ELECTRONIC SUPPLEMENTARY INFORMATION

Spying on the Boron-Boron Triple Bond Using Spin-Spin Coupling Measured from ^{11}B Solid-State NMR Spectroscopy

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Experimental

Synthesis

Compounds **1**,[1] **2**,[2] **3**,[3] and **4**[4] were prepared as previously described.

Solid-State NMR Spectroscopy

For all NMR experiments, the samples were packed into 4 mm o.d. MAS rotors under an inert atmosphere immediately prior to running the experiments. The experiments were performed using a Bruker AVANCE 500 NMR spectrometer using a Bruker triple-resonance 4 mm MAS probe. The ^{11}B *J*-resolved and DQF-*J*-resolved spectra were obtained using the previously published pulse sequences[5,6] and used 15 μs central-transition selective 90° pulses and a DQF time of 4 to 6 ms. A 2 s recycle delay was used in all cases and the samples were spun at a 10 kHz MAS frequency. Between 25 and 42 t_1 increments of 500 μs were performed for the 2D acquisition; between 128 and 2048 scans were acquired in each increment. The final spectra were obtained by magnitude processing.

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DFT Calculations

All DFT calculations were performed using the Amsterdam Density Functional program (ADF, ver. 2009).[7] DFT calculations were performed using the generalised gradient approximation (GGA) DFT functional of Perdew, Burke, and Ernzerhof (PBE)[8] using triple-zeta polarised Slater-type basis sets (TZP). The NBO/NLMO analysis was performed using the NBO 5.0 program,[9] which is included with ADF. The results of the NLMO decomposition of the *J* couplings are given in Table S1.

Table S1. Results from the NLMO analysis of the $J(^{11}B, {}^{11}B)$ coupling constants

Compound	σ_{BB} contribution to J / %	s_B contribution to J / %	σ_{BB} s-character / %	σ_{BB} NBO energy / a.u.
1	33.1	64.4	52.5	-0.399
2	36.3	74.0	50.7	-0.410
3	34.6	69.7	32.5	-0.309
4	33.9	81.4	31.5	-0.314

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