Supporting Information

Divalent *closo*-monocarborane solvates for solid-state ionic conductors.

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Figure S1:(a) ¹H, (b) ¹¹B and (c) ¹¹B{¹H} NMR of Me₃NH[CB₁₁H₁₂] and hydrated divalent salts $Zn[CB_{11}H_{12}]_2 \cdot xH_2O$, Mg[CB₁₁H₁₂]_2 \cdot xH_2O, and Ca[CB₁₁H₁₂]_2 \cdot xH_2O. Me₃NH[CB₁₁H₁₂] and

 $Zn[CB_{11}H_{12}]_2 \cdot xH_2O$ samples were analysed in CD₃CN. Mg[CB₁₁H₁₂]₂ \cdot xH₂O, and Ca[CB₁₁H₁₂]₂ \cdot xH₂O were analysed in D₂O. Solvents differ due to solubility issues...



Figure S2: ¹H NMR of (a) $Me_3NH[CB_{11}H_{12}]$, (b) $Mg[CB_{11}H_{12}]_2$ and (c) $Mg[CB_{11}H_{12}]_2$ ·3en in DMSO-*d6*.



Figure S3: ¹¹B NMR of (a) $Me_3NH[CB_{11}H_{12}]$, (b) $Mg[CB_{11}H_{12}]_2$ and (c) $Mg[CB_{11}H_{12}]_2$ ·3en in DMSO-*d6*.



Figure S4: ¹¹B{¹H} NMR of (a) Me₃NH[CB₁₁H₁₂], (b) Mg[CB₁₁H₁₂]₂ and (c) Mg[CB₁₁H₁₂]₂·3en in DMSO-*d6*.



Figure S5: ${}^{13}C{}^{1}H$ NMR of Mg[CB₁₁H₁₂]₂ in DMSO-*d6*.



Figure S6: ¹H-¹³C HSQC of Mg[CB₁₁H₁₂]₂ in DMSO-*d6*.



Figure S7: ${}^{13}C{}^{1}H$ NMR of Mg[CB₁₁H₁₂]₂·3en in DMSO-*d6*.

Table S1: Estimation of residual water for $Mg[CB_{11}H_{12}]_2 \cdot xH_2O$, $Ca[CB_{11}H_{12}]_2 \cdot xH_2O$ and $Zn[CB_{11}H_{12}]_2 \cdot xH_2O$ dried at different temperatures. Estimation was calculated from thermogravimetric analysis (TGA) residual masses.

| Sample | Temp dried | Initial mass | Residual (%) | Ratio mol M[CB ₁₁ H ₁₂] ₂ | Ratio mol | In text notation |
|---|---------------|-----------------|-----------------|--|------------------|---|
| | (°C) | (mg) | . , | | H ₂ O | |
| Mg[CB ₁₁ H ₁₂] ₂ ·xH ₂ O | 100 | 5.00 | 84.7% | 1 | 3.1 | $Mg[CB_{11}H_{12}]_2 \cdot 3.1H_2O$ |
| $Ca[CB_{11}H_{12}]_2 \cdot xH_2O$ | 100 | 3.55 | 90.7% | 1 | 1.9 | $Ca[CB_{11}H_{12}]_2 \cdot 1.9H_2O$ |
| $Ca[CB_{11}H_{12}]_2 \cdot xH_2O$ | 125 | 4.57 | 95.7% | 1 | 0.8 | $Ca[CB_{11}H_{12}]_2 \cdot 0.8H_2O$ |
| $Zn[CB_{11}H_{12}]_2.\cdot xH_2O$ | 100 | 4.67 | 86.5% | 1 | 3.0 | $Zn[CB_{11}H_{12}]_2 \cdot 3H_2O$ |
| $Zn[CB_{11}H_{12}]_2 \cdot xH_2O$ | 150 | 4.18 | 90.9% | 1 | 1.9 | $Zn[CB_{11}H_{12}]_2 \cdot 1.9H_2O$ |
| $Ca[B_{12}H_{12}]\cdot xH2O$ | 100 | 3.08 | 85.7% | 1 | 1.7 | Ca[B ₁₂ H ₁₂]·1.7H2O |
| $Zn[B_{12}H_{12}]\cdot xH2O$ | 100 | 1.85 | 80.8% | 1 | 2.7 | $Zn[B_{12}H_{12}] \cdot 2.7H2O$ |



Figure S8: FTIR of (a) $Me_3NH[CB_{11}H_{12}]$, (b) $Zn[CB_{11}H_{12}]_2 \cdot xH_2O$, (c) $Mg[CB_{11}H_{12}]_2 \cdot xH_2O$ and (d) $Ca[CB_{11}H_{12}]_2 \cdot xH_2O$. All samples were dried at 100 °C before analysis.



Figure S9: Raman spectra for (a) $Me_3NH[CB_{11}H_{12}]$, (b) $Na[CB_{11}H_{12}]$, (c) $Zn[CB_{11}H_{12}]_2.xH_2O$, (d) $Mg[CB_{11}H_{12}]_2.xH_2O$ and (e) $Ca[CB_{11}H_{12}]_2.xH_2O$. Purple boxes indicate features attributed to the anion $[CB_{11}H_{12}]^-$, whereas blue boxes are due to the cation Me_3NH^+ . All samples were dried at 100 °C before analysis.



Figure S10: FTIR of Mg[CB₁₁H₁₂]₂ and Mg[CB₁₁H₁₂]₂·3en. All samples were briefly exposed to air during measurement. All samples were dried at 100 °C for 1 hour before analysis.



Figure S11: pXRD of (a) Me₃NH[CB₁₁H₁₂], (b) Na[CB₁₁H₁₂], (c) Zn[CB₁₁H₁₂]₂·xH₂O, (d) Mg[CB₁₁H₁₂]₂·xH₂O, and (e) Ca[CB₁₁H₁₂]₂·xH₂O. Me₃NH[CB₁₁H₁₂] was prepared in air using a standard pXRD holder, whereas Na[CB₁₁H₁₂], Zn[CB₁₁H₁₂]₂·xH₂O, Mg[CB₁₁H₁₂]₂·xH₂O and Ca[CB₁₁H₁₂]₂·xH₂O were prepared in an Ar filled glovebox using air-tight dome holders to prevent the absorption of atmospheric moisture. All samples were dried at 100 °C before analysis. CuK α radiation source (λ = 1.5406 Å) Data was collected from 5 – 60° 2 ϑ at 0.02° steps over 1 hour.



Figure S12: SR-XRD of Mg[CB₁₁H₁₂]₂ compared to the Topas refinement of the data. The energy of the X-ray beam was 16 keV (λ = 0.774954(1) Å)



Figure S13: SR-XRD of Mg[CB₁₁H₁₂]₂·3en compared to the Topas refinement of the data. The energy of the X-ray beam was 16 keV (λ = 0.774954(1) Å)

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| H18 H 8 0.88200 0.70390 0.54930 N6 N 8 0.72360 0.60590 0.48260 H19 H 8 0.72880 0.55900 0.47910 H20 H 8 0.66330 0.61740 0.45840 C5 C 8 0.80000 0.70370 0.46190 H21 H 8 0.85300 0.72470 0.44810 H22 H 8 0.73500 0.72470 0.44810 H23 H 8 0.86270 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| N6 N 8 0.72360 0.60590 0.48260 H19 H 8 0.72880 0.55900 0.47910 H20 H 8 0.66330 0.61740 0.45840 C5 C 8 0.80000 0.70370 0.46190 H21 H 8 0.85300 0.72600 0.43090 H22 H 8 0.73500 0.72470 0.44810 C6 C 8 0.79780 0.63590 0.44300 H23 H 8 0.86270 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| H19 H 8 0.72880 0.55900 0.47910 H20 H 8 0.66330 0.61740 0.45840 C5 C 8 0.80000 0.70370 0.46190 H21 H 8 0.85300 0.72600 0.43090 H22 H 8 0.73500 0.72470 0.44810 C6 C 8 0.79780 0.63590 0.44300 H23 H 8 0.86270 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| H20 H 8 0.66330 0.61740 0.45840 C5 C 8 0.80000 0.70370 0.46190 H21 H 8 0.85300 0.72600 0.43090 H22 H 8 0.73500 0.72470 0.44810 C6 C 8 0.79780 0.63590 0.44300 H23 H 8 0.86270 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| C5 C 8 0.80000 0.70370 0.46190 H21 H 8 0.85300 0.72600 0.43090 H22 H 8 0.73500 0.72470 0.44810 C6 C 8 0.79780 0.63590 0.44300 H23 H 8 0.79000 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| H21 H 8 0.85300 0.72600 0.43090 H22 H 8 0.73500 0.72470 0.44810 C6 C 8 0.79780 0.63590 0.44300 H23 H 8 0.86270 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| H22 H 8 0.73500 0.72470 0.44810 C6 C 8 0.79780 0.63590 0.44300 H23 H 8 0.86270 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| C6 C 8 0.79780 0.63590 0.44300 H23 H 8 0.86270 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| H23 H 8 0.86270 0.61500 0.45810 H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| H24 H 8 0.79000 0.63100 0.38570 B1a B 8 0.49000 0.79700 0.75600 |
| B1a B 8 0.49000 0.79700 0.75600 |
| |
| B2a B 8 0.50000 0.86000 0.69900 |
| B3a B 8 0.57000 0.92000 0.74000 |
| B4a B 8 0.61000 0.89000 0.82300 |
| B5a B 8 0.44000 0.82000 0.83400 |
| B6a B 8 0.56000 0.81000 0.83300 |

Table S2: Structural parameters for Mg[CB₁₁H₁₂]₂·3en at 25.1 °C in space group *Pbca* from Topas refinement of SR-XRD data.

| B7a | В | 8 | 0.40000 | 0.85000 | 0.75000 |
|------|---|---|---------|---------|---------|
| B8a | В | 8 | 0.45000 | 0.92000 | 0.74000 |
| B9a | В | 8 | 0.52000 | 0.94100 | 0.81700 |
| B10a | В | 8 | 0.51000 | 0.87700 | 0.87400 |
| B11a | В | 8 | 0.41000 | 0.90000 | 0.82300 |
| H1a | Н | 8 | 0.65000 | 0.82000 | 0.73000 |
| H2a | Н | 8 | 0.50000 | 0.75000 | 0.73000 |
| H3a | Н | 8 | 0.51000 | 0.85000 | 0.63700 |
| H4a | Н | 8 | 0.63000 | 0.94000 | 0.71000 |
| H5a | Н | 8 | 0.68000 | 0.89000 | 0.84000 |
| H6a | Н | 8 | 0.39000 | 0.79000 | 0.87000 |
| H7a | Н | 8 | 0.60000 | 0.77000 | 0.86000 |
| H8a | Н | 8 | 0.33000 | 0.84000 | 0.72000 |
| H9a | Н | 8 | 0.42000 | 0.96000 | 0.71000 |
| H10a | Н | 8 | 0.50000 | 0.99000 | 0.84000 |
| H11a | Н | 8 | 0.51000 | 0.88000 | 0.93600 |
| H12a | Н | 8 | 0.35000 | 0.92000 | 0.85000 |
| C1a | С | 8 | 0.59000 | 0.84000 | 0.75300 |
| B1b | В | 8 | 0.18000 | 0.96400 | 0.11500 |
| B2b | В | 8 | 0.14000 | 0.97500 | 0.03000 |
| B3b | В | 8 | 0.07500 | 0.91000 | 0.00400 |
| B4b | В | 8 | 0.08000 | 0.85700 | 0.08000 |
| B5b | В | 8 | 0.25600 | 0.90000 | 0.11300 |
| B6b | В | 8 | 0.14000 | 0.89000 | 0.14400 |
| B7b | В | 8 | 0.25000 | 0.95000 | 0.04000 |
| B8b | В | 8 | 0.19000 | 0.92000 | - |
| | | | | | 0.02700 |
| B9b | В | 8 | 0.15000 | 0.84600 | 0.00200 |
| B10b | В | 8 | 0.19000 | 0.83500 | 0.09000 |
| B11b | В | 8 | 0.26000 | 0.87000 | 0.03000 |
| H1b | Н | 8 | 0.02000 | 0.95000 | 0.11000 |
| H2b | Н | 8 | 0.18000 | 1.01000 | 0.15000 |
| H3b | Н | 8 | 0.11000 | 1.02400 | 0.01000 |
| H4b | Н | 8 | 0.01000 | 0.91000 | - |
| | | | | | 0.03000 |
| H5b | Н | 8 | 0.01000 | 0.83000 | 0.09000 |
| H6b | Н | 8 | 0.32000 | 0.90000 | 0.15000 |
| H7b | Н | 8 | 0.12000 | 0.88000 | 0.20300 |
| H8b | Н | 8 | 0.31000 | 0.99000 | 0.03000 |
| H9b | Н | 8 | 0.20000 | 0.93000 | - |
| | | _ | | | 0.08700 |
| H10b | Н | 8 | 0.14000 | 0.80000 | - |
| | | | | | 0.04000 |
| H11b | Н | 8 | 0.21000 | 0.78500 | 0.11000 |
| H12b | Н | 8 | 0.33000 | 0.85000 | 0.00000 |
| C1b | С | 8 | 0.07800 | 0.93000 | 0.09000 |



Scheme S1: Mechanism for the hydroxylation of (a) $Mg(H_2O)_3[B_{12}H_{12}]$ proposed by Shore et al.¹, and (b), is proposed for $Mg[CB_{11}H_{12}]_2 \cdot xH_2O$.



Figure S14: ¹¹B NMR (CD₃CN) of the $[CB_{11}H_{12}]^-$ anion (purple) and $[12-OH-CB_{11}H_{11}]^-$ anion (red).



Figure S15: ¹H NMR of Mg[CB₁₁H₁₂]₂ dried at 100 °C (bottom) and Mg[CB₁₁H₁₂]₂ heated under vacuum to 215 °C (top) in DMSO-*d6*. Inset shows a closer observation of peaks between 2.9 and 1.8 ppm.



Figure S16: SR-XRD *in situ* ramp of Mg[CB₁₁H₁₂]₂·3en from 25 °C to 300 °C.



Figure S17: Linear sweep voltammetry (LSV) of (a) Mg[CB₁₁H₁₂]₂·3.1H₂O, (b) Mg[CB₁₁H₁₂]₂, and (c) Mg[CB₁₁H₁₂]₂·3en. For LSV, cells were prepared as Mg/electrolyte/electrolyte+C/Pt and were analysed at 100 °C at 50 μ V/s due to the low conductivity of the salts. Open circuit voltage (OCV) values were 0.96 V for Mg[CB₁₁H₁₂]₂·3.1H₂O, 1.08 V for Mg[CB₁₁H₁₂]₂, and 0.51 V for Mg[CB₁₁H₁₂]₂·3en.



Figure S18: Linear sweep voltammetry (LSV) of Ca[CB₁₁H₁₂·1.9H₂O. For LSV cells were prepared as Ca/Ca[CB₁₁H₁₂]₂·1.9H₂O@100 °C/Ca[CB₁₁H₁₂]₂·1.9H₂O@100 °C+C/Pt with a scan rate of 50 μ V s⁻¹. LSV was measured at 100 °C due to the low ionic conductivity at lower temperatures.¹⁸ OCV for Ca[CB₁₁H₁₂]₂·1.9H₂O was 1.26 V.



Figure S19: Ionic conductivities of $Zn[CB_{11}H_{12}]_{2}xH_{2}O$, $Zn[B_{12}H_{12}]\cdot xH_{2}O$ and mixtures with different stoichiometry's. Each sample molar ratio is indicated by the number in front, for example $0.7Zn[B_{12}H_{12}]\cdot xH_{2}O + 0.3Zn[CB_{11}H_{12}]_{2}\cdot xH_{2}O$. The samples labelled + BM were prepared by ball milling the mixtures together for 1 hour in a stainless steel planetary ball mill (Across Industries). Ball sizes were 0.6 mm with a ball to sample mass ratio of 33:1. The sample, $0.7Zn[B_{12}H_{12}]\cdot xH_{2}O + 0.3Zn[CB_{11}H_{12}]_{2}\cdot xH_{2}O$ was prepared by dissolving the

appropriate amounts of $Zn[B_{12}H_{12}]\cdot xH_2O$ and $Zn[CB_{11}H_{12}]_2\cdot xH_2O$ in deionised water and drying 16 hours at 100 °C.

NMR data for $Zn[B_{12}H_{12}]$, $Ca[B_{12}H_{12}]$ and $Zn[B_{12}H_{12}]\cdot xH_2O + Zn[CB_{11}H_{12}]_2\cdot xH_2O$ mixed samples.



Figure S20: ¹H NMR for Ca[B₁₂H₁₂]·*x*H₂O



Figure S21: ¹¹B NMR (top) ad ¹¹B{¹H} NMR (bottom) for Ca[B₁₂H₁₂]·xH₂O.



Figure S22: ¹H NMR for Zn[B₁₂H₁₂]·*x*H₂O



Figure S23: ¹¹B NMR (top) and ¹¹B{¹H} NMR (bottom) for $Zn[B_{12}H_{12}]\cdot xH_2O$.



Figure S24: ¹H NMR of (a) $0.7Zn[B_{12}H_{12}] \cdot xH_2O + 0.3Zn[CB_{11}H_{12}]_2 \cdot xH_2O$, (b) $0.7Zn[B_{12}H_{12}] \cdot xH_2O + 0.3Zn[CB_{11}H_{12}]_2 \cdot xH_2O + BM$, (c) $0.5Zn[B_{12}H_{12}] \cdot xH_2O + 0.5Zn[CB_{11}H_{12}]_2 \cdot xH_2O + BM$, and (d) $0.3Zn[B_{12}H_{12}] \cdot xH_2O + 0.7Zn[CB_{11}H_{12}]_2 \cdot xH_2O$.



Figure S25: ¹¹B NMR of (a) $0.7Zn[B_{12}H_{12}] \cdot xH_2O + 0.3Zn[CB_{11}H_{12}]_2 \cdot xH_2O$, (b) $0.7Zn[B_{12}H_{12}] \cdot xH_2O + 0.3Zn[CB_{11}H_{12}]_2 \cdot xH_2O + BM$, (c) $0.5Zn[B_{12}H_{12}] \cdot xH_2O + 0.5Zn[CB_{11}H_{12}]_2 \cdot xH_2O + BM$, and (d) $0.3Zn[B_{12}H_{12}] \cdot xH_2O + 0.7Zn[CB_{11}H_{12}]_2 \cdot xH_2O$.



Figure S26: ¹¹B{¹H} NMR of (a) $0.7Zn[B_{12}H_{12}] \cdot xH_2O + 0.3Zn[CB_{11}H_{12}]_2 \cdot xH_2O$, (b) $0.7Zn[B_{12}H_{12}] \cdot xH_2O + 0.3Zn[CB_{11}H_{12}]_2 \cdot xH_2O + BM$, (c) $0.5Zn[B_{12}H_{12}] \cdot xH_2O + 0.5Zn[CB_{11}H_{12}]_2 \cdot xH_2O + BM$, and (d) $0.3Zn[B_{12}H_{12}] \cdot xH_2O + 0.7Zn[CB_{11}H_{12}]_2 \cdot xH_2O$.



Figure S27: ¹H NMR of Me₃NH[12-OH-CB₁₁H₁₁] in acetone-d6



Figure S28: ${}^{11}B$ (top) and ${}^{11}B{}^{1}H$ (bottom) NMR of Me₃NH[12-OH-CB₁₁H₁₁] in acetone-d6.





Figure S29: Nyquist plots for Ca[CB₁₁H₁₂]₂·*x*H₂O dried at 100 °C, 125 °C and 150 °C.



Figure S30: Nyquist plots for Zn[CB₁₁H₁₂]₂·*x*H₂O dried at 100 °C and 150 °C.



Figure S31: Nyquist plots for Zn[CB₁₁H₁₂]₂·xH₂O@100 °C + BM (ball milling).



Figure S32: Nyquist plots for Mg[CB₁₁H₁₂]₂·xH₂O@100 °C and Mg[CB₁₁H₁₂]₂·3en.

References

1 X. Chen, H. K. Lingam, Z. Huang, T. Yisgedu, J. C. Zhao and S. G. Shore, Thermal decomposition behavior of hydrated magnesium dodecahydrododecaborates, *J. Phys. Chem. Lett.*, 2010, **1**, 201–204.