

New insights into Frustrated Lewis Pairs: Structural investigations of intramolecular phosphane-borane adducts by using modern Solid State NMR techniques and DFT calculations

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Supporting Information

General Procedures. All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried with the procedure according to Grubbs (A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518-1520) or were distilled from appropriate drying agents and stored under an argon atmosphere. NMR spectra were recorded on a *Bruker* AV 300 (¹H: 300 MHz, ¹³C: 76 MHz, ³¹P: 121 MHz, ¹¹B: 96 MHz, ¹⁹F: 282 MHz) and on a *Agilent* DD2- 600 MHz (¹H: 600 MHz, ¹³C: 151 MHz, ¹⁹F: 564 MHz, ¹¹B: 192 MHz, ³¹P: 243 MHz). ¹H NMR and ¹³C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ¹⁹F NMR: chemical shifts δ are given relative to CFCl₃ (external reference), ¹¹B NMR: chemical shifts δ are given relative to BF₃·Et₂O (external reference), ³¹P NMR: chemical shifts δ are given relative to H₃PO₄ (85% in D₂O) (external reference). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Melting points and decomposition points were obtained with a DSC 2010 (*TA Instruments*). HRMS was recorded on GTC Waters Micromass (Manchester, UK).

X-Ray crystal structure analyses. Data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.*

1990, A46, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122), graphics XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 50 % probability, *R*-values are given for the observed reflections, *wR*²-values are given for all reflections.

Materials. B(C₆F₅)₃ (**12**) [(a) Wang, C.; Erker, G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics*, **2005**, 24, 4760–4773. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, 2, 245–250. (c) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212.], propynyl lithium [(a) Bender, S. L.; Detty, M. R.; Haley, N. F. *Tetrahedron Lett.* **1982**, 23, 1531 –1534. (b) Starowieyski, K. B.; Chojnowski, A.; Kusmierek, Z. **1980**, 192, 147 – 154. (c) Jäger, V.; Viehe, H. G. *Methoden Org. Chem. (Houben-Weyl)*, 4th edition **1977**, V/2a, 123.], diphenyl(propynyl)phosphane [(a) Miller, A. D.; Johnson, S. A.; Tupper, K. A.; McBee, J. L.; Tilley, T. D. *Organometallics* **2009**, 28, 1252–1262. (b) Samb, A.; Demerseman, B.; Dixneuf, P. H.; Mealli, C. *Organometallics* **1988**, 7, 26–33. See also: Spies, P.; Fröhlich, R.; Kehr, G.; Erker, G.; Grimme, S. *Chem. Eur. J.* **2008**, 14, 333-343.] and compound **6** [Ekkert, O.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2011**, 133, 4610.] were synthesised according to literature procedure.

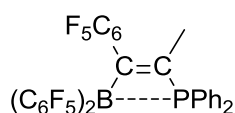
Synthesis of Diphenyl(propynyl)phosphine.

Propynyl lithium (1.00 g, 21.7 mmol) was suspended in diethylether (15 ml) and cooled to -78°C and chlorodiphenylphosphane (4.01 ml, 21.7 mmol) was added. Subsequently the suspension was stirred for 3h at room temperature. The solvent was removed in vacuum and the residue was extracted (under argon) with pentane (30 ml) via filter cannula. Evaporation of pentane gave the product (3.60 g, 16.1 mmol, 74%) as a red oil.

¹H NMR (300 MHz, 300 K, C₆D₆): δ = 7.72 (m, 4H, Ph), 7.05 (m, 6H, Ph), 1.52 (d, ⁴*J*_{PH} = 1.7 Hz, 3H, CH₃).

¹³C{¹H} NMR (76 MHz, 300 K, C₆D₆): δ = 137.7 (d, ¹*J*_{PC} = 7.4 Hz, *i*-Ph), 132.9 (d, ²*J*_{PC} = 21.0 Hz, *o*-Ph), 129.0 (*p*-Ph), 128.8 (d, ³*J*_{PC} = 7.4 Hz, *m*-Ph), 106.1 (d, ²*J*_{PC} = 4.4 Hz, CH₃C≡), 76.0 (d, ¹*J*_{PC} = 3.2 Hz, ≡C^P), 4.9 (d, ³*J*_{PC} = 1.2 Hz, CH₃).

³¹P{¹H} NMR (121 MHz, 300 K, C₆D₆): δ = -32.1 (*v*_{1/2} ~ 2 Hz).



Synthesis of 6. B(C₆F₅)₃ (**12**) (0.420 g, 0.821 mmol) and diphenyl(propynyl)phosphane (0.184 g, 0.821 mmol) were dissolved in toluene (20 ml) and stirred for 6h at 70 °C. Subsequently the solvent was

removed and the residue was washed twice with pentane (15 ml) and filtered via cannula. After crystallization from dichloromethane / pentane, compound **6** (0.307 g, 0.417 mmol, 51%) was obtained as a white solid. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **6** in dichloromethane at -36 °C. **Anal. Calc.** for C₃₃H₁₃BF₁₅P: C, 53.84; H, 1.78. Found: C, 54.51; H, 1.58. **HRMS:** Calc. for (C₃₃H₁₃BF₁₅P)CF₃COO: 849.04710. Found: 849.04789. **IR** (KBr): $\tilde{\nu}$ / cm⁻¹ = 3066 (br m), 2919 (w), 2616 (w), 2400 (w), 1645 (m), 1518 (s), 1467 (s), 1286 (m), 1096 (s), 970 (s), 691 (m). **M.p.** (DSC): 218 °C. **Decomp.** (DSC): 259 °C.

¹H NMR (600 MHz, 298 K, C₆D₆): δ = 7.21 (m, 4H, *o*-Ph), 6.93 (m, 2H, *p*-Ph), 6.86 (m, 4H, *m*-Ph), 1.65 (d, ³*J*_{PH} = 12.0 Hz, CH₃).

¹³C{¹H} NMR (151 MHz, 298 K, C₆D₆): δ = 161.8 (br, ^BC=), 148.4 (dm, ¹*J*_{FC} ~ 240 Hz, *o*-BC₆F₅), 143.5 (dm, ¹*J*_{FC} ~ 245 Hz, *o*-C₆F₅), 141.5 (d, ¹*J*_{PC} = 52.0 Hz, =C^P), 140.7 (dm, ¹*J*_{FC} ~ 250 Hz, *p*-C₆F₅), 140.4 (dm, ¹*J*_{FC} ~ 250 Hz, *p*-BC₆F₅), 137.9 (dm, ¹*J*_{FC} ~ 250 Hz, *m*-C₆F₅), 137.5 (dm, ¹*J*_{FC} ~ 250 Hz, *m*-BC₆F₅), 132.3 (d, ⁴*J*_{PC} = 3.0 Hz, *p*-Ph), 132.1 (d, ²*J*_{PC} = 9.0 Hz, *o*-Ph), 129.3 (d, ³*J*_{PC} = 10.5 Hz, *m*-Ph), 125.0 (d, ¹*J*_{PC} = 43.0 Hz, *i*-Ph), 116.0 (br s, *i*-BC₆F₅), 114.9 (br m, *i*-C₆F₅), 15.1 (d, ²*J*_{PC} = 2.4 Hz, CH₃).

¹⁹F{¹H} NMR (564 MHz, 298 K, C₆D₆): δ = -130.0 (m, 4F, *o*), -156.4 (m, 2F, *p*), -163.8 (m, 4F, *m*) (B(C₆F₅)₂) [$\Delta\delta^{19}\text{F}_{m,p}$ = 7.4], -139.3 (m, 2F, *o*), -154.6 (t, ³*J*_{FF} = 21.5 Hz, 1F, *p*), -162.0 (m, 2F, *m*) (C₆F₅).

¹¹B{¹H} NMR (192 MHz, 298 K, C₆D₆): δ = -5.5 (*v*_{1/2} ~ 280 Hz).

³¹P{¹H} NMR (243 MHz, 298 K, C₆D₆): δ = 15.1 (*v*_{1/2} ~ 80 Hz).

TOCSY (600 MHz, 298 K, C₆D₆): $\delta^1\text{H}_{\text{irr.}} / \delta^1\text{H}_{\text{res.}}$ = 7.21 / 6.93, 6.86 (*o*-Ph / *p*, *m*-Ph).

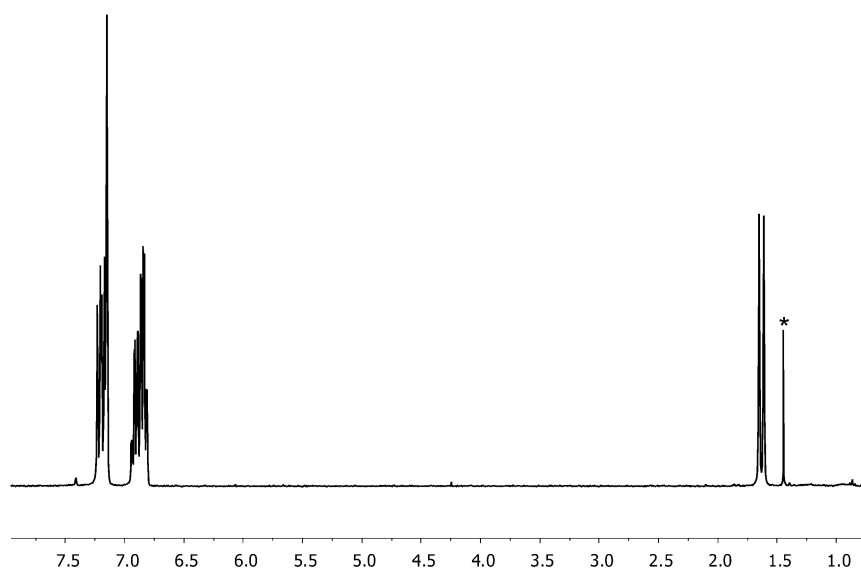
NOE (600 MHz, 298 K, C₆D₆)[selected experiments]: $\delta^1\text{H}_{\text{irr.}} / \delta^1\text{H}_{\text{res.}}$ = 7.21 / 6.86, 1.65 (*o*-Ph / *m*-Ph, CH₃), 1.65 / 7.21 (CH₃ / *o*-Ph).

¹H, ¹H GCOSY (600 MHz / 600 MHz, 298 K, C₆D₆): $\delta^1\text{H} / \delta^1\text{H}$ = 6.86 / 7.21, 6.93 (*m*-Ph / *o*-, *p*-Ph).

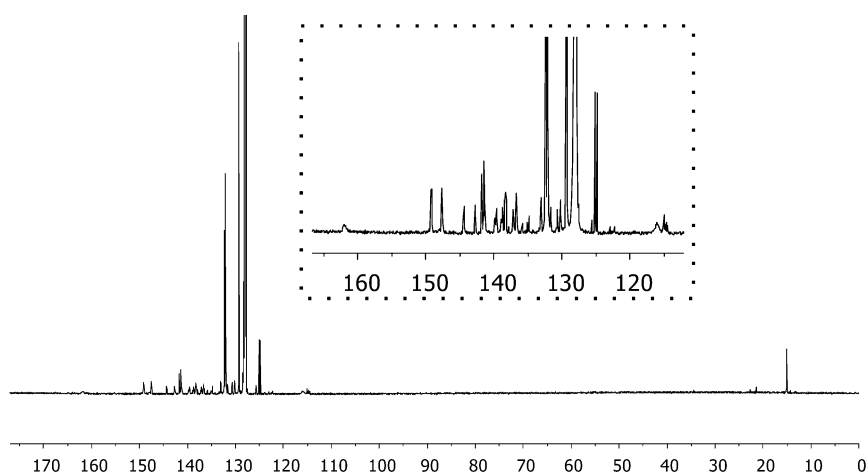
¹H, ¹³C GHSQC (600 MHz / 151 MHz, 298 K, C₆D₆): $\delta^1\text{H} / \delta^{13}\text{C}$ = 7.21 / 132.1 (*o*-Ph), 6.93 / 132.3 (*p*-Ph), 6.86 / 129.3 (*m*-Ph), 1.65 / 15.1 (CH₃).

¹H, ¹³C GHMBC (600 MHz / 151 MHz, 298 K, C₆D₆): $\delta^1\text{H} / \delta^{13}\text{C}$ = 7.21 / 132.1, 132.3 (*o*-Ph / *o*-, *p*-Ph), 6.93 / 132.1 (*p*-Ph / *o*-Ph), 6.86 / 132.1, 129.3, 125.0 (*m*-Ph / *o*-, *m*-, *i*-Ph), 1.65 / 161.8, 141.5 (CH₃ / ^BC=, =C^P).

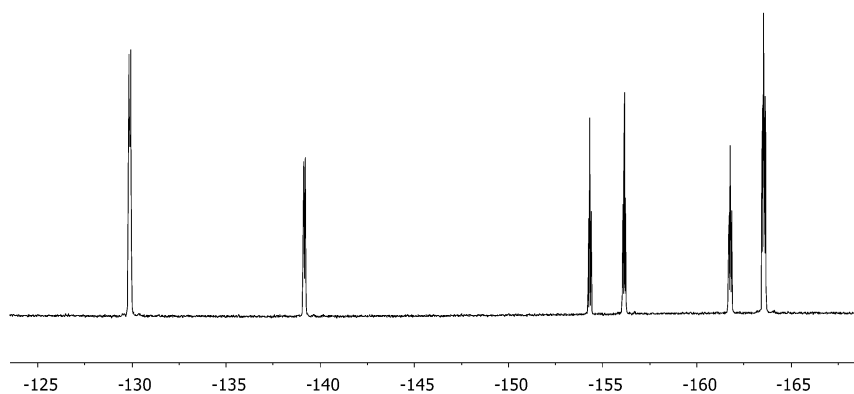
$^{19}\text{F}, ^{19}\text{F}$ GCOSY (564 MHz / 564 MHz, 298 K, C_6D_6)[selected traces]: $\delta^{19}\text{F} / \delta^{19}\text{F} = -163.8 / -156.4, -130.0$ (*m* / *p*, *o*) ($\text{B}(\text{C}_6\text{F}_5)_2$), $-162.0 / -154.6, -139.3$ (*m* / *p*, *o*) (C_6F_5).



^1H NMR (300 MHz, 300 K, C_6D_6) of **6**



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 298 K, C_6D_6) of **6**



^{19}F NMR (282 MHz, 300 K, C_6D_6) of **6**.



Solid State NMR and DFT calculations

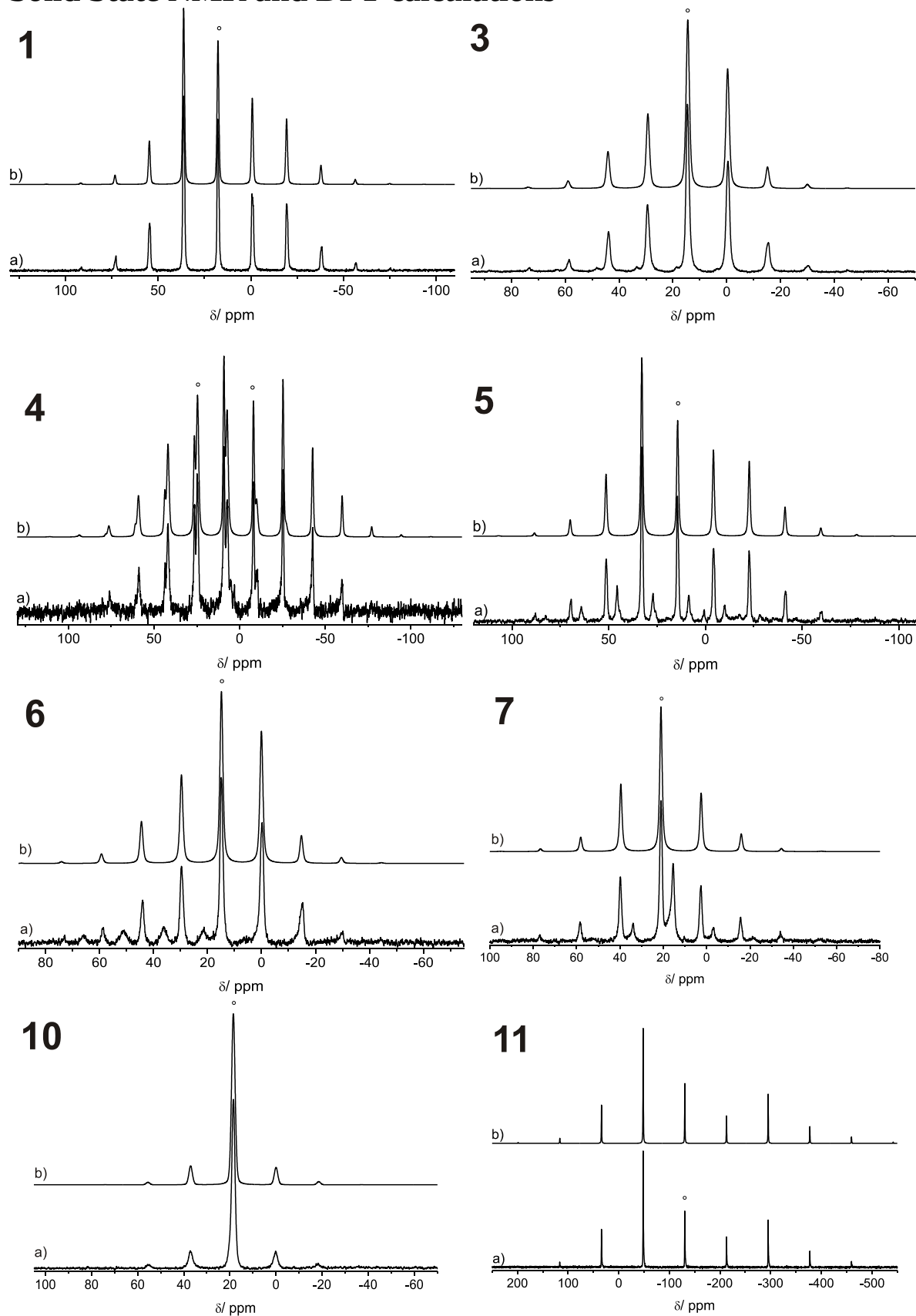


Figure S1: Slow-spinning $^{31}\text{P}\{^1\text{H}\}$ CPMAS experiments with spinning rates ranging in-between 2.4 to 3 kHz (a) and simulated CSA pattern ignoring impurities (b). The isotropic peak positions are labeled by open circles.

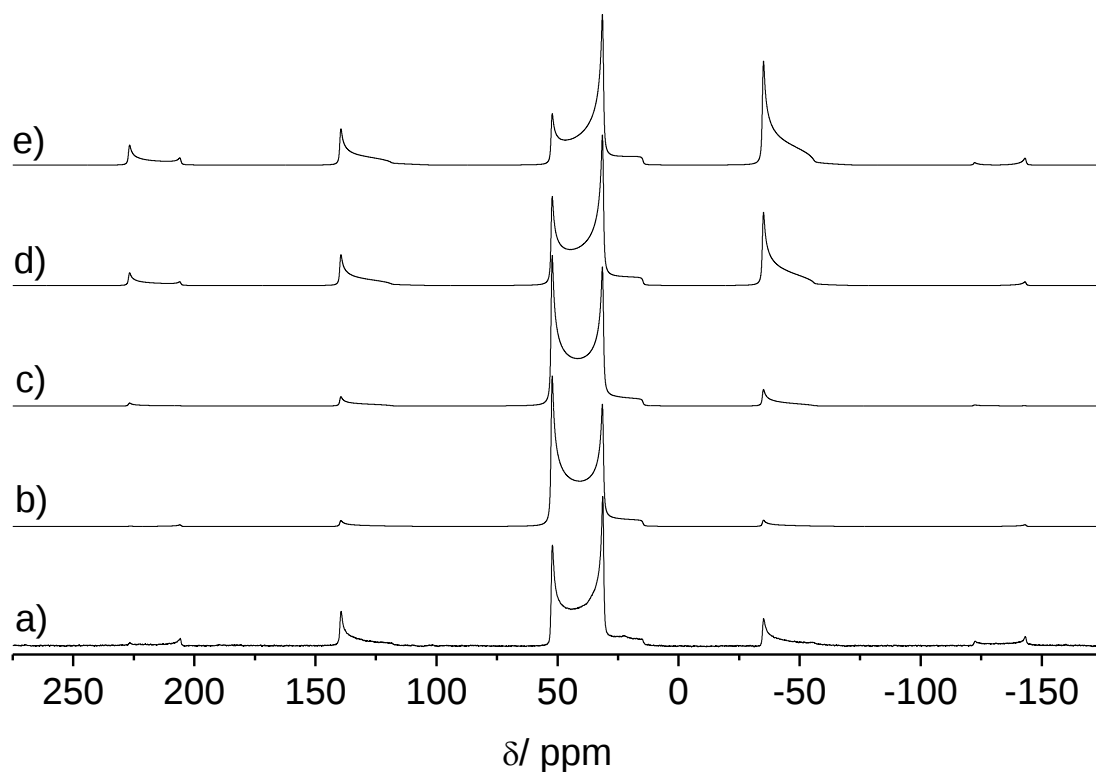


Figure S2: ^{11}B MAS spectrum for the educt of the 1,1-carboboration $\text{B}(\text{C}_6\text{F}_5)_3$ (**12**) acquired at 11.7 T with a rotation frequency of 14 kHz (a) and simulated spectra using the SIMPSON program package with a C_Q of 4.259 MHz, an η value of 0.02 and different chemical shift anisotropies: $\Delta\sigma = 0$ ppm (b), $\Delta\sigma = 180$ ppm (c), $\Delta\sigma = 300$ ppm (d) and $\Delta\sigma = 360$ ppm (e). The intensity distribution of the central transition is strongly influenced by the chemical shift anisotropy.

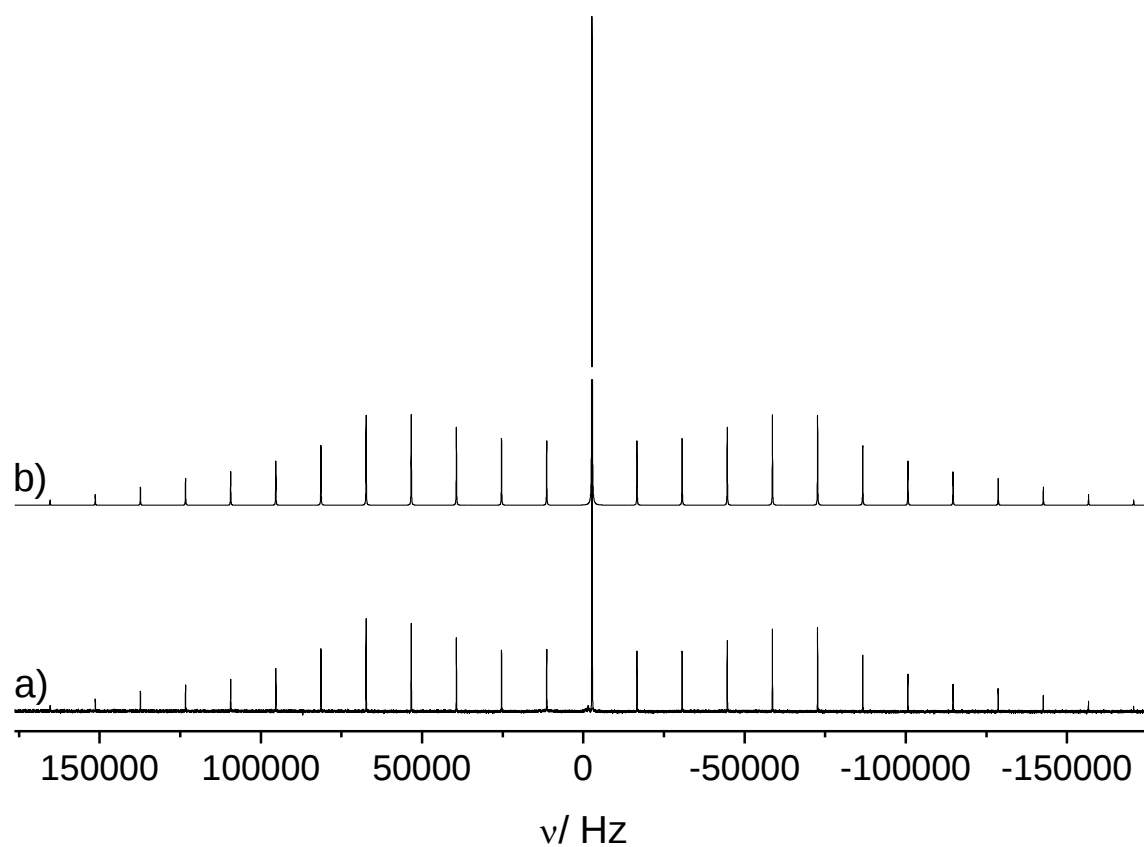


Figure S3: ^{11}B SATRAS spectrum of compound **11** (a) and corresponding SIMPSON simulation (b) with the following simulation parameters: $\delta_{\text{CS}}^{\text{iso}} = -16.7$ ppm, $C_Q = 0.33$ and $\eta = 0.3$.

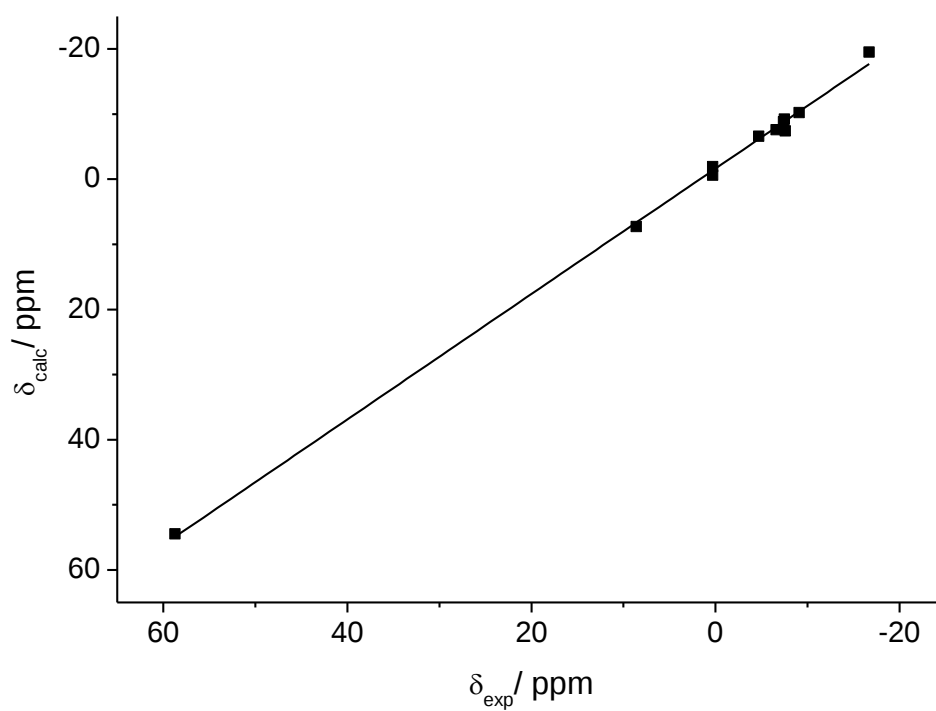


Figure S4: Correlation between experimentally and quantum-chemically (B3-LYP, def2-TZVP, except **9**) determined ^{11}B chemical shifts (referenced to $\text{BF}_3 \cdot \text{Et}_2\text{O}$). The linear regression belongs to an R^2 value of 0.998.

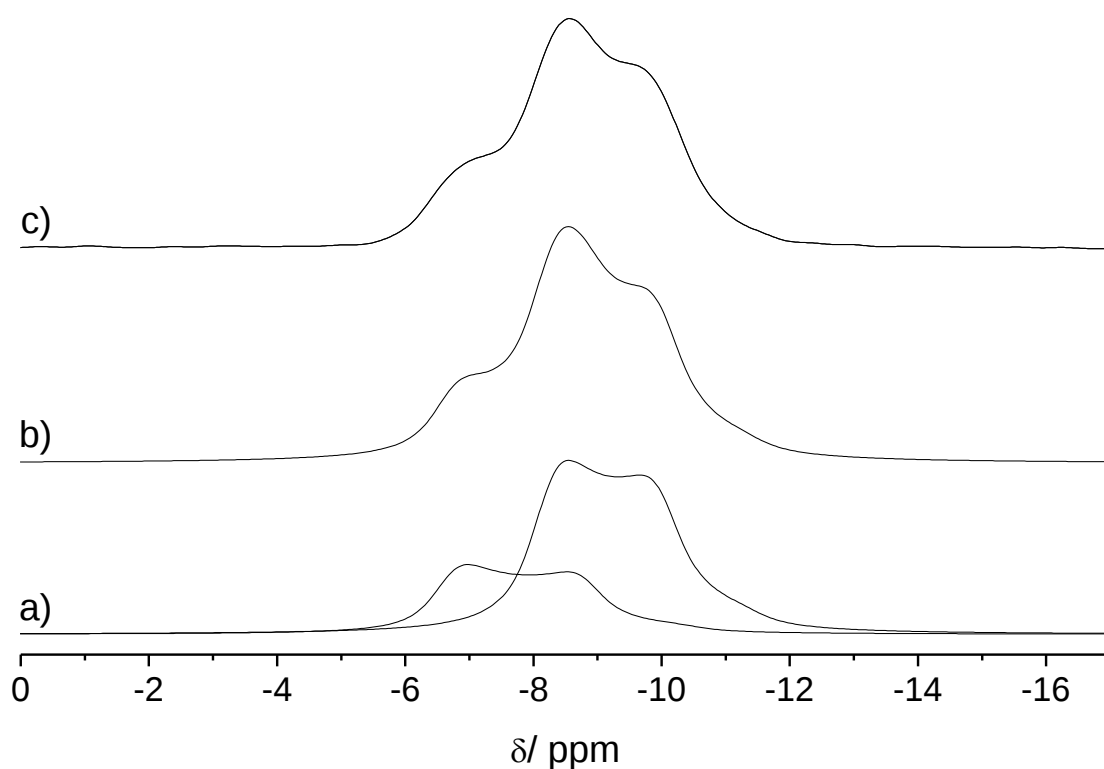


Figure S5: ^{11}B MAS spectrum of compound **2** acquired at 11.7 T (c), simulated spectrum (b) and individual contributions of the simulation (a) showing two boron sites. For simulations the quadrupolar parameters determined via the MQMAS experiment were chosen ($C_Q = 1.25$ MHz, $\eta = 0.18$ (A) and $C_Q = 1.36$ MHz, $\eta = 0.15$ (B)). The intensity ratio is determined as A:B = 2.3:1.

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B 0
S 6 1.00
8564.8660687 0.22837198155E-03
1284.1516263 0.17682576447E-02
292.27871604 0.91407080516E-02
82.775469176 0.36342638989E-01
27.017939269 0.11063458441
9.8149619660 0.23367344321
S 2 1.00
3.9318559059 0.41818777978
1.6595599712 0.22325473798
S 1 1.00
0.35762965239 1.0000000
S 1 1.00
0.14246277496 1.0000000
S 1 1.00
0.60560594768E-01 1.0000000

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S	1	1.00	
		2.9400000	1.0000000
S	1	1.00	
		8.3110000	1.0000000
P	4	1.00	
		22.453875803	0.50265575179E-02
		5.1045058330	0.32801738965E-01
		1.4986081344	0.13151230768
		0.50927831315	0.33197167769
P	1	1.00	
		0.18147077798	1.0000000
P	1	1.00	
		0.64621893904E-01	1.0000000
P	1	1.00	
		6.0160000	1.0000000
P	1	1.00	
		22.8910000	1.0000000
D	1	1.00	
		0.66100000	1.0000000
D	1	1.00	
		0.19900000	1.0000000
D	1	1.00	
		13.0150000	1.0000000
F	1	1.00	
		0.49000000	1.0000000

Figure S6: Slightly modified def2-TZVP basis set of boron used for the calculations of EFGs. The basis functions marked in red are taken from the cc-pCVTZ basis set.

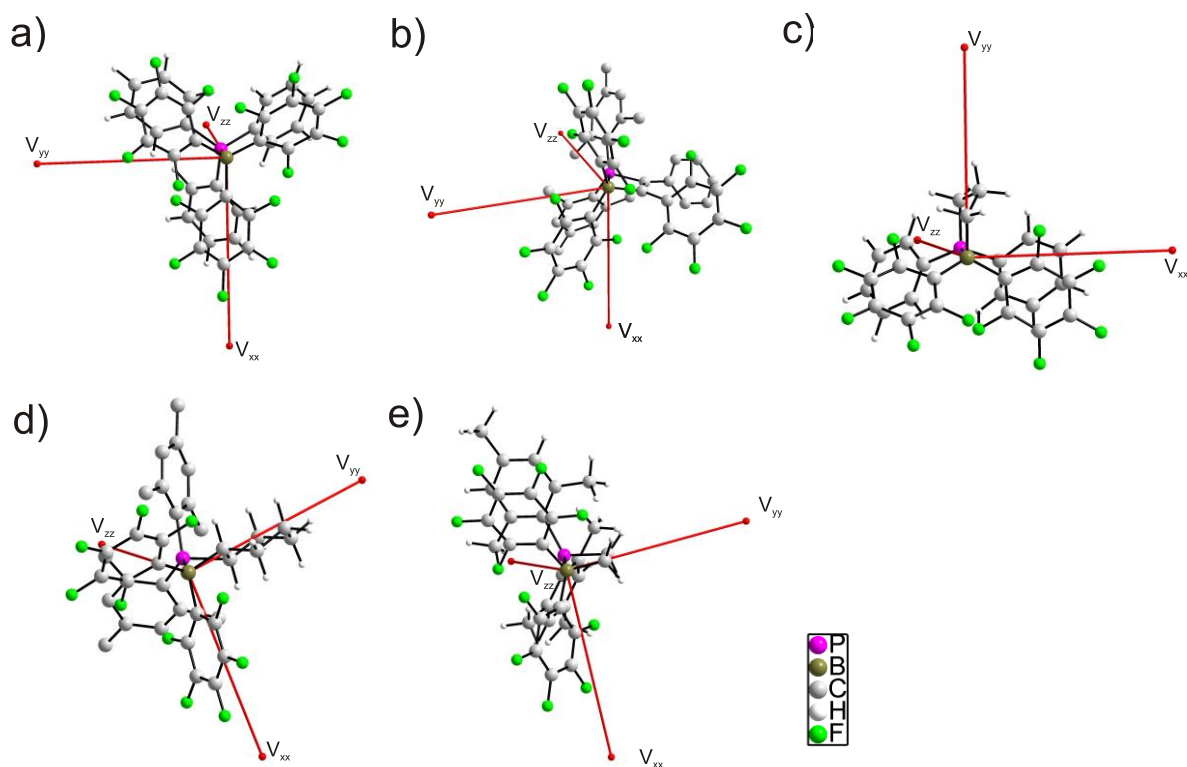


Figure S7: Tensor orientations of the ^{11}B electric field gradients for **10** (a), **1** (b), **7** (c), **8** (d) and **9** (e) obtained by DFT calculations on a GGA level (B97-D) with a slightly modified def2-TZVP basis set (for details see experimental section). In nearly all cases a slight deviation from parallel alignment between the largest principal component V_{zz} and the B $\cdots$ P vector is observed (for detailed values see Table 1).

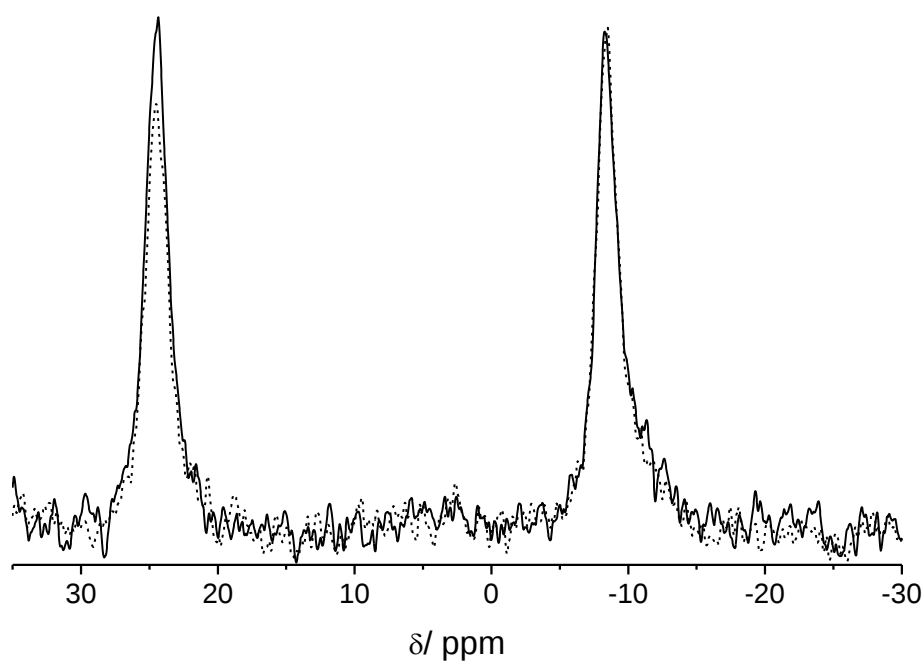


Figure S8: Single data point of a $^{31}\text{P}\{^{11}\text{B}\}$ REDOR experiment acquired at 9.4 T with a rotor frequency of 10 kHz and an evolution time of 0.4 ms (continuous line: S_0 , dotted line: S) for **4**. The signal at 24 ppm shows a significant dephasing due to heteronuclear dipolar interactions leading to the assignment of this resonance to the phosphorus site forming the adduct with boron. This is also confirmed by DFT calculations of magnetic shieldings on the B3-LYP/def2-TZVP level of theory: $\delta(\text{P}\dots\text{B})= 23.6$ ppm and $\delta(\text{PPh}_2)= -10.1$ ppm.

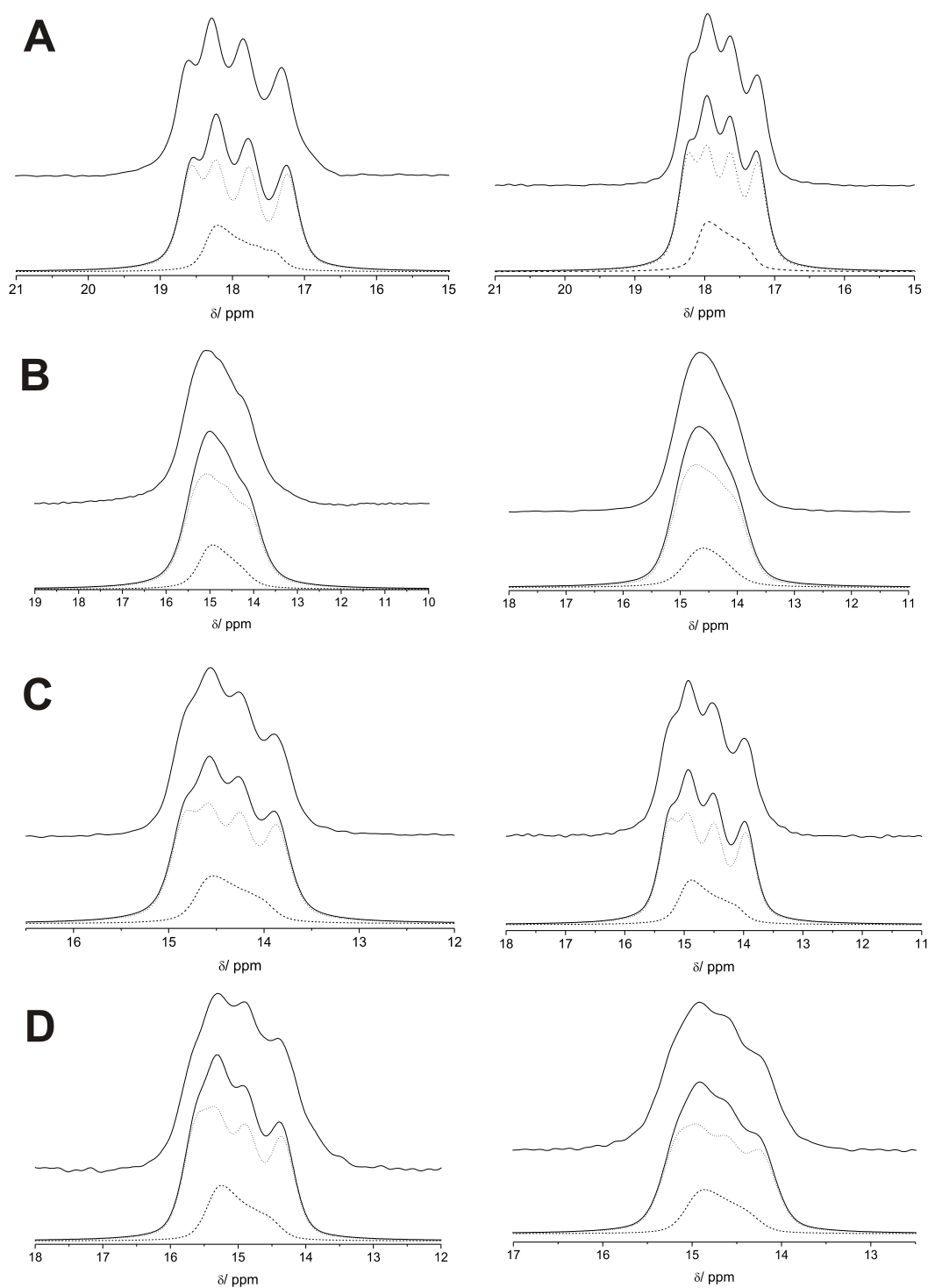


Figure S9: Top: $^{31}\text{P}\{^1\text{H}\}$ CPMAS spectra acquired at 7.1 T with the SW-TPPM-15 decoupling scheme (left) and at 9.4 T with the TPPM-15 decoupling sequence (right) for compound **1** (A), **3** (B), **5** (C) and **6** (D). Bottom: Peak deconvolution (straight line) consisting of ^{31}P , ^{11}B coupling (dotted line) and ^{31}P , ^{10}B coupling (dashed line).

	WBI (CAO basis) ^a	WBI (NAO basis) ^b	occupancy (bond B...P) ^b	percentage of the NBO on the natural atomic hybrid localized at P/% ^b	percentage of the NBO on the natural atomic hybrid localized at B/% ^b
1	0.91	0.78	1.89	63.8	36.2
2	0.77	0.79	1.88	62.0	38.0
3	0.73	0.81	1.89	61.9	38.1
4	0.74	0.82	1.89	61.4	38.6
5	0.87	0.79	1.88	63.1	36.9
6	0.75	0.81	1.89	61.4	38.6
7	0.82	0.82	1.90	62.1	37.9
8	0.60	0.75	1.89	67.7	32.3
9	0.72	0.66	1.88	71.9	28.1
10	0.78	0.77	1.89	64.1	35.9

Table S10: Calculated Wiberg bond order indices (WBI) and results of a Natural Bond Orbital (NBO) analysis of the B...P bond for the bridged B/P adducts illustrating a significant covalent interaction. ^a: DFT (TPSS-D3/def2-TZVP), ^b: Obtained from an NBO analysis (TPSS/def2-TZVP). The NBO analysis reveals in all cases a real covalent bond between the Lewis acid and base functionalities.

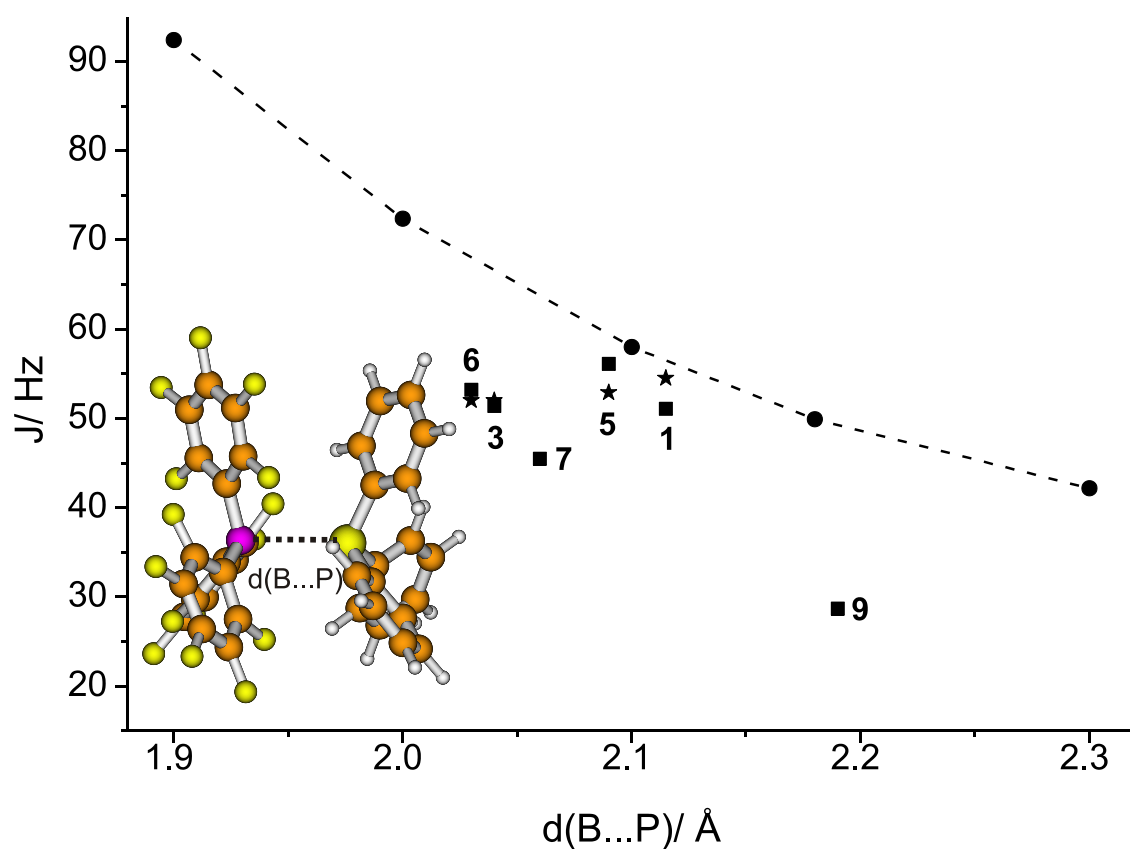


Figure S11: DFT calculated $^{31}\text{P}\cdots^{11}\text{B}$ J coupling constants (B3-LYP, TZVP) for the Lewis acid/-base adduct **10** with varied boron phosphorus distances in the framework of the crystal structure. The data show a strong distance-dependence of the coupling constants (filled circles). Filled stars show the experimentally determined coupling constants of the substituted vinylene linked intramolecular B/P adducts, while filled squares represent DFT calculated values.

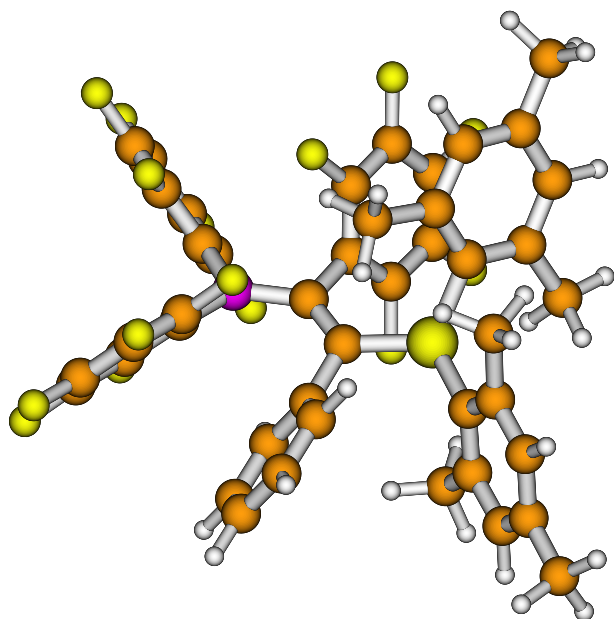


Figure S12: Model of **1** in which the Lewis acid and –base moiety are oriented *trans* to each other (dihedral angle 173°). The structure was obtained by a full geometry optimization (TPSS-D3, def2-TZVP). The 3J coupling (B3-LYP, TZVP) is determined as 18.3 Hz.

References

- (43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09* Gaussian, Inc., Wallingford CT, 2009.