Supporting Information

Magnesium Boryl Reactivity with 9-BBN and Ph₃B: Rational B–B’ Bond Formation and Diborane Isomerization
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anie_201709902_sm_miscellaneous_information.pdf
Author Contributions

A.P. Investigation: Equal; Methodology: Equal
C.M. Formal analysis: Equal; Investigation: Equal; Writing—review & editing: Supporting
M.M. Formal analysis: Equal; Investigation: Equal; Writing—review & editing: Supporting.
Experimental Procedures

1. General considerations and starting materials

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in J Young tap NMR tubes made up and sealed in a Glovebox. NMR spectra were collected on a Bruker AV300 spectrometer operating at 300.2 MHz (1H), 75.5 MHz (13C), 96.3 MHz (11B) or an Agilent ProPulse spectrometer operating at 500 MHz (1H), 126 MHz (13C), 160.4 MHz (11B). The spectra were referenced relative to residual solvent resonances or an external BF3.OEt2 standard (11B). Solvents (toluene, hexane) were dried by passage through a commercially available (Innovative Technologies) solvent purification system, under nitrogen and stored in ampoules over molecular sieves. Di-n-butylmagnesium (1.0 M solution in n-heptane), bis(pinacolato)diborane, 9-BBN and BPh3 were purchased from Sigma-Aldrich Ltd. and the BPh3 was sublimed before use. [HC{(Me)CN(2,6-Pr2C6H4)}2MgBu] (5) and [HC{(Me)CN(2,6-Pr2C6H4)}3Mg{pinBB(n-Bu)pin}] (6) were synthesized by literature procedures.11,12 Elemental analysis was carried out at Elemental Microanalysis Ltd., Okehampton, Devon. UK.

2. Synthetic, spectroscopic and analytical data for new compounds

Compound 9

In a J Young NMR tube, d8-toluene (0.5 mL) was added to a mixture of (5) (200 mg, 0.4 mmol) and bis(pinacolato)diborane (107 mg, 0.4 mmol). After 2 hours, 0.5 equivalents of 9-BBN dimer (48.9 mg, 0.2 mmol) were added. After a further 2 hours, the solvent was removed under reduced pressure and the solid was washed with hexane to yield compound 9 (160 mg, 57.8%). Colorless crystals suitable for X-ray diffraction analysis were obtained from a saturated toluene solution at –35°C. 1H NMR (300 MHz, d8-tol.): δ 7.12 (m, 6H, Ar-H), 4.78 (s, 1H, NC(CH2)CH), 3.34 (m, 2H, JHII = 6.9 Hz, CH(CH3)2), 3.21 (m, 2H, JHII = 6.9 Hz, CH(CH3)2), 1.62 (s, 6H, NC(CH2)CH), 2.05-1.40 (m, 13 H, CH2 and CH from 9-BBN), 1.36 (d, 6H, JHII = 6.9 Hz, CH(CH3)2), 1.32 (d, 6H, JHII = 6.9 Hz, CH(CH3)2), 1.19 (d, 6H, JHII = 6.9 Hz, CH(CH3)2), 1.15 (s, 12H, B(OCH3)2), 1.03 (br s, 2H, BH2). 13C{1H} NMR (75 MHz, d8-tol.): δ 171.0 (NC(CH3)CH), 145.2 (Cipso), 143.1 (Cortho), 143.1 (Cortho), 126.3 (Cpara), 126.6 (Cmeta), 124.8 (Cmeta), 94.7 (NC(CH3)CH), 84.7 (B(OCH3)2), 36.8 (CH2 9-BBN), 33.9 (CH2 9-BBN), 29.2 (CH(CH3)2), 28.4 (CH(CH3)2), 26.4 (B(OCH3)2), 26.3 (B(OCH3)2), 26.1 (CH(CH3)2), 25.6 (CH(CH3)2), 25.3 (9-BBN), 25.3 (9-BBN), 25.2 (NC(CH3)). 11B{1H} NMR (96 MHz, d8-tol): δ –22.8 ppm. Elemental analysis: Found C, 74.46; H, 9.64; N, 4.09 %. C43H46B2MgN2O2 requires: C, 74.75; H, 9.92; N, 4.05 %.
Compound 10

In a J Young NMR tube, d₈-toluene (0.5 mL) was added to a mixture of compound (5) (50 mg, 0.1 mmol) and bis(pinacolato)diboron (25.4 mg, 0.1 mmol). After 2 hours, an equimolar equivalent of triphenylborane (24.2 mg, 0.1 mmol) was added. The solution was left at room temperature for 2 days. The solvent was removed under reduced pressure and the solid was washed with hexane to yield compound 10 as a colorless solid (50 mg, 61%). Colorless crystals suitable for X-ray diffraction analysis were obtained from a saturated hexane solution at -35°C. ¹H NMR (500 MHz, d₈-tolu.) δ 7.84 (m, 4H, CH Ar), 7.67 (m, 2H, CH Ar), 7.21 (m, 4H, CH Ar), 7.07 (m, 6H, CH Ar), 6.99 (m, 3H, CH Ar), 6.85 (m, 1H, CH Ar), 6.40 (m, 2H, CH Ar), 4.58 (s, 1H, NC(CH₃)CH), 2.90 (m, 2H, CH(CH₃)₂), 2.71 (m, 2H, CH(CH₃)₂), 1.42 (s, 6H, NC(CH₃)CH), 1.30 (m, 12H, CH₃), 1.25 (s, 6H, CH₃), 1.04 (d, 6H, CH₃), 1.00 (m, 12H, CH₃) ppm. ¹³C [¹H] NMR (126 MHz, d₈-tolu.) δ 170.6 (NC(CH₃)CH), 144.8, 142.7, 142.0, 134.70 (CH Ar), 133.8 (CH Ar), 131.4 (CH Ar, correlated with resonance at 6.40 ppm in ¹H NMR by HSQC), 126.7 (CH Ar), 125.9 (CH Ar, correlated with resonance at 6.85 ppm in ¹H NMR by HSQC), 124.3 (CH Ar), 124.1 (CH Ar), 123.0 (CH Ar), 95.8 (NC(CH₃)CH), 88.9 (B(OC(CH₃)₂)₂), 81.6 (B(OC(CH₃)₂)₂), 28.0 (CH(CH₃)₂), 27.5 (CH(CH₃)₂), 26.3 (CH₃), 25.5 (NC(CH₃)CH), 25.4 (CH₃), 25.1 (CH₃), 24.5 (CH₃), 23.7 (CH₃) ppm. ¹¹B NMR (160 MHz, d₈-tolu.) δ -14.6 ppm. Despite multiple attempts an accurate microanalysis could not be obtained for this compound.

Compounds 11 and 12

A solution of compound 9 was heated in d₈-toluene at 110°C for 3 days. Analysis by ¹H and ¹¹B NMR spectroscopy at this point indicated the formation of two new compounds, 11 and 12 in an approximate 1:0.7 ratio. Crystallization from the reaction solution provided a mixture of crystals of both compounds suitable for X-ray diffraction analysis. Removal of volatiles from the reaction mixture and washing of the resultant colorless solid with n-hexane effected separation of compound 11 to leave a solid sample that displayed only ¹H NMR resonances associated with compound 12. The n-hexane filtrate was dried under vacuum and redissolved in d₈-toluene. The ¹H and ¹¹B spectra displayed resonances only for compound 11. (11): ¹H NMR (500 MHz, d₈-tolu.) δ 7.08 (m, aromatic CH), 4.89 (s, 1H, NC(CH₃)CH), 3.12 (m, 2H, J₉₁₁ = 6.3 Hz, CH(CH₃)₂), 1.66 (s, 6H, NC(CH₃)CH), 1.34 (d, 12H, J₉₁₁ = 6.3 Hz, CH(CH₃)₂), 1.15 (d, 12H, J₉₁₁ = 6.3 Hz, CH(CH₃)₂), 1.08 (s, 12H, B(OC(CH₃)₂)₂ ppm (other CH₂ and CH from 9-BBN in the baseline). ¹³C NMR (126 MHz, d₈-tolu.) δ 170.2 (NC(CH₃)CH), 141.6, 135.9, 126.0 (CH Ar), 123.8 (CH Ar), 123.6 (CH Ar), 122.9 (CH Ar), 94.9 (NC(CH₃)CH), 81.6 (B(OC(CH₃)₂)₂), 35.1, 33.2, 28.5 (CH(CH₃)₂), 24.5 (B(OC(CH₃)₂)₂), 23.9 (CH₃), 23.8 (CH₃), 23.3 (NC(CH₃)) ppm. ¹¹B NMR (160 MHz, d₈-tolu.) δ -17.7 ppm. (12) ¹H NMR (500 MHz, d₈-tolu.) δ 7.13- 6.99 (m, aromatic CH), 4.85 (s, 1H , NC(CH₃)CH), 3.47 (m, 2H, J₉₁₁ = 6.7 Hz, CH(CH₃)₂), 3.23 (m, 2H, J₉₁₁ = 6.7 Hz, CH(CH₃)₂), 1.63 (s, 6H, NC(CH₃)CH), 1.45 (d, 6H, J₉₁₁ = 6.7 Hz, CH(CH₃)₂), 1.20 (m, 34H, CH(CH₃)₂ + B(OC(CH₃)₂)₂ + CH₂), 1.08 (s, 2H, BH₂) (other CH₂ and CH from 9-BBN in the baseline). ¹³C NMR (126 MHz, d₈-tolu.) δ 170.3
(NC(CH₃)CH), 146.4, 144.6, 142.7, 142.4, 141.6, 135.9, 125.3 (CH Ar), 124.1(CH Ar), 124.0 (CH Ar), 123.8 (CH Ar), 123.6 (CH Ar), 122.9 (CH Ar), 95.4 (NC(CH₃)CH), 85.8 (B(O(CH₃)₂)₂), 34.7, 32.5, 32.4, 31.6, 28.2 (CH(CH₃)₂), 27.8 (CH(CH₃)₂), 25.8, 25.7, 25.3, 24.5 (NC(CH₃)), 24.4 (NC(CH₃)), 24.2, 23.3, 22.7, 22.0. ¹¹B NMR (160 MHz, d₈-tol.) δ –22.5.

Figure S1: ¹H NMR (500 MHz) spectrum of compound 9.
Figure S2: $^{13}$C{\textsuperscript{1}H} NMR spectrum (126 MHz) of compound 9.

Figure S3: $^{11}$B NMR spectrum (160.4 Mz) of compound 9.
Figure S4: $^1$H NMR (500 MHz) spectrum of compound 10.

Figure S5: $^{13}$C{$^1$H} NMR (126 MHz) spectrum of compound 10.
**Figure S6:** $^{11}$B NMR (160.4 MHz) spectrum of compound 10.

**Figure S7:** $^1$H NMR (500 MHz) spectrum of a mixture of compounds 11 and 12 after heating a sample of compound 9 at 110 °C for 4 days.
Figure S8: $^{11}$B NMR (160.4 MHz) spectrum of a mixture of compounds 11 and 12 after heating a sample of compound 9 at 110 °C for 4 days.

Figure S9: $^1$H NMR (500 MHz) spectrum of compound 11.
Figure S10: $^{13}$C{$^1$H} NMR (126 MHz) spectrum of compound 11.

Figure S11: $^{11}$B NMR (160.4 MHz) spectrum of compound 11.
Figure S12: $^1$H NMR (500 MHz) spectrum of 12.

Figure S13: $^{13}$C{$^1$H} NMR (126 MHz) spectrum of compound 12.
Figure S14: $^1$B NMR (160.4 MHz) NMR spectrum of compound 12.
**Computational Details / Methodology**

DFT calculations were run with Gaussian 09 (Revision D.01).³ Mg centers were described with the Stuttgart RECPs and associated basis sets,⁴ and 6-31G** basis sets were used for all other atoms (BS1).⁵ Initial BP86⁶ optimizations were performed using the ‘grid = ultrafine’ option, with all stationary points being fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). All energies were recomputed with a larger basis set (BS2) featuring 6-311++G** on all atoms. Corrections for the effect of toluene (ε = 2.3741) solvent were run using the polarizable continuum model and BS1.⁷ Single-point dispersion corrections to the BP86 results employed Grimme’s D3 parameter set with Becke-Johnson damping as implemented in Gaussian.⁸

**Breakdown of Energy Contributions**

The following tables detail the evolution of the relative energies as the successive corrections to the initial SCF energy are included. Terms used are:

- **ΔE_{BS1}**: SCF energy computed with the BP86 functional with BS1
- **ΔH_{BS1}**: Enthalpy at 0 K with BS1
- **ΔG_{BS1}**: Free energy at 298.15 K and 1 atm with BS1
- **ΔG_{BS1/tol}**: Free energy corrected for toluene solvent with BS1
- **ΔG_{BS1/tol+D3}**: Free energy corrected for toluene and dispersion effects with BS1
- **ΔG_{tol}**: Free energy corrected for basis set (BS2), dispersion effects and toluene solvent

**Energy Tables**

**Table S1** – Computed relative energies (kcal/mol) for the reaction of complex 9. Data in bold are those used in the main text. All energies are quoted relative to 9 at 0.0 kcal/mol.

|     | ΔE_{BS1} | ΔH_{BS1} | ΔG_{BS1} | ΔG_{BS1/tol} | ΔG_{BS1/tol+D3} | ΔE_{BS2} | ΔG_{tol} |
|-----|----------|----------|----------|--------------|-----------------|----------|----------|
| 9   | 0.0      | 0.0      | 0.0      | 0.0          | 0.0             | 0.0      | 0.0      |
| 9_{Xray} | 0.0  | 0.1      | 0.3      | -0.3         | 3.7             | 0.2      | 3.8      |
| 11  | -6.5     | -6.7     | -3.6     | -3.1         | -6.9            | -6.4     | -6.7     |
| 12  | -4.4     | -4.8     | -1.8     | -1.1         | -5.0            | -4.5     | -5.1     |
| 13a | 18.8     | 16.2     | 14.7     | 14.4         | 22.1            | 16.1     | 19.4     |
| 13b | 23.1     | 20.8     | 20.3     | 20.3         | 24.6            | 21.0     | 22.5     |
| 13c | 23.7     | 21.4     | 20.8     | 20.7         | 25.0            | 21.4     | 22.8     |
| 13d | 33.0     | 29.9     | 28.2     | 27.9         | 34.2            | 30.5     | 31.7     |
Computational Structural Discussion

Two different conformers of 9, the unsymmetrical diborane anion complex with a {Bpin} and a 9-BBN unit, have been computationally optimised. The X-ray crystal structure, 9\text{Xray}, is slightly raised in free energy by 3.8 kcal mol\(^{-1}\), compared to the computationally built geometry 9. Comparison of the structures by overlaying the two geometries (mapping the equivalent Mg centres, nacnac ligands and B atoms to be aligned), shows the majority of misalignment is due to the 9-BBN unit position (Figure S1). Upon closer inspection the conformational difference can be best described by the torsion O-B_{Bpin}-B_{9BBN}-H (shown in red in Figure S2), which is \(\sim 5^\circ\) for the crystal structure geometry (9\text{Xray}, magenta) and \(\sim 47^\circ\) for the computationally optimised structure 9 (shown in blue / elemental colours).

Looking at the breakdown in energy corrections for the two structures, the difference in \(\Delta G_{\text{tot}}\) arises from dispersion contributions, with the computed 9 involving more favourable and closer contacts between the 9-BBN unit and the Dipp groups of the nacnac ligand in comparison to the solid state structure 9\text{Xray}.

Figure S1 – Overlay of 9 (blue) and 9\text{Xray} (magenta) in Mercury, with the unaligned part of the structure (9-BBN unit) circled in green

Figure S2 – Overlay of 9 (blue / elemental colours) and 9\text{Xray} (magenta) in Mercury
Four intermediates of 13 were optimised (see Figure S3) highlighting the incredible conformational freedom the cyclooctenyl ring can access after “de-hydroboration”.

**Figure S3** – DFT-computed geometries for the addition of MeI to complex 11. Bond lengths given in Ångstroms.
**Cartesian Coordinates and Computed Energies (in Hartrees)**

9 (comp)

**SCF (BP86) Energy = -1990.21226964**
**Enthalpy UK = -1989.202017**
**Enthalpy 298K = -1989.144188**
**Free Energy 298K = -1989.293198**

**Lowest Frequency = 6.93310 cm⁻¹**
**Second Frequency = 17.1422 cm⁻¹**

**SCF (Toluene) Energy = -1990.21787291**
**SCF (BP86-D3BJ) Energy = -1990.51772581**
**SCF (BS2) Energy = -2189.93124956**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 0.05635 | 0.09441 | 0.16354 |
| C    | -1.14003 | 1.69919 | 0.88674 |
| O    | -1.83794 | 3.52411 | -0.32793 |
| H    | -0.59040 | -1.72100 | 0.98409 |
| N    | 1.98407 | 0.01463 | 0.95480 |
| C    | -0.64279 | -3.06317 | 3.10722 |
| H    | -0.93091 | -2.64945 | 0.08887 |
| Mg   | 0.14034 | -3.81645 | 3.29941 |
| C    | -1.50964 | -3.57209 | 2.66674 |
| C    | -0.09534 | -1.94672 | 2.22067 |
| C    | 0.97586 | -1.21843 | 2.81286 |
| C    | 1.15024 | -1.47128 | 3.86317 |
| C    | 2.01591 | -0.45314 | 2.22132 |
| C    | 3.23922 | -0.21663 | 3.09753 |
| C    | 4.00284 | -0.99401 | 2.92212 |
| C    | 2.96551 | -0.25075 | 4.16327 |
| C    | 3.71344 | 0.75222 | 2.87811 |
| C    | 3.22483 | 0.45236 | 0.35498 |
| C    | 3.51366 | 1.84012 | 0.20212 |
| C    | 4.72202 | 2.22923 | -0.40785 |
| C    | 4.94055 | 3.29745 | -0.51657 |
| C    | 5.64686 | 1.28719 | -0.86646 |
| C    | 6.58273 | 1.60883 | -1.33531 |
| C    | 5.35624 | -0.07270 | -0.72184 |
| C    | 6.07259 | -0.81690 | -1.08802 |
| C    | 4.16104 | -0.05154 | -0.12245 |
| C    | 3.91027 | -2.02349 | -0.05672 |
| C    | 2.94882 | -2.19079 | 0.45848 |
| C    | 3.79336 | -2.61025 | -1.48197 |
| C    | 2.97546 | -2.13459 | -0.20480 |
| C    | 3.60276 | -3.69695 | -1.44117 |
| C    | 4.72595 | -2.45775 | -0.52579 |
| C    | 5.06850 | -2.77303 | 0.73275 |
| C    | 5.98920 | -2.69625 | 0.23109 |
| C    | 4.76098 | -3.84597 | 0.81354 |
| C    | 5.12981 | -2.37604 | 1.75461 |
| C    | 2.57723 | 2.92955 | 0.71505 |
| C    | 1.67072 | 2.42415 | 1.08802 |
| C    | 2.15382 | 3.90505 | -0.40446 |
| C    | 3.01920 | 4.46426 | -0.80151 |
| C    | 1.43228 | 4.64997 | -0.02347 |
| C    | 1.67875 | 3.37035 | -1.24223 |
| C    | 3.20778 | 3.70093 | 1.88386 |
| C    | 3.47027 | 3.03000 | 2.73399 |
| C    | 2.51290 | 4.46798 | 2.28444 |
| C    | 4.13122 | 4.21866 | 1.58461 |
| C    | -1.55403 | -2.65773 | 0.43950 |
| C    | -2.94849 | -2.50456 | 0.70021 |
| C    | -3.84880 | -3.45695 | 0.18270 |
| C    | -4.91786 | -3.34782 | 0.39664 |
| C    | -3.40946 | -4.53512 | -0.58965 |
| C    | -4.12422 | -5.26858 | -0.97775 |
| H    | -2.04548 | -4.65832 | -0.87101 |
| H    | -1.69968 | -5.49434 | -1.48718 |

**Sime**

SCF (BP86) Energy = -1990.21225054
Enthalpy UK = -1989.2025078
Enthalpy 298K = -1989.144117
Free Energy 298K = -1989.292677
Lowest Frequency = 13.4997 cm⁻¹
Second Frequency = 19.7085 cm⁻¹
SCF (Toluene) Energy = -1990.21778452
SCF (BP86-D3BJ) Energy = -1990.50653646
SCF (BS2) Energy = -2189.93039234

Mg 0.06021 0.03451 0.29749
H 0.04078 -0.31055 -1.51488
C 1.75439 -2.31156 -2.21617
O 0.00729 -1.93539 1.00741
N -0.80879 -3.78284 -0.09309
C 1.76280 1.05915 0.89468
N -1.34628 1.55553 1.08579
C 2.84728 2.29381 2.76477
H 3.05916 1.78366 2.07870
H 0.03852 1.90668 2.74332
H 0.04861 2.34350 3.74037
C -0.95177 1.90493 2.25655
C -1.95276 2.64210 3.13816
H 1.94964 3.72226 2.91043
C -1.67729 2.53318 4.19918
H -2.98045 2.28086 2.98814
C -2.63929 1.73856 0.55437
C -2.79605 3.00778 -0.08125
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C -5.84842 0.57438 1.7369
C -3.54527 0.85243 0.63666
C -3.67069 -0.49642 1.34533
C -2.60178 -0.69138 1.53597
C -4.22752 -1.65490 0.48985
C -5.30858 -1.53737 0.30005
C -4.09982 -2.62039 1.01155
C -3.71728 -1.72390 -0.48402
C -4.38788 -0.45267 2.71583
C -3.96770 0.32341 3.37693
C -4.30296 -1.42352 3.23606
C -5.46296 -0.23591 2.58670
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C -1.33111 4.18944 -1.76329
C -1.05938 3.23319 -2.23983
C -0.49432 4.89665 -1.89878
C -2.20195 4.59698 -2.30582
C -1.94727 5.37379 0.38805
H -2.79757 5.87661 -0.10536
C -1.07199 6.04073 0.29997
C -2.19667 5.28025 1.45825
C 3.05359 1.12924 0.23819
C 3.32046 2.18938 -0.67811
C 4.60517 2.29202 -1.24733
H 4.81468 3.11711 -1.93700
C 5.61300 1.36800 -0.95773
H 6.06719 1.47119 -1.40492
C 5.32450 0.29604 -0.10884
H 6.09922 -0.45105 0.09762
C 4.05854 0.14955 0.49159
C 3.00272 -0.78444 1.36149
H 2.77742 -1.12384 0.73526
C 4.75838 -1.15885 2.58129
SCF (BS2) Energy = -2189.94143998
Mg 0.08706 0.03067 -0.08477
H 0.59427 1.25383 -1.50348
H 0.30126 -0.62058 -2.20113
O -0.81587 2.00623 0.66059
O -1.75948 4.03707 0.07784
N 1.96343 -0.32745 0.76360
N -0.92038 -1.47292 0.62249
C 3.16705 -0.52412 2.93871
H 3.77707 0.33925 2.62959
H 3.81063 -1.41542 2.85127
H 2.89276 -0.41578 3.99963
C 1.91716 -0.65485 2.07503
C 0.76783 -1.16004 2.73961
H 0.92031 -1.35132 3.80579
C -0.43389 -1.72599 2.21663
C -1.11781 -2.72649 3.14086
H -2.19345 -2.82628 2.94073
H -0.96397 -2.44815 4.19548
H -0.66709 -3.72564 3.00603
C -2.06432 -2.23846 0.52836
C -1.86325 -3.45744 -0.18260
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H -5.14927 -4.38183 -0.62784
C -4.48095 -2.56144 2.34517
H -5.49958 -2.20998 0.54238
C -3.93934 1.76958 0.76295
C -3.68752 0.43877 1.45563
H -2.73500 0.11402 1.50303
C -4.20649 -0.62995 2.90024
H -5.14418 -2.13156 2.90410
C -4.42000 0.34653 3.37054
C -3.48057 -1.15979 3.53773
C -4.69069 0.42128 0.65381
C -4.37140 0.54774 0.39322
H -4.79078 1.42296 1.10888
H -5.69900 -0.02830 0.64532
C -0.47815 3.99402 -0.54441
C 0.27182 -3.26254 -0.19017
C -0.19347 -5.34504 0.15160
H -0.27910 -5.26537 1.24863
H 0.82476 -5.69949 -0.08596
H -0.90188 -6.12427 -0.18085
C -0.04212 -4.12439 -0.21709
H -1.07484 -4.81667 0.24961
H 0.67195 -4.51488 -2.33863
H -0.45079 -3.14672 -2.52787
C 3.26891 -0.27174 0.14381
C 3.98846 1.48773 -0.08753
C 5.27211 -1.42813 -0.66224
H 5.81886 -2.36207 -0.83464
C 5.85818 -0.21328 -1.02873
H 6.86024 -0.18820 -1.46959
C 5.13264 0.96701 -0.83796
C 5.58234 1.92281 -1.13398
C 3.84896 0.96561 -0.26421
C 3.15757 2.31445 -0.07627
H 2.12545 2.11255 0.26214
C 3.07037 3.10241 -1.40194
H 4.07139 3.36850 -1.78371
H 2.51787 4.04804 -1.25916
H 2.55228 2.51592 -2.17717
C 3.8441 3.15562 1.01043
H 3.96511 2.63243 0.33814
H 3.36136 4.12622 1.15726

12
SCF (BP86) Energy = -1990.21925273
Enthalpy 0K = -1990.209669
Enthalpy 298K = -1989.152602
Free Energy 298K = -1989.296050
Lowest Frequency = 23.6126 cm⁻¹
Second Frequency = 27.9983 cm⁻¹
STOL (Toluene) Energy = -1990.2368997
SCF (BP86-D3BJ) Energy = -1990.5259977
SCF (BS2) Energy = -2189.93843073
Mg -0.06946 -0.01509 0.11238
H -0.81322 0.98611 -1.88234
H -0.11010 0.89366 -1.96135
O 0.67661 -2.01507 -0.66207

-S16-
O  1.76716 -4.01264 -0.23196
N -1.89579  0.38214 -0.81639
N  1.04730  1.42211 -0.94192
C  -3.01356  0.64535 -0.03296
H  -3.69882 -0.16001 -2.71754
H  -2.70705  0.42014 -0.07423
H  -3.58958  1.58550 -0.03003
C  -1.79016  0.71746 -2.12577
C  -0.59728  1.73788  2.74612
H  -0.70641  1.36816 -3.81737
C  0.61385  1.68686 -2.18792
C  1.38119  2.63596 -3.10128
H  0.96429  3.65542 -0.03154
H  1.27253  2.33122 -4.15448
H  2.44809  2.69840 -2.8582
C  2.19119  2.15432 -0.43256
C  3.51208  1.62436 -0.56257
C  4.60339  2.37980 -0.09135
H  5.61584  1.97809 -0.20819
C  4.42338  3.62535  0.51732
H  5.28511  4.20126  0.87077
C  3.12560  4.11527  0.68420
H  2.97561  5.07990  1.18157
C  1.99778  3.40134  0.23166
H  0.61724  4.00213  0.49838
H  -0.14079  3.28099  0.14572
C  0.39900  4.21508  2.01452
H  0.47760  3.26123  2.56193
H  -0.59907  4.64168  2.20822
C  1.14453  4.91189  2.43566
C  0.41291  5.32665 -0.27283
C  1.13454  6.09563  0.05534
H  -0.60119  5.72708 -0.09854
H  0.54331  5.19248 -1.35998
C  3.79275  0.27005 -1.21174
H  2.82126 -0.24034 -1.30879
C  4.70966 -0.62133 -0.34324
C  5.73564 -0.21952 -0.28785
H  4.78469 -1.63456 -0.77742
H  4.32989 -0.71541  0.68681
C  4.40020  0.41993 -2.62645
H  3.73457  0.97244 -3.30921
C  4.59935 -0.56969 -0.07526
H  5.36019  0.96419 -2.58187
C  -3.21655  0.36061 -0.23064
C  -3.82022 -0.86160  0.19146
C  -5.11002 -0.63415  0.75801
H  -5.57250 -1.77815  1.06665
C  -5.81468  0.36023  0.92517
H  -6.81867  0.35822  1.36233
C  -5.21009  1.55904  0.53687
H  -5.74487  2.50357  0.68740
C  -3.92209  1.59037 -0.03059
C  -3.31480  2.96479 -0.32543
H  -2.34045  2.81721 -0.82091
C  -3.06011  3.71365  1.00304
C  -4.00739  3.89859  1.53951
C  -2.85803  4.69269  0.81528
H  -2.40566  3.12984  1.67003
C  -4.19374  3.83123 -1.25655
H  -4.42108  3.32517 -2.20996
H  -3.68189  4.78067 -1.49158
H  -5.15754  4.08643 -0.78191
C  -3.15507 -2.22508 -0.01390
H  -2.11704 -2.04702 -0.31984
C  -3.49487 -3.04756 -1.11734
H  -4.92850 -3.23639 -0.79448
H  -3.39477 -4.03022 -1.22662

SCF (BP66) Energy = -1990.18238168
Enthalpy OK = -1989.176161
Enthalpy 298K = -1989.117083
Free Energy 298K = -1989.269776

Spectrum:

-13a

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Enthalpy OK = -1989.176161
Enthalpy 298K = -1989.117083
Free Energy 298K = -1989.269776

Spectrum:

-13a

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-13a

SCF (BP66) Energy = -1990.18238168
Enthalpy OK = -1989.176161
Enthalpy 298K = -1989.117083
Free Energy 298K = -1989.269776

Spectrum:

-13a

SCF (BP66) Energy = -1990.18238168
Enthalpy OK = -1989.176161
Enthalpy 298K = -1989.117083
Free Energy 298K = -1989.269776

Spectrum:
| C  | 1.61526  | -0.77167  | 2.82766  |
| H  | 2.01049  | -0.84781  | 3.84416  |
| C  | 2.52446  | -0.19754  | 1.89627  |
| C  | 3.91480  | 0.10361   | 2.44167  |
| H  | 4.57984  | -0.77059  | 2.33632  |
| H  | 3.85991  | 0.34477   | 3.51508  |
| C  | 4.38681  | 0.93687   | 1.90351  |
| C  | 3.32612  | 0.24330   | -0.32729 |
| C  | 3.59394  | 3.52898   | 2.72857  |
| C  | 4.64166  | 1.67306   | -1.81353 |
| H  | 4.84468  | 2.66465   | -2.23291 |
| C  | 5.43303  | 0.58812   | -2.19965 |
| H  | 6.24717  | 0.72152   | -2.91970 |
| C  | 5.16558  | -0.67151  | 1.65555  |
| H  | 5.77458  | -1.52936  | -1.96256 |
| C  | 4.12453  | -0.87338  | -0.72890 |
| C  | 3.86852  | -2.30426  | -0.24874 |
| H  | 3.05253  | 2.28111   | 0.49353  |
| C  | 3.40698  | -3.18607  | -1.43147 |
| H  | 2.50635  | -2.77239  | -1.91339 |
| C  | 3.17905  | -4.21084  | -1.08919 |
| C  | 4.19403  | -3.25869  | -2.20242 |
| C  | 5.10672  | -2.93935  | 0.42559  |
| H  | 5.93736  | -3.06256  | -0.29147 |
| C  | 4.85907  | -3.94059  | 0.81909  |
| H  | 5.48470  | -2.32979  | 1.26338  |
| C  | 2.82123  | 2.78018   | -0.47283 |
| C  | 1.98228  | 2.45037   | 0.16403  |
| C  | 2.23096  | 3.54071   | -1.68033 |
| C  | 3.02450  | 3.96843   | -2.31793 |
| C  | 1.59769  | 4.37759   | -1.33735 |
| C  | 1.60859  | 2.88009   | -2.30416 |
| C  | 3.71701  | 3.71794   | 0.37173  |
| C  | 4.08093  | 3.22279   | 1.28811  |
| C  | 3.16933  | 4.62944   | 0.67144  |
| C  | 4.60045  | 4.03968   | -0.20704 |
| C  | -1.45336 | -2.32555  | 1.33901  |
| C  | -2.75312 | -1.96869  | 1.50523  |
| C  | -3.80762 | -2.89168  | 1.66366  |
| H  | -4.80447 | -2.61821  | 2.02756  |
| C  | -3.61188 | -4.14231  | 1.07091  |
| C  | -4.44271 | -4.84955  | 0.97835  |
| C  | -2.34455 | -4.46871  | 0.57991  |
| C  | -2.18986 | -5.43819  | 0.09340  |
| C  | -1.25701 | -3.57969  | 0.68927  |
| C  | 0.08303  | -3.99867  | 0.08340  |
| C  | 0.77847  | -1.14671  | 0.18431  |
| C  | -0.07157 | -4.31377  | -1.42269 |
| H  | -0.76267 | -5.15830  | -1.58954 |
| H  | 0.89951  | -4.58937  | -1.86594 |
| H  | -0.46876 | -3.44562  | -1.97528 |
| C  | 0.69900  | -5.20310  | 0.83170  |
| H  | 0.86302  | -4.98026  | 1.89969  |
| H  | 1.67281  | -5.48034  | 0.39096  |
| H  | 0.04188  | -6.08872  | 0.77240  |
| C  | -3.06364 | -6.06892  | 2.42539  |
| H  | -2.11791 | -0.04187  | 2.49262  |
| C  | -3.64086 | -0.72126  | 3.85498  |
| H  | -4.61521 | -1.24048  | 3.85634  |
| H  | -3.80177 | 0.28143   | 4.28932  |
| H  | -2.96893 | -1.27675  | 4.53090  |
| C  | -4.03516 | 0.18394   | 1.51911  |
| C  | -3.60259 | 0.35795   | 0.51996  |
| C  | -4.28365 | 1.16195   | 1.96910  |
| H  | -4.98507 | -0.36155  | 1.38240  |
| C  | 0.812668 | -1.33666  | 1.31257  |
| C  | -1.53231 | 4.17272   | 1.21788  |
| C  | -3.16550 | 4.13323   | 1.39563  |

SCF (BP86) Energy = -1990.17551234
Enthalpy 0K = -1990.168890
Enthalpy 298K = -1990.110043
Free Energy 298K = -1990.260801
Lowest Frequency 13.5884 cm⁻¹
Second Frequency = 17.3542 cm⁻¹
SCF (Toluene) Energy = -1990.18111348
SCF (BP86-D3BJ) Energy = -1990.46914757
SCF (BS2) Energy = -2189.89785376

Mg 0.14275 -0.11991 -0.18222
O -0.099634 -1.73603 -1.07111
O -1.74400 -3.57491 0.09520
N -0.329681 1.63333 -1.18359
N 2.15950 +0.13648 -0.71406
C 0.19430 2.77272 -3.39041
C 0.41781 2.75661 -4.30360
H -0.15786 3.78789 -2.96075
H -1.24719 2.59387 -3.66435
H 0.29248 1.74540 -2.37781
C 1.41632 0.96646 -2.77423
C 1.71950 1.11604 -3.81390
C 2.35417 0.22726 -1.99996
C 3.60608 0.11008 -2.07076
C 4.39669 0.70324 -2.58483
H 3.48907 -0.23444 -3.78797
### SCF (BP86) Energy

| H        | C         | O         | Mg         | Na         |
|----------|-----------|-----------|------------|------------|
| 1.08302  | 1.49670   | 2.97771   | 0.22188   | 0.23879    |
| 1.09712  | 1.46592   | 0.77797   | 0.35070   | 2.3573    |
| 0.95828  | 0.75930   | 0.7777    | 0.35042   | 3.94509   |
| 0.31979  | 0.31562   | 0.77495   | 0.35042   | 3.94509   |
| 0.23879  | 0.22188   | 0.23879   | 0.35042   | 3.94509   |
| 0.75930  | 0.31562   | 0.77495   | 0.35042   | 3.94509   |
| 0.7777   | 0.35070   | 2.3573    | 0.35042   | 3.94509   |
| 0.7777   | 0.35070   | 2.3573    | 0.35042   | 3.94509   |
| 0.35070  | 0.35042   | 3.94509   | 0.35042   | 3.94509   |

### SCF (Toluene) Energy

| H        | C         | O         | Mg         | Na         |
|----------|-----------|-----------|------------|------------|
| 1.08302  | 1.49670   | 2.97771   | 0.22188   | 0.23879    |
| 1.09712  | 1.46592   | 0.77797   | 0.35070   | 2.3573    |
| 0.95828  | 0.75930   | 0.7777    | 0.35042   | 3.94509   |
| 0.31979  | 0.31562   | 0.77495   | 0.35042   | 3.94509   |
| 0.23879  | 0.22188   | 0.23879   | 0.35042   | 3.94509   |
| 0.75930  | 0.31562   | 0.77495   | 0.35042   | 3.94509   |
| 0.7777   | 0.35070   | 2.3573    | 0.35042   | 3.94509   |
| 0.7777   | 0.35070   | 2.3573    | 0.35042   | 3.94509   |
| 0.35070  | 0.35042   | 3.94509   | 0.35042   | 3.94509   |

### SCF (BP86-D3BJ) Energy

| H        | C         | O         | Mg         | Na         |
|----------|-----------|-----------|------------|------------|
| 1.08302  | 1.49670   | 2.97771   | 0.22188   | 0.23879    |
| 1.09712  | 1.46592   | 0.77797   | 0.35070   | 2.3573    |
| 0.95828  | 0.75930   | 0.7777    | 0.35042   | 3.94509   |
| 0.31979  | 0.31562   | 0.77495   | 0.35042   | 3.94509   |
| 0.23879  | 0.22188   | 0.23879   | 0.35042   | 3.94509   |
| 0.75930  | 0.31562   | 0.77495   | 0.35042   | 3.94509   |
| 0.7777   | 0.35070   | 2.3573    | 0.35042   | 3.94509   |
| 0.7777   | 0.35070   | 2.3573    | 0.35042   | 3.94509   |
| 0.35070  | 0.35042   | 3.94509   | 0.35042   | 3.94509   |

### Enthalpy 0K

| H        | C         | O         | Mg         | Na         |
|----------|-----------|-----------|------------|------------|
| 2.18580  | 0.64580   | 0.11391   | 0.96603    | 0.96603    |
| 0.11391  | 0.96603   | 2.18580   | 0.64580   | 0.11391   |
| 0.96603  | 0.96603   | 0.11391   | 0.96603   | 0.96603   |

### Second Frequency

| H        | C         | O         | Mg         | Na         |
|----------|-----------|-----------|------------|------------|
| 1.2116   | 3.81543   | 2.85891   | 3.75294   | 3.75294   |
| 2.85891  | 3.75294   | 1.2116    | 3.81543   | 2.85891   |
| 3.75294  | 3.75294   | 1.2116    | 3.81543   | 2.85891   |

### SCF (BS2) Energy

| H        | C         | O         | Mg         | Na         |
|----------|-----------|-----------|------------|------------|
| -1.1083  | -1.7742   | -0.3085   | -0.23879   | -0.23879   |
| -0.3085  | -0.23879  | -1.1083   | -1.7742   | -0.3085   |
| -0.23879 | -0.23879  | -1.1083   | -1.7742   | -0.3085   |

### Total SCF Energies

| H        | C         | O         | Mg         | Na         |
|----------|-----------|-----------|------------|------------|
| -2.37359 | -5.94951  | -0.98592  | -2.37359   | -5.94951   |
| -0.98592 | -2.37359  | -5.94951  | -2.37359   | -5.94951   |
| -2.37359 | -5.94951  | -0.98592  | -2.37359   | -5.94951   |

### Other Energies

| H        | C         | O         | Mg         | Na         |
|----------|-----------|-----------|------------|------------|
| -2.37359 | -5.94951  | -0.98592  | -2.37359   | -5.94951   |
| -0.98592 | -2.37359  | -5.94951  | -2.37359   | -5.94951   |
| -2.37359 | -5.94951  | -0.98592  | -2.37359   | -5.94951   |

### Notes

- SCF (BP86) Energy = \(-1990.17452978\)
- Enthalpy 0K = \(-1989.167970\)
- Enthalpy 298K = \(-1989.109029\)
- Free Energy 298K = \(-1989.260107\)
- Lowest Frequency = 15.9939 cm\(^{-1}\)
- Second Frequency = 19.6725 cm\(^{-1}\)
- SCF (Toluene) Energy = \(-1990.18025624\)
- SCF (BP86-D3BJ) Energy = \(-1990.46812491\)
- SCF (BS2) Energy = \(-2189.897909474\)
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | 1   | 2   | 3   |
| H    | 4   | 5   | 6   |
| C    | 7   | 8   | 9   |
| H    | 10  | 11  | 12  |
| C    | 13  | 14  | 15  |
| H    | 16  | 17  | 18  |
| C    | 19  | 20  | 21  |
| H    | 22  | 23  | 24  |

**SCF (BP86) Energy = -1990.15965826**

**Enthalpy 0K = -1989.154360**

**Enthalpy 298K = -1989.095038**

**Free Energy 298K = -1989.248192**

**Lowest Frequency = 10.5504 cm⁻¹**

**Second Frequency = 16.6256 cm⁻¹**

**SCF (toluene) Energy = -1990.1655614**

**SCF (B3LYP-D3BJ) Energy = -1990.45012874**

**SCF (BS2) Energy = -2189.88263520**
Single Crystal X-ray Diffraction Analysis

Data were collected for compounds 9 - 12 on a SuperNova, Dual Cu at zero, EosS2 diffractometer. The crystals were all kept at 150(2) K during data collection. Using Olex2, the structures were solved via the olex2.solve routine and refined with the ShelXL refinement package using Least Squares minimization. For compound 9, H2 and H40 (attached to B2 and C40, respectively) were located and refined without restraints. From the raw data for compound 11 it was evident that the diffraction pattern resulted from a twin – wherein the second component was small. The twin angle was determined to be in the region of 178° and, as such, most reflections were overlapped. Data integration to account for the twin was carried with as small a mask as possible in an effort to maximize the quality of the arising data sets. The $R$(int) for the data extracted pertaining to the minor component was poor and, after parallel refinements, the results presented here are based solely on the data arising from the major component in the sample. Overall, we have here an unambiguous characterization of this material, and a credible convergence. Residual electron density is in the region of C40-C42, for which some soft ADP restraints were included in the model. There is either some minor disorder in this region – or the maxima are artifacts of the crystal quality/twinning. In any event, it was not possible to attain a chemically sensible disorder model for this region with an accompanying enhancement of the residuals. H2a and H2b were located and refined freely, subject to being equidistant from B2. For 12 the hydrogens attached to B2 and C36 were located and refined without restraints. A further crystal resulting from a toluene solution of a mixture of 11 and 12 was found to represent an average of these two structural isomers. In particular, C38-C42 were each found to be disordered in a 78:22 ratio. ADP restraints were applied to the fractional occupancy carbons in the final least squares. H36 was located and refined subject to being a distance of 0.98 Å from C36, while H2A and H2A (attached to B2) were located and refined freely.
### Table S1: Single crystal X-ray diffraction analysis of compounds 9 – 12 and the 78:22 co-crystal of 11 and 12.

| Compound | 9 | 10 | 11 | 12 | 11/12 |
|----------|---|----|----|----|------|
| **Empirical formula** | C_{60}H_{38}B_{2}Mg_{2}N_{8}O_{2} | C_{60}H_{38}B_{2}Mg_{2}N_{8}O_{2} | C_{60}H_{38}B_{2}Mg_{2}N_{8}O_{2} | C_{60}H_{38}B_{2}Mg_{2}N_{8}O_{2} | C_{60}H_{38}B_{2}Mg_{2}N_{8}O_{2} |
| **Formula weight** | 690.92 | 811.02 | 690.92 | 690.92 | 690.92 |
| **Temperature/K** | 150.00(10) | 150.00(10) | 150.01(10) | 298.15 | 150.00(10) |
| **Crystal system** | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| **Space group** | P2_1/n | P2_1/n | P2_1/n | P2_1/n | P2_1/n |
| **a/Å** | 10.4806(1) | 12.1210(7) | 9.9486(2) | 9.9657(1) | 9.94853(16) |
| **b/Å** | 20.9444(1) | 16.8031(8) | 21.5144(4) | 21.5829(2) | 21.5169(5) |
| **c/Å** | 19.3236(1) | 12.9376(9) | 19.0011(3) | 18.8992(2) | 18.9880(4) |
| **α°** | 90 | 90 | 90 | 90 | 90 |
| **β°** | 100.418(1) | 116.747(8) | 92.140(2) | 92.242(1) | 92.0642(18) |
| **γ°** | 90 | 90 | 90 | 90 | 90 |
| **U/Å³** | 4171.79(5) | 2353.1(3) | 4064.12(13) | 4061.89(7) | 4061.95(14) |
| **Z** | 4 | 2 | 4 | 4 | 4 |
| **ρ_{calc} g/cm³** | 1.100 | 1.145 | 1.129 | 1.130 | 1.130 |
| **μ/mm⁻¹** | 0.629 | 0.634 | 0.645 | 0.646 | 0.646 |
| **F(000)** | 1512.0 | 876.0 | 1512.0 | 1512.0 | 1512.0 |
| **Crystal size/mm³** | 0.313 × 0.124 × 0.122 | 0.08 × 0.058 × 0.043 | 0.187 × 0.127 × 0.088 | 0.284 × 0.239 × 0.182 | 0.21 × 0.08 × 0.065 |
| **2θ range for data collection/°** | 6.28 to 146.26 | 7.62 to 147.346 | 6.208 to 144.258 | 6.218 to 146.896 | 6.21 to 146.59 |
| **Index ranges** | -10 ≤ h ≤ 13, -25 ≤ k ≤ -15 ≤ l ≤ 11, -20 ≤ k ≤ -16, -12 ≤ l ≤ 15 | -12 ≤ h ≤ 12, -25 ≤ k ≤ 26, -23 ≤ l ≤ 23 | -12 ≤ h ≤ 11, -24 ≤ k ≤ 26, -23 ≤ l ≤ 23 | -9 ≤ h ≤ 12, -25 ≤ k ≤ 26, -21 ≤ l ≤ 23 |
| **Reflections collected** | 48301 | 16025 | 55552 | 55827 | 30529 |
| **Independent reflections, R_{int}** | 8324 [R_{int} = 0.0290, R_{eq} = 0.0175] | 8292 [R_{int} = 0.0533, R_{eq} = 0.0927] | 8018 [R_{int} = 0.0897, R_{eq} = 0.0536] | 8171 [R_{int} = 0.0510, R_{eq} = 0.0280] | 8072 [R_{int} = 0.0495, R_{eq} = 0.0451] |
| **Data/restraints/parameters** | 83240/473 | 8292/1555 | 8018/25473 | 8171/0477 | 8072/49522 |
| **Goodness-of-fit on F²** | 1.024 | 1.035 | 1.050 | 1.038 | 1.033 |
| **Final R1, wR2 [I>2σ (I)]** | R₁ = 0.0372, wR₂ = 0.0958 | R₁ = 0.0547, wR₂ = 0.0950 | R₁ = 0.0855, wR₂ = 0.2399 | R₁ = 0.0490, wR₂ = 0.1279 | R₁ = 0.0555, wR₂ = 0.1359 |
| **Final R1, wR2 [all data]** | R₁ = 0.0407, wR₂ = 0.0984 | R₁ = 0.0788, wR₂ = 0.1049 | R₁ = 0.1081, wR₂ = 0.2567 | R₁ = 0.0561, wR₂ = 0.1335 | R₁ = 0.0742, wR₂ = 0.1464 |
| **Largest diff. peak/hole / e Å⁻³** | 0.32/o.26 | 0.20/o.20 | 0.97/o.30 | 0.61/o.32 | 0.38/o.34 |
| **Flack Parameter** | -0.06(6) | -0.06(6) | -0.06(6) | -0.06(6) | -0.06(6) |
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