8	–287.6	–266.5	–17.6	–17.4	–18.8	–17.4	–17.5	–16.7	–6.2	[c]
[1-H_2N-6-HO-*closo*-1-$CB_{11}F_{10}$]$^-$	exp.	–255.8	–254.9	–263.1	–265.0	–262.2	–251.9	–18.1	–18.1	–19.7	–17.3	–18.1	–16.7	–10.4	2
	calc.	–292.8	–291.2	–295.4	–297.0	–294.8	–280.0	–20.2	–20.3	–22.0	–18.4	–18.5	–17.7	–10.6	2

		F2+3	F5	F7	F8+11	F9+10	F12	B2+3	B4+6	B5	B7	B8+11	B9+10	B12	
[1-NC-4,6-$(HO)_2$-*closo*-1-$CB_{11}F_9$]$^-$	calc.	–288.2	–285.0	–289.1	–289.4	–286.2	–265.5	–17.2	–18.7	–17.0	–17.5	–16.8	–16.7	–6.0	[c]
[1-H_2N-4,6-$(HO)_2$-*closo*-1-$CB_{11}F_9$]$^-$	exp.	–254.8	–254.0	–262.9	–263.8	–262.0	–251.1	–17.7	–19.8	–17.7	–17.3	–17.0	–16.6	–10.2	2
	calc.	–290.7	–292.9	–296.1	–299.2	–295.2	–279.4	–19.4	–22.4	–19.5	–18.1	–17.9	–17.2	–11.3	2

[a] GIAO-B3LYP/6-311++G(2d,p) with geometries calculated at the B3LYP/6-311++G(d,p) level of theory. [b] δ in ppm. [c] This work. [d] Assignment based on calculated chemical shifts. [e] Measured in CH_3CN containing a small amount of aqueous HCl (1 mol L^{-1}).

Table S2 Calculated NBO,[a] APT[b] and Mulliken[c] partial charges of [1-NC-*closo*-1-$CB_{11}X_{11}$]$^-$ (X = H (**1**), F (**2**), Cl (**3**), Br (**4**), I (**5**))

	[1-NC-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1**)			[1-NC-*closo*-1-$CB_{11}F_{11}$]$^-$ (**2**)			[1-NC-*closo*-1-$CB_{11}Cl_{11}$]$^-$ (**3**)			[1-NC-*closo*-1-$CB_{11}Br_{11}$]$^-$ (**4**)			[1-NC-*closo*-1-$CB_{11}I_{11}$]$^-$ (**5**)		
	NBO	APT	Mulliken	NBO	APT	Mulliken	NBO	APT	Mulliken	NBO	APT	Mulliken	NBO	APT	Mulliken
N	–0.36	–0.44	–0.12	–0.28	–0.33	–0.17	–0.26	–0.26	–0.13	–0.25	–0.24	–0.13	–0.25	–0.22	–0.08
C	0.37	0.28	–1.13	0.33	0.21	–0.06	0.33	0.12	–0.48	0.33	0.09	0.21	0.33	0.07	–0.07
$C_{cluster}$	–0.66	–0.21	–2.08	–0.71	–0.34	–0.97	–0.78	–0.32	2.29	–0.83	–0.34	1.66	–0.91	–0.38	2.47
B2–6	0.03	0.15	–0.24	0.54	0.60	–0.30	0.18	0.40	–0.92	0.09	0.34	–0.45	–0.07	0.26	–0.64
B7–11	–0.17	0.07	0.61	0.35	0.51	–0.48	–0.03	0.27	1.04	–0.13	0.20	–0.19	–0.30	0.11	–0.17
B12	–0.13	0.12	0.00	0.38	0.61	–0.48	0.03	0.37	2.35	–0.06	0.30	0.15	–0.23	0.20	–0.17
X2–6	0.04	–0.15	–0.30	–0.46	–0.58	0.45	–0.08	–0.38	–0.36	0.02	–0.31	0.06	0.19	–0.22	0.10
X7–11	0.05	–0.18	–0.40	–0.47	–0.63	0.39	–0.11	–0.39	–0.60	–0.01	–0.32	0.00	0.16	–0.23	0.06
X12	0.04	–0.18	–0.33	–0.47	–0.64	0.38	–0.11	–0.41	–0.79	–0.01	–0.33	0.00	0.16	–0.24	0.05

References

S1 S. V. Ivanov, J. J. Rockwell, O. G. Polyakov, C. M. Gaudinski, O. P. Anderson, K. A. Solntsev and S. H. Strauss, *J. Am. Chem. Soc.*, 1998, **120**, 4224-4225.

S2 M. Finze, G. J. Reiss and M. Zähres, *Inorg. Chem.*, 2007, **46**, 9873-9883.