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ARTICLE

Formation, Structural Characterization, and Reactions of a Unique Cyclotrimeric Vicinal Lewis Pair Containing $(C_6F_5)_2P$ -Lewis Base and $(C_6F_5)BH$ -Lewis Acid Components

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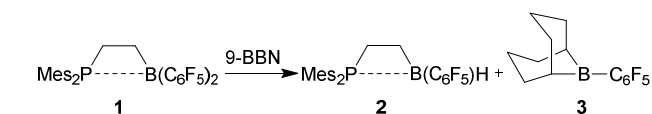
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The synthesis of the new vicinal frustrated Lewis pair **5** containing a $(C_6F_5)_2P$ -Lewis base and a $(C_6F_5)BH$ -Lewis acid functionality is described. It forms a unique cyclotrimer (**5**)₃ which was structurally characterized by X-ray crystallography and high-resolution solid state NMR spectroscopy. The relevant NMR Hamiltonian parameters (¹¹B and ³¹P chemical shielding tensors, ¹¹B quadrupolar coupling tensors, and ³¹P-¹¹B spin-spin coupling constants indicate significant intramolecular covalent B⋯P interactions, consistent with results from density functional theory (DFT) calculations. In addition, the ¹¹B/³¹P and ³¹P/³¹P three-spin geometries are accurately reproduced by suitable high-resolution hetero- and homonuclear dipolar NMR experiments. As predicted from the bonding character portrayed by the solid state NMR results, the cyclotrimer (**5**)₃ possesses only moderate catalytic activity. However, it undergoes an addition reaction with pyridine and hydroboration reactions with benzaldehyde and *tert*-butylacetylene. The products of the hydroboration reactions form stable adducts with pyridine.

Introduction

Frustrated Lewis pairs are comprised of pairs of co-existing Lewis acids and Lewis bases,¹ which are prevented from covalent adduct formation owing to either steric hindrance²⁻⁴ or specific electronic effects.⁵ The co-existent Lewis acid/base pairs can undergo a variety of remarkable cooperative reactions with added substrates. Dihydrogen activation is a most prominent and often observed frustrated Lewis pair (FLP) feature^{2,6} and, consequently, protocols for metal-free FLP-catalyzed hydrogenation reactions have been developed.⁷ FLPs were also shown to add to a great variety of other small molecules, including CO₂,⁸ SO₂,⁹ and nitrogen oxides.¹⁰ Intramolecular FLPs play an important role in this chemistry.³ Recently we introduced additional functionalities at vicinal P/B FLPs. This can be done by modifying the C₂-framework that is bridging between the phosphane and borane sites,¹¹ but also by direct modification of the Lewis acid and Lewis base components. Previously, we introduced the much less Lewis basic $(C_6F_5)_2P$ -building block⁵ and we converted the $(C_6F_5)_2B$ -group to $(C_6F_5)BH$ by treatment with 9-BBN.¹² This resulted in

an effective C₆F₅/H exchange with formation of the (C_6F_5) -9-BBN product (**3**) and the new P/BH FLP **2** (see Scheme 1). We have now realized both features in one system containing the $(C_6F_5)_2P$ and the $(C_6F_5)BH$ functionalities in a saturated vicinal FLP. This new system shows some rather unique features that will be described and discussed in this article.



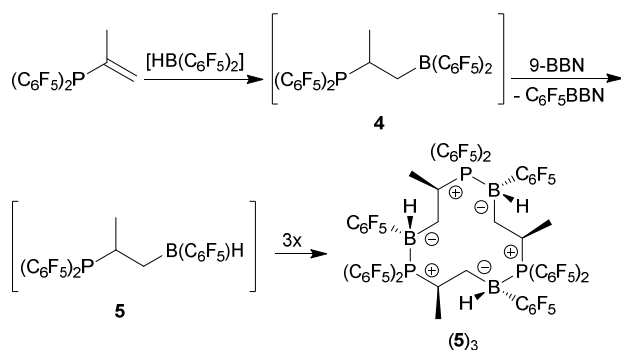
Scheme 1

Results and Discussion

Formation and structural characterization of the vicinal $(C_6F_5)_2P/B(C_6F_5)H$ FLP

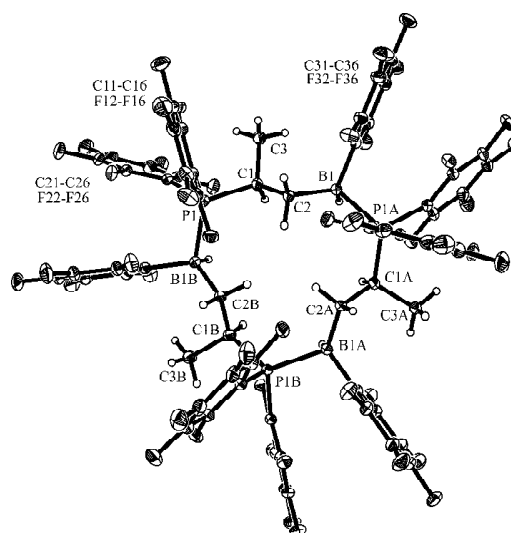
We previously showed that the hydroboration of $(C_6F_5)_2P-C(CH_3)=CH_2$ with Piers' borane $[HB(C_6F_5)_2]$ ¹³ yields the vicinal $(C_6F_5)_2P/(C_6F_5)_2B$ -FLP **4**.⁵ Compound **4** shows some typical FLP reactions. However, it turns out to be less reactive

than e. g. its analogue **1** featuring the stronger basic Mes_2P -Lewis base component. Since the FLP **1** readily underwent the (C_6F_5) vs. H exchange reaction (see Scheme 1)¹² we also treated the $(\text{C}_6\text{F}_5)_2\text{P}/(\text{C}_6\text{F}_5)_2\text{B}$ -FLP **4** with the 9-BBN reagent. For that purpose compound **4** was generated in situ from **1** and $[\text{HB}(\text{C}_6\text{F}_5)_2]$ (toluene solution, 15 min. r.t.). Then 9-BBN was added and the mixture stirred overnight at room temperature. This resulted in the anticipated $\text{C}_6\text{F}_5/\text{H}$ exchange reaction at the borane site, and it left the $(\text{C}_6\text{F}_5)_2\text{P}$ -unit untouched. The resulting product (**5**)₃ forms during the reaction time as an insoluble precipitate that was isolated in 45% yield. The product was characterized by C,H-elemental analysis, by X-ray diffraction and by solid state NMR spectroscopy (see below).



Scheme 2

The X-ray crystal structure analysis confirms that one C_6F_5 substituent at boron was replaced by hydride. However, the resulting vicinal P/B FLP $(\text{C}_6\text{F}_5)_2\text{P}-\text{C}(\text{CH}_3)-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)\text{H}$ (**5**) was not found as such but it had become a subunit of its cyclotrimer (**5**)₃. The trimer is formed from three symmetry equivalent monomeric units. Each of them features a close to anti-periplanar $[\text{P}]-\text{CHMe}-\text{CH}_2-[\text{B}]$ conformation [dihedral angle $\text{P1}-\text{C1}-\text{C2}-\text{B1}$ $169.2(2)^\circ$]. The three P/B FLP monomers are each connected by P-B bonds ($\text{B1}-\text{P1A}$: $2.006(3)$ Å). The trimer shows three symmetry equivalent stereogenic centers (at C1) and three symmetry-equivalent hydridoborate centers; the overall structure of (**5**)₃ possesses the symmetry C_3 . Within the cyclic structure the $\text{B1}-\text{B1A}$ separation is 5.109 Å, and the $\text{P1}-\text{P1A}$ distance is found to be 5.758 Å. There are three boron - phosphorus distances: the direct $\text{B1}-\text{P1A}$ bond (see above), the $\text{B1}-\text{P1}$ separation of 4.236 Å within the monomeric P/B FLP unit and the transannular $\text{B1}-\text{P1B}$ distance which amounts to 6.149 Å (see Fig. 1). The central core of compound (**5**)₃ does not deviate much from co-planarity. The $\text{P1}\cdots\text{P1A}\cdots\text{P1B}$ and the $\text{B1}\cdots\text{B1A}\cdots\text{B1B}$ planes are only 0.421 Å apart. The planes of the C_6F_5 groups at both boron and phosphorus are oriented more or less normal to the central core plane of the cyclotrimer.

Figure 1: A projection of the C_3 -symmetric P/BH cyclotrimer (**5**)₃ (thermal ellipsoids are shown with 15% probability).

Characterization of the cyclotrimer (**5**)₃ by solid state NMR spectroscopy

Solid-State NMR techniques provide a significant understanding of the reactivity and catalytic activities of P/B FLPs in terms of structure and bonding. Many systems still possess weak covalent interactions between the two Lewis centers moderating the FLP reactivity^{11c,14} and various solid-state NMR parameters such as ^{11}B quadrupolar coupling constants, ^{11}B isotropic chemical shifts and $^{11}\text{B}-^{31}\text{P}$ spin-spin coupling constants can serve to quantify the “degree of frustration” of the investigated P/B systems. Based on these parameters, three groups of P/B systems can be differentiated: (i) classical Lewis adducts showing no FLP reactivity (e.g. the adduct between PPh_3 and $\text{B}(\text{C}_6\text{F}_5)_3$),^{15,16} (ii) P/B systems with weak interactions between the centers (such as vinylene-bridged FLPs)^{11a} showing moderate FLP reactivities and (iii) non-interacting FLPs (e.g. the norbornylene-bridged intramolecular P/B system),¹⁷ being extremely reactive. Solid-state NMR can serve as a principal tool for understanding its reactivity in terms of structure and bonding properties classifying the reactivity. REDOR-type techniques^{11c,18} allow a very accurate determination of $\text{P}\cdots\text{B}$ distances which are a very important structural parameter for understanding the potential of those systems in FLP-type cooperative reactions. The recently proposed new homonuclear re-coupling technique called DQ-DRENAR (Double-Quantum based Dipolar Recoupling Effects Nuclear Alignment Reduction)^{19,20} allows the determination of homonuclear P-P distances which opens up the possibility of analyzing the long-range $^{31}\text{P}-^{31}\text{P}$ dipolar interactions for proving the presence of oligomeric structures. Due to the insolubility of the cyclic trimer (**5**)₃ in all common organic solvents, solid-state NMR is a key technique for its structural characterization, including the assessment of B/P intramolecular interaction strengths. Figure 2 shows the $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum of (**5**)₃.

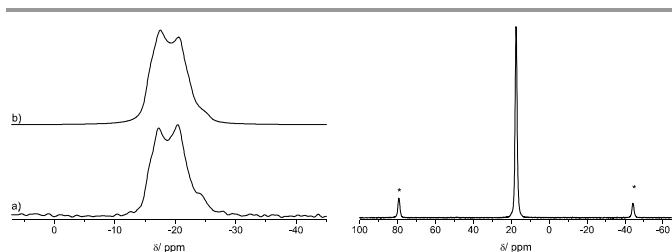


Figure 2: Left: $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum of $(\mathbf{5})_3$ acquired at 9.4 T with a spinning frequency of 13.0 kHz (a) and corresponding line shape simulation (b, for details see Table 1). Right: $^{31}\text{P}\{^1\text{H}\}$ CPMAS NMR spectrum of $(\mathbf{5})_3$ measured at 9.4 T and a spinning frequency of 10.0 kHz.

One single resonance is detected, confirming the crystallographic identity of the three boron atoms within the cyclotrimeric structure. The line shape is dominated by second order quadrupolar perturbations. The corresponding parameters (quadrupolar coupling constant $C_Q = 1.69$ MHz and EFG asymmetry parameter $\eta_Q = 0.35$) as well as the isotropic chemical shift $\delta_{\text{iso}} = -14.6$ ppm are typical for a four-coordinated boron atom with an unsymmetrical ligation pattern. These data are in excellent agreement with the DFT calculated ones based on the crystallographic data (see Table 1) and the C_Q and δ_{iso} values agree well with values determined for characteristic intermolecular Lewis acid/ Lewis base adducts (e.g. PPh_3 and $\text{B}(\text{C}_6\text{F}_5)_3$).^{11c}

Table 1: Experimentally and quantum chemically determined ^{11}B and ^{31}P solid state NMR parameters.

	$\delta_{\text{iso}}^{\text{CS}}(^{11}\text{B})$ $\pm 0.5/\text{ppm}$	$C_Q \pm 3\%$ /MHz	η_Q ± 0.1	$\delta_{\text{iso}}^{\text{CS}}(^{31}\text{P})$ $\pm 0.5/\text{ppm}$	$\Delta\sigma(^{31}\text{P})$ $\pm 10/\text{ppm}$	$\eta_\sigma(^{31}\text{P})$ ± 0.1
Exp.	-14.6	1.69	0.35	17.4	99.3	0.57
Calc.	-17.6 ^a	1.67 ^b	0.36 ^b	26.4 ^a	86.9 ^c	0.62 ^c

^a: B3-LYP/def2-TZVP, ^b: B97-D/def2-TZVP(mod.), ^c: B3-LYP/TZVP. The following convention is used: $\Delta\sigma = \sigma_{zz} - 1/2(\sigma_{xx} + \sigma_{yy})$, $\eta_\sigma = (\sigma_{yy} - \sigma_{xx}) / (\sigma_{zz} - \sigma_{\text{iso}})$ and $|\sigma_{zz} - \sigma_{\text{iso}}| > |\sigma_{xx} - \sigma_{\text{iso}}| > |\sigma_{yy} - \sigma_{\text{iso}}|$.

The principal component of the ^{11}B electric field gradient tensor (V_{zz}) lies nearly parallel to the B-P bond vector indicating that the EFG is strongly dominated by the covalent interactions among the two Lewis functionalities (the angle between V_{zz} , B and P is determined to 14.5°). Altogether, the ^{11}B MAS-NMR data indicate rather strong interactions between the Lewis centers preventing any FLP-type reaction behavior. The $^{31}\text{P}\{^1\text{H}\}$ CP-MAS NMR spectrum (see Figure 2) reveals also one single resonance at 17.4 ppm and the field-independent linewidths indicate the influence of non-resolved ^{31}P - ^{11}B spin-spin interactions on the MAS-NMR line shape (FWHM (7.05 T) = 188 Hz, FWHM (9.4 T) = 192 Hz). An attempt to measure $^1\text{J}(^{31}\text{P}-^{11}\text{B})$ by a heteronuclear J-resolved experiment was thwarted by very short ^{11}B and ^{31}P spin-spin relaxation times. Using GAUSSIAN09, this value was calculated to be 61.8 Hz ($^1\text{J} = 32.2$ Hz, $^3\text{J} = 29.6$ Hz) on a B3-LYP/TZVP level

of theory which in general gives results in close agreement with experimental data. The data in Table 2, calculated via ADF (Amsterdam Density Functional), reveal that the ^1J and ^3J coupling contributions to the isotropic $\text{J}(^{31}\text{P}-^{11}\text{B})$ value are of comparable size.

Table 2: DFT-calculated ^1J and ^3J -coupling tensors for $\mathbf{1}$ (BP-6(PBE)/TZ2P).

	$\text{J}_{\text{iso}}(^{31}\text{P}-^{11}\text{B})/\text{Hz}$	J_{xx}/Hz	J_{yy}/Hz	J_{zz}/Hz	J_{xy}/Hz	$\Delta\text{J}/\text{Hz}$	η_{J}
^1J	26.4	-8.7	-0.03	87.9	-0.24	92.2	0.14
^3J	31.9	27.9	28.8	38.9	-0.04	10.6	0.13

The following convention is used: $\Delta\text{J} = \text{J}_{zz} - 1/2(\text{J}_{xx} + \text{J}_{yy})$, $\eta_{\text{J}} = (\text{J}_{yy} - \text{J}_{xx}) / (\text{J}_{zz} - \text{J}_{\text{iso}})$ and $|\text{J}_{zz} - \text{J}_{\text{iso}}| > |\text{J}_{xx} - \text{J}_{\text{iso}}| > |\text{J}_{yy} - \text{J}_{\text{iso}}|$.

The Wiberg bond order index²¹ close to one (0.85 in the Cartesian Atomic Orbital, CAO, and 0.89 in the Natural Atomic Orbital, NAO, basis) also suggests the presence of a covalent boron-phosphorus single bond. The B-P internuclear distance of the trimer $(\mathbf{5})_3$ has been determined by $^{11}\text{B}\{^{31}\text{P}\}$ REDOR^{11c,18} and $^{31}\text{P}\{^{11}\text{B}\}$ REAPDOR^{14,22} experiments (see Figure 3). The numerical simulations (taking all the intramolecular B...P distances within the cyclotrimer, $d = 2.01$ Å, 4.24 Å, and 6.15 Å, into consideration) leads in both experiments to a very good overall agreement with the prediction from the crystal structure. Upon close inspection of these results, one notices a slight discrepancy, which could be remedied, in principle, by assuming a slightly longer distance of 2.04 Å than the crystallographically found distance of 2.006(0) Å.

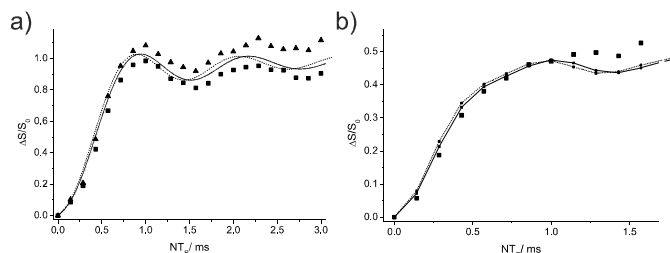


Figure 3: (a) $^{11}\text{B}\{^{31}\text{P}\}$ REDOR curve of $(\mathbf{5})_3$ measured at 7.05 T with a spinning frequency of 14.0 kHz. The squares represent REDOR data and the triangles compensated REDOR data (calibration factor $a=1$). (b) $^1\text{H} \rightarrow ^{31}\text{P}\{^{11}\text{B}\}$ CP-REAPDOR curve of $(\mathbf{5})_3$ (for the conditions see (a)). The curves in (a) and (b) represent numerical simulations: the dashed curves belong to simulations based on the crystallographically determined B-P distances (assuming a four-spin system) and the experimentally determined ^{31}P CSA parameters, while the solid curves represent simulations that additionally include a ΔJ -value of 100 Hz.

As previously discussed, such discrepancies between simulated and experimental REDOR data can arise from the effect of non-zero contributions of the J-anisotropy ($\Delta\text{J} \sim 100$ Hz).^{11c,14} Therefore, the numerically simulated REDOR and REAPDOR curves assuming a ΔJ value of 100 Hz indicate a perfect agreement with the experimental data. This result is also consistent with DFT calculations of the full J-coupling tensor of $(\mathbf{5})_3$ yielding a ΔJ value of 92 Hz and $\eta_{\text{J}} = 0.14$, on a BP-86(PBE)/TZ2P level of theory (see Table 2). In any event, our results highlight the fact that strong intermolecular B-P bonds are formed between the monomeric units, which are even slightly shorter than in the classical Lewis adduct between PPh_3 and $\text{B}(\text{C}_6\text{F}_5)_3$.

The geometry of (**5**)₃ can be further characterized on the basis of the homonuclear dipole-dipole interactions between the constituent ³¹P nuclei within the cyclotrimer. To this end, a new homonuclear recoupling technique, denoted DQ-DRENAR (Double-Quantum based Dipolar Recoupling Enables Nuclear Alignment Reduction) was used. This method uses a symmetry-based POST-C7 pulse sequence for the stimulation of DQ-coherences, thereby leading to a “drainage” of z-magnetization. To distinguish this decrease from that caused by other sources (relaxation, experimental imperfections) a corresponding reference experiment is carried out, in which the DQ-Hamiltonian is absent and the difference between both signal functions is recorded. Figure 4 compares the ³¹P-³¹P DQ-DRENAR curve of (**5**)₃ with the simulation based on a three-spin system in a trigonal geometry with P-P distances of 5.758(0) Å. The simulation includes the effect of the chemical shift anisotropy on the DRENAR curve, which is quite considerable in the present case. For the initial data range ($\Delta S/S_0 < 0.2$) excellent agreement between simulation and experiment can be noted. For longer mixing times a significant deviation is observed due to the fact that the first order approximation on which the simulation is based fails. Since the intermolecular P-P distances between different molecular units in monomeric P/B systems are significantly longer, the DRENAR results are clearly consistent with the trigonal P-P-P geometry suggested by the crystallographic data. Further work in our laboratory is in

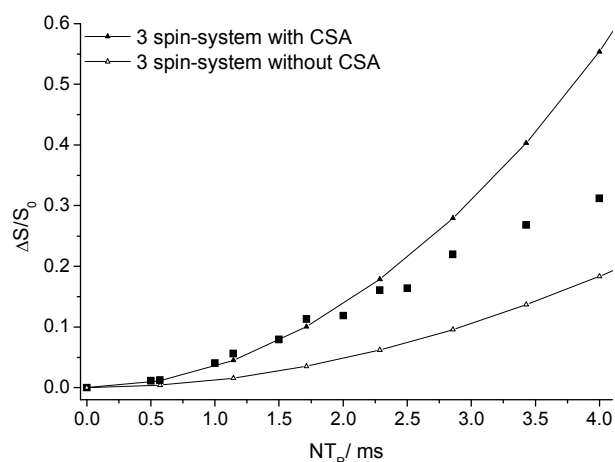


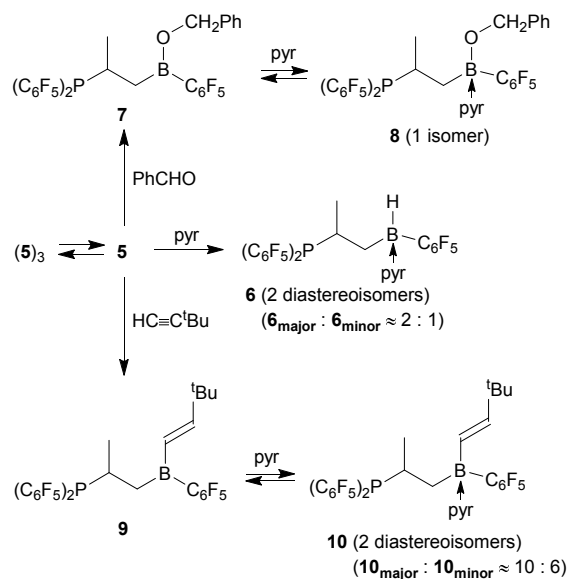
Figure 4: ³¹P-³¹P DQ-DRENAR curve of **1** measured at 7.05 T with a spinning frequency of 7.0 kHz and SIMPSON simulations based on a three spin-system with and without ³¹P CSA effects.

progress for developing new DRENAR-based techniques which allow an analysis of the oscillatory parts usually observed for longer evolution times. This part, which was not accessible in the present application, is quite sensitive to the detailed spin geometry. Overall, the results of the present study clearly show the utility of this solid-state NMR approach for the study of weakly interacting spins at longer intermolecular distances, which will be important in future studies of other

intermolecular P/B-based FLP assemblies and polymeric systems.

Reactions of the Cyclotrimer (**5**)₃

From a small series of chemical reactions we have obtained evidence that the monomer might be available from (**5**)₃ by equilibration. We have isolated the corresponding trapping products in a few cases. The reaction of (**5**)₃ with pyridine is a typical example. A suspension of the trimer was stirred with 3 molar equivalents of pyridine overnight. The resulting product was then recrystallized from pentane at -34°C to give compound **6** as a white solid. It was isolated in 43% yield. The X-ray crystal structure analysis (see below) showed that we had obtained and isolated the pyridine adduct to the boron atom of the FLP monomer **5**. This has resulted in the formation of a stereogenic boron center. Together with the already present persistent carbon chirality center in the α -position to phosphorus this may give rise to a pair of diastereomers. The NMR analysis of the product in solution actually showed that both diastereomers are present in a ratio of **6**_{major}:**6**_{minor} = 2:1, as revealed by the observation of a pair of slightly different sets of NMR signals (see Table 3). In the ¹⁹F NMR spectra we have e.g. observed separate sets of *o*- and *p*-¹⁹F NMR signals of the single C₆F₅-ligand at boron for the two isomers (the *m*-C₆F₅B resonances are overlapping). The C₆F₅ substituents at phosphorus are diastereotopic and, consequently, give rise to a pair of separate ¹⁹F NMR features for each diastereoisomer. Accordingly, we also observe two pairs of *p*-C₆F₅[P] ¹⁹F NMR resonances for each diastereomer (in a ca. 2:1 intensity ratio). Actually each of these signals appears as a triplet of triplets due to the coupling of each *p*-C₆F₅[P] fluorine nucleus with a pair of adjacent *m*- and *o*- fluorine atoms (the spectra are depicted in the Supporting Information). We also observe the broad ¹H NMR [B]-H resonance of both **6**_{major,minor} at δ 3.71.



Scheme 3

The single crystals that we used for the X-ray crystal structure determination of compound **6** contained only a single diastereomer (see Fig. 5). It shows a tricoordinate phosphorus atom that has a pair of C₆F₅ substituents and the C1 carbon atom of the bridge bound to it, resulting in a trigonal-pyramidal geometry ($\Sigma\text{P1}^{\text{CCC}} = 308.6^\circ$). Carbon atom C1 represents a stereogenic center. The boron atom is tetra-coordinated. It has a C₆F₅-group, the pyridine donor ligand, carbon atom C2 of the bridge and the hydride bound to it in a pseudotetrahedral coordination geometry ($\Sigma\text{B1}^{\text{NCC}} = 330.0^\circ$).

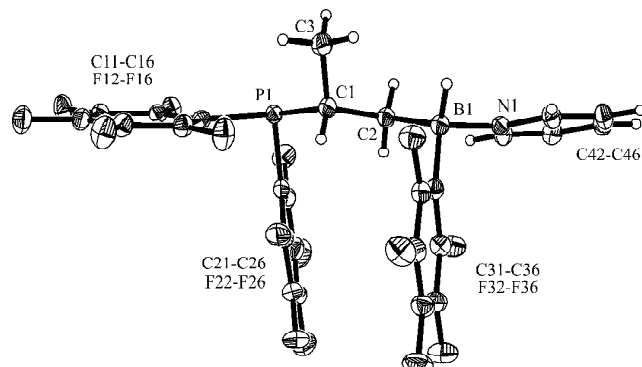


Figure 5: A view of the molecular structure of one diastereomer of the pyridine adduct **6** (thermal ellipsoids are shown with 15% probability).

Table 3: Selected NMR parameters^a of compounds (C₆F₅)₂PCH(Me)CH₂B(C₆F₅)R(L)

Compd	δ_{major}	δ_{minor}	7	8	9	δ_{major}	δ_{minor}
R	H		OCH ₂ Ph			CH=CH ^t Bu	
L	pyr		-	pyr	-	pyr	
³¹ P	-37.7	-36.9	-35.5	-36.1	-36.4	-37.7	-35.7
¹⁰ B	-5.1	-5.1	48.5	10.5	71.5	0.4	0.4
¹ H BCH ₂	1.08	1.06	1.39	1.29	1.83	1.03	1.31
	0.81			1.00	1.61		0.91
¹ H CH	3.00	2.93	3.62	2.86	3.64	3.10	2.92
¹³ C BCH ₂	25.6	26.8	27.9	25.9	33.1	28.7	28.7
¹³ C CH	25.9	25.9	23.6	24.5	25.3	25.3	25.3

^a NMR spectra in CD₂Cl₂, chemical shifts in ppm (δ -scale)

Compound **5** contains an active [B]H borane functionality, which reacts e. g. with benzaldehyde. Treatment of a suspension of (**5**)₃ in dichloromethane overnight at room temperature with a stoichiometric amount of PhCHO gave product **7**, which we isolated in 76% yield (see Scheme 3). The compound is characterized by a ¹⁰B NMR signal at δ 48.5 indicating the presence of a planar-tricoordinate Lewis acidic boron center. Again the C₆F₅ groups at phosphorus are diastereotopic due to the adjacent carbon chirality center. The newly formed OCH₂Ph substituent at boron gives rise to an AB ¹H NMR pattern of the methylene group (δ 5.12/5.11 [¹³C: 71.4]). For additional data see Table 3 and the Supporting Information.

Compound **7** adds pyridine to give the respective [B]-pyridine adduct **8**, which was isolated as an oil in 84% yield. The ¹H/¹³C NMR spectra show the typical signals of the [P]CHMeCH₂[B]

subunit (see Table 3), the signals of the OCH₂Ph substituent and the resonances of the coordinated pyridine unit (for details see the Supporting Information). In this case we have apparently monitored the NMR signals of only a single diastereoisomer. Consequently, the ¹⁹F NMR spectrum of **8** shows three sets of C₆F₅ resonances in a 1:1:1 intensity ratio: two originating from the pair of diastereotopic C₆F₅ groups at phosphorus and one from the single C₆F₅ substituent at boron (the spectra are depicted in the Supporting Information).

The [B]H functionality of compound **5** can be used for hydroboration.²³ As a typical example we treated a suspension of the trimer (**5**)₃ with *tert*-butylacetylene in CD₂Cl₂ overnight. Compound **9** was obtained as a colorless oil and recovered in 90% yield. It features a typical ¹⁰B NMR signal of a planar-tricoordinate borane Lewis acid (δ 71.5) and a ¹H NMR AX pattern of the newly formed *trans*-[B]-CH=CH-^tBu moiety (δ 6.82, 6.45, ³J_{HH} = 17.7 Hz). It also shows the typical set of ¹⁹F NMR signals of the three C₆F₅-groups at boron and phosphorus. Compound **9** also added pyridine. After crystallization from pentane at -34°C we obtained the [B]-pyridine adduct **10** in 63% yield as a mixture of two diastereoisomers in a 10:6 ratio. Both these isomers show ¹⁰B NMR signals typical of four-coordinate pseudotetrahedral boron (see Table 3) and ³¹P NMR signals typical of three-coordinate trigonal pyramidal phosphorus. Each isomer shows the typical ¹H NMR features of a *trans*-CH=CH-^tBu substituent at boron (for details see the Supporting Information).

We have obtained crystals of one diastereoisomer by slow crystallization from heptane/dichloromethane solution. In the crystal this diastereoisomer of **10** shows an extended antiperiplanar conformation of the central unit with a dihedral angle P1-C1-C2-B1 of -177.1(3)°. The phosphorus atom features a three-coordinate trigonal pyramidal coordination geometry ($\Sigma\text{P1}^{\text{CCC}} = 308.3^\circ$). It has a single C₆F₅ substituent bonded to it in addition to carbon atom C2 of the bridge and the newly added pyridine ligand (see Fig. 6). The fourth coordination position is taken by the σ -CH=CH-^tBu substituent. It features a *trans* disubstituted C=C double bond (C4-C5: 1.303(5) Å, θ B1-C4-C5-C6: -172.8(4)°); at its distal carbon atom C5 we find the bulky ^tBu substituent attached.

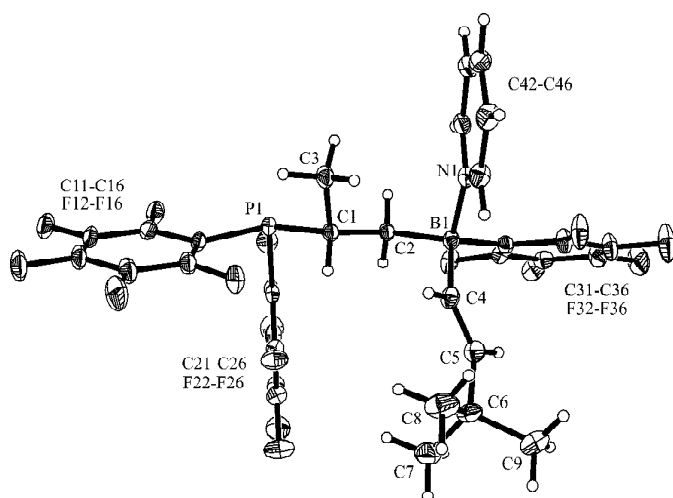


Figure 6: A view of the molecular structure of one diastereoisomer of **10** (thermal ellipsoids are shown with 15% probability).

Conclusions

In this study we have prepared the vicinal intramolecular Lewis acid/Lewis base pair **5** that is characterized by having a $P(C_6F_5)_2$ moiety of rather low Lewis basicity and a $B(C_6F_5)H$ Lewis acid component. Previous studies had shown that the $P(C_6F_5)_2/B(C_6F_5)_2$ pairs do not undergo intra- or intermolecular P/B adduct formation, probably because the Lewis basicity of the former group is too low, although those systems showed a limited set of FLP reactions.⁵ Our new vicinal $P(C_6F_5)_2/B(C_6F_5)H$ Lewis pair **5** behaves differently: it features strong P-B interactions that result in the formation of the observed unique cyclotrimer (**5**)₃. We think that two features may be responsible for this behavior: first the presence of the small $B(C_6F_5)H$ Lewis acid moiety that will encourage adduct formation and second, the very low solubility of the cyclotrimerization product that will remove the new vicinal FLP **5** from any equilibrium situation by precipitation of (**5**)₃.

The trimeric structure based on intermolecular P/B interactions has been verified by modern solid-state NMR techniques. Those studies reveal strong P-B covalent interactions as reflected by ¹¹B solid-state NMR parameters which are very similar to those values observed for classical Lewis acid/-base adducts. ¹¹B{³¹P} REDOR and ³¹P{¹¹B} REAPDOR measurements allow an accurate determination of the corresponding P-B distances, which agree well with the crystallographically determined values if non-zero anisotropic contributions of the J-coupling tensor are taken into account. The recently developed DQ-DRENAR sequence was applied for the first time in FLP-related systems for measuring the weak long-range ³¹P-³¹P homonuclear three-spin dipolar interaction within the cyclotrimer. Thus, our studies suggest that this technique will be useful for exploring P-P distance geometries in oligomeric and polymeric FLP-based systems.

Despite its apparent stability and its low solubility the system (**5**)₃ undergoes typical hydroboration reactions of the pendant

$B(C_6F_5)H$ moiety. The products are monomeric and do not show any appreciable P-B interaction any more as revealed by their characteristic NMR parameters. This behavior leaves room for the chemical functionalization of the system **5**, so we shall see if derivatives of **5** and related $B(C_6F_5)H$ containing P/B systems will become useful in the development of frustrated Lewis pair chemistry.

Experimental Part

Solid-state NMR experiments were performed on a BRUKER Avance 400 and a BRUKER Avance III 300 machine equipped with 4 mm double and triple resonance probes. ¹¹B{¹H} MAS NMR studies were conducted at a Larmor frequency of 128.4 MHz. The single-pulse spectrum was acquired at a spinning frequency of 13.0 kHz and a relaxation delay of 5 s, using a 45 degree excitation pulse (2.0 μs in length) applying the TPPM-15 ¹H decoupling scheme during acquisition.²⁴ ³¹P{¹H} CPMAS NMR experiments were conducted at 7.05 T and 9.4 T with rotation frequencies of 3.0-10.0 kHz using the following acquisition parameters: ¹H 90° pulses of 5.0- 5.5 μs length, contact time 5 ms, relaxation delays 2-5 s. {¹H}→¹¹B{³¹P} CP-REDOR and {¹H}→³¹P{¹¹B} CP-REAPDOR experiments were conducted at 7.05 T using radio frequency power levels corresponding to 180° pulses of 8.0 μs length for ¹¹B and for ³¹P, respectively. A spinning frequency of 14.0 kHz was used in both cases. For creating a reproducible magnetization in each experiment, a pre-saturation comb consisting of sixty 90° pulses was applied. ¹H decoupling was achieved by using the TPPM-15 scheme during the evolution and data acquisition period with rf fields corresponding to a ¹H nutation frequency of 53 kHz. In case of the REAPDOR experiments the ¹¹B resonance was excited for one third of the rotor period during the dipolar evolution time. Simulations of REDOR and REAPDOR curves were done with the SIMPSON code.²⁵ DQ-DRENAR measurements were conducted at 7.05 T applying a rotation frequency of 7.0 kHz. All line shape simulations were performed using the DMFIT software (version 2011).²⁶

DFT calculations. All calculations were carried out using the program packages TURBOMOLE (version 6.3)^{27,28} and GAUSSIAN (version GAUSSIAN09).²⁹ The geometry was taken from the crystal structure and the positions of the hydrogen atoms were optimized on a DFT meta-GGA (TPSS)³⁰ level of theory applying the recently developed D3(BJ) dispersion correction³¹ and Ahlrich's def2-TZVP³² basis set. All geometry optimizations were performed within the TURBOMOLE program suite. In all TURBOMOLE SCF calculations an energy convergence criterion of 10⁻⁷ E_h and in all geometry optimizations an energy convergence criterion of 5*10⁻⁷ E_h was chosen. The integration grid was set to m4³³ and the RI approximation^{34,35} was used.

The calculation of the ¹¹B electric field gradient was performed on a GGA DFT level (functional B97-D)³⁶ using the program package GAUSSIAN09. The def2-TZVP basis set obtained from the EMSL data base^{37,38} was modified in such a way that

tighter basis functions on the boron atom (extracted from the cc-pCVTZ basis set,^{39,40} for details see ref. 11c) were included for having a more accurate description of the region near the boron nucleus. The GAUSSIAN output files were analysed by using the program EFGShield,⁴¹ version 2.2, for determination of C_Q and η values and visualizing the orientation of the electric field gradient tensor in the molecular geometry by using the DIAMOND software.⁴² The magnetic shielding calculations were performed within the GIAO (gauge independent atomic orbitals) framework.^{43,44} For ^{11}B , magnetic shieldings were calculated on the B3-LYP^{45,46} level of theory with the def2-TZVP basis set using the TURBOMOLE program package. Chemical shifts are referenced to $\text{BF}_3(\text{OEt}_2)$ by using B_2H_6 ($\delta(\text{B}_2\text{H}_6)=16.6$ ppm vs. $\text{BF}_3/\text{Et}_2\text{O}$) as an external standard ($\sigma^{\text{B3-LYP}}(\text{B}_2\text{H}_6)=84.23$ ppm).⁴⁷⁻⁵⁰ ^{31}P chemical shifts were calculated with the B3-LYP functional and the def2-TZVP basis set. Chemical shifts were referenced to phosphoric acid ($\sigma^{\text{B3-LYP}}=274.31$ ppm). ^{31}P chemical shift anisotropy (CSA) parameters were calculated on the B3-LYP TZVP⁵¹ level of theory using the program package GAUSSIAN09. $^{31}\text{P}/^{11}\text{B}$ indirect spin spin coupling constants were calculated on a B3-LYP TZVP level of theory using the program package GAUSSIAN09. Wiberg bond order indices⁵² in the Cartesian Atomic Orbital (CAO) basis were calculated from the TPSS Kohn-Sham determinants by using the TURBOMOLE program package and those in the Natural Atomic Orbitals (NAO) basis by using the Natural Bonding Orbitals (NBO) program (version 3.1)⁵³ as included in GAUSSIAN09.

J- anisotropies ΔJ were calculated using the program package ADF and the CPL program included therein.⁵⁴⁻⁵⁶ For the J coupling tensors the Fermi contact (FC), paramagnetic spin orbit (PSO), diamagnetic spin orbit (DSO), as well as spin dipolar interaction (SD) contributions were considered. The GGA functional BP-86^{57,58} was used for the SCF run together with the PBE^{59,60} functional for determining the first-order perturbed MOs in the calculation of NMR properties. Those calculations were performed with the TZ2P basis set⁶¹. The integration keyword was set to 6.0 and an SCF convergence criterion of $10^{-7} E_{\text{H}}$ was used for the spin-spin coupling constant calculations.

Preparation of Compound (5)₃

$(\text{C}_6\text{F}_5)_2\text{P}-\text{C}(\text{CH}_3)\text{H}=\text{CH}_2$ (80.0 mg, 0.20 mmol, 1.0 eq) and bis(pentafluorophenyl)borane (68.1 mg, 0.20 mmol, 1.0 eq) were dissolved in toluene (10 mL). After stirring for 15 min 9-BBN (24.0 mg, 0.20 mmol, 1.0 eq) was added. The solution was stirred overnight and the formed colourless precipitate was isolated and dried *in vacuo* (53.2 mg, 45%). Crystals suitable for the X-ray single crystal structure analysis were obtained simultaneously with the isolated colourless precipitate. Mp: 192 °C (DSC). Anal. calc. for $\text{C}_{63}\text{H}_{21}\text{B}_3\text{F}_{45}\text{P}_3$ (1758.12 g/mol): C 43.04, H 1.20; found: C 42.99, H 1.39. IR (KBr) $\tilde{\nu} = 2353$ (m, B-H).

Preparation of Compounds **6**_{major} and **6**_{minor}

Pyridine (7.0 μL , 0.09 mmol, 3.0 eq) was added to a suspension of compound (**5**)₃ (50.0 mg, 0.03 mmol, 1.0 eq) in dichloromethane (10 mL) and stirred overnight. Then all volatiles were removed *in vacuo* and the remaining solid was dissolved in pentane (ca. 5 mL) and the formed suspension stored at -34 °C. After two days the formed colourless precipitate was isolated and dried *in vacuo* (24.1 mg, 43%). In the CD_2Cl_2 solution of the obtained solid two diastereomers **6**_{major} and **6**_{minor} were observed (major/minor $\sim 2/1$). Crystals suitable for the X-ray single crystal structure analysis were obtained by slow crystallisation from a dichloromethane solution of compound **6**. Anal. calc. for $\text{C}_{26}\text{H}_{12}\text{BF}_{15}\text{NP}$ (665.15 g/mol): C 46.95, H 1.82, N 2.11; found: C 47.39, H 1.93, N 2.19. IR (KBr) $\tilde{\nu} = 2419$ (w, B-H). **6**_{major}: ^1H NMR (500 MHz, CD_2Cl_2 , 299 K): $\delta = 8.55$ (m, 2H, *o*-Py), 8.05 (m, 1H, *p*-Py), 7.60 (m, 2H, *m*-Py), 3.71 (br d, $^1J_{\text{BH}} \sim 90$ Hz, 1H, BH), 3.00 (m, 1H, CH), 1.20 (dd, $^4J_{\text{PH}} = 21.2$ Hz, $^3J_{\text{HH}} = 6.7$ Hz, 3H, CH_3), 1.08, 0.81 (each m, each 1H, CH_2B). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 299 K): $\delta = 147.0$ (*o*-Py), 141.4 (*p*-Py), 126.3 (*m*-Py), 25.9 (m, CH), 25.6 (br, CH_2B), 18.5 (d, $^2J_{\text{PC}} = 26.1$ Hz, CH_3), [C_6F_5 not listed]. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 299 K): $\delta = -37.7$ (quin, $^3J_{\text{PF}} = 30.6$ Hz). ^{10}B NMR (54 MHz, CD_2Cl_2 , 299 K): $\delta = -5.1$ ($\nu_{1/2} \sim 150$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2 , 299 K): $\delta = -129.4$ (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -151.5 (tm, $^3J_{\text{FF}} = 20.4$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -162.1 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.6$]; -130.0 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{B}}$), -152.1 (tm, $^3J_{\text{FF}} = 20.4$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{B}}$), -161.9 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{B}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 9.8$]; -134.4 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{B}}$), -159.5 (t, $^3J_{\text{FF}} = 19.9$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{B}}$), -165.0 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{B}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{B}} = 5.5$]. **6**_{minor}: ^1H NMR (500 MHz, CD_2Cl_2 , 299 K): $\delta = 8.55$ (m, 2H, *o*-Py), 8.11 (m, 1H, *p*-Py), 7.64 (m, 2H, *m*-Py), 3.67 (br, 1H, BH), 2.93 (m, 1H, CH), 1.16 (dd, $^4J_{\text{PH}} = 21.2$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 3H, CH_3), 1.06, 1.00 (each m, each 1H, CH_2B). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 299 K): $\delta = 147.1$ (*o*-Py), 141.6 (*p*-Py), 126.5 (*m*-Py), 26.8 (br, CH_2B), 25.9 (m, CH), 18.2 (d, $^2J_{\text{PC}} = 25.3$ Hz, CH_3), [C_6F_5 not listed]. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 299 K): $\delta = -36.9$ (quin, $^3J_{\text{PF}} = 28.4$ Hz). ^{10}B NMR (54 MHz, CD_2Cl_2 , 299 K): $\delta = -5.1$ ($\nu_{1/2} \sim 150$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2 , 299 K): $\delta = -129.7$ (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -151.6 (tm, $^3J_{\text{FF}} = 20.6$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.76 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.2$]; -129.8 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{B}}$), -151.8 (tm, $^3J_{\text{FF}} = 20.3$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{B}}$), -161.80 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{B}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.1$]; -133.3 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{B}}$), -159.7 (t, $^3J_{\text{FF}} = 20.1$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{B}}$), -165.0 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{B}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{B}} = 5.3$].

Preparation of Compound 7

Benzaldehyde (8.6 μL , 0.09 mmol, 3.0 eq) was added to a suspension of compound (**5**)₃ (50.0 mg, 0.03 mmol, 1.0 eq) in CD_2Cl_2 (0.8 mL) and reacted overnight. Then all volatiles were removed and the obtained solid was dried *in vacuo* to give compound **7** (47.1 mg, 76%). Anal. calc. for $\text{C}_{28}\text{H}_{13}\text{BF}_{15}\text{OP}$ (692.17 g/mol): C 48.59, H 1.89; found: C 48.63, H 1.82. ^1H NMR (500 MHz, CD_2Cl_2 , 299 K): $\delta = 7.38$ (m, 2H, *m*-Ph), 7.32 (m, 1H, *p*-Ph), 7.31 (m, 2H, *o*-Ph), 5.12, 5.11 (each d, $^2J_{\text{HH}} = 12.7$ Hz, each 1H, CH_2O), 3.62 (m, 1H, CH), 1.39 (m, 2H, CH_2B), 1.17 (dd, $^4J_{\text{PH}} = 20.1$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, 3H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 299 K): $\delta = 137.9$ (*i*-Ph), 129.0 (*m*-Ph), 128.4 (*p*-Ph), 127.1 (*o*-Ph), 71.4 (CH_2O), 27.9 (br, CH_2B), 23.6 (m, CH), 19.6 (d, $^2J_{\text{PC}} = 24.0$ Hz, CH_3), [C_6F_5 not listed]. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 299 K): $\delta = -35.5$ (quin, $^3J_{\text{PF}} = 30.4$ Hz). ^{10}B NMR (54 MHz, CD_2Cl_2 , 299 K): $\delta = 48.0$ ($\nu_{1/2} \sim 450$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2 , 299 K): $\delta = -129.9$ (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -150.7 (tm, $^3J_{\text{FF}} = 20.4$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.2 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.5$]; -129.8 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -150.6 (br t, $^3J_{\text{FF}} = 19.1$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.2 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.6$]; -133.3 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{B}}$), -152.5 (tm, $^3J_{\text{FF}} = 19.6$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{B}}$), -161.5 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{B}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{B}} = 9.0$].

Preparation of Compound 8

Benzaldehyde (8.6 μL , 0.09 mmol, 3.0 eq) was added to a suspension of compound (**5**)₃ (50.0 mg, 0.03 mmol, 1.0 eq) in dichloromethane (10 mL) and stirred overnight. Then pyridine (7.0 μL , 0.09 mmol, 3.0 eq) was added and the reaction mixture was stirred overnight again. All volatiles were removed *in vacuo* and the remaining residue was dissolved in pentane (ca. 5 mL) and stored at -34 °C. After two days the formed oil was isolated and dried *in vacuo* (55.4 mg, 84%). Anal. calc. for $\text{C}_3\text{H}_{18}\text{BF}_{15}\text{NOP}$ (771.27 g/mol): C 51.39, H 2.35, N 1.82; found: C 51.65, H 2.23, N 1.74. ^1H NMR (500 MHz, CD_2Cl_2 , 299 K): $\delta = 8.68$ (br m, 2H, *o*-Py), 8.05 (br m, 1H, *p*-Py), 7.60 (br m, 2H, *m*-Py), 7.33 (m, 2H, *o*-Ph), 7.30 (m, 2H, *m*-Ph), 7.21 (m, 1H, *p*-Ph), 4.52, 4.29 (each d, $^2J_{\text{HH}} = 13.0$ Hz, each 1H, CH_2O), 2.86 (m, 1H, CH), 1.29, 1.00 (each m, each 1H, CH_2B), 1.10 (dd, $^4J_{\text{PH}} = 21.7$ Hz, $^3J_{\text{HH}} = 6.2$ Hz, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 299 K): $\delta = 145.9$ (*o*-Py), 142.0 (*i*-Ph), 140.7 (*p*-Py), 128.4 (*m*-Ph), 127.0 (*p*-Ph), 126.7 (*o*-Ph), 125.7 (*m*-Py), 65.9 (CH_2O), 25.9 (br, CH_2B), 24.5 (m, CH), 18.5 (d, $^2J_{\text{PH}} = 23.5$ Hz, CH_3), [C_6F_5 not listed]. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 299 K): $\delta = -36.1$ (quin, $^3J_{\text{PF}} = 27.5$ Hz). ^{10}B NMR (54 MHz, CD_2Cl_2 , 299 K): $\delta = 10.5$ ($\nu_{1/2} \sim 150$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2 , 299 K): $\delta = -129.2$ (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -151.0 (tm, $^3J_{\text{FF}} = 20.5$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.5 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.4$]; -129.8 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -151.7 (tm, $^3J_{\text{FF}} = 19.8$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.7 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.0$]; -133.0 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{B}}$), -157.8 (t, $^3J_{\text{FF}} = 19.6$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{B}}$), -164.2 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{B}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{B}} = 6.4$].

Preparation of Compound 9

tert-Butylacetylene (5.3 μL , 0.09 mmol, 3.0 eq.) was added to a suspension of compound (**5**)₃ (25.0 mg, 0.03 mmol, 1.0 eq) in CD_2Cl_2 (0.8 mL) and reacted overnight. All volatiles were removed *in vacuo* to obtain compound **9** as a colourless oil (25.7 mg, 90%). Anal. calc. for $\text{C}_{27}\text{H}_{17}\text{BF}_{15}\text{P}$ (668.19 g/mol): C 48.53, H 2.56; found: C 47.09, H 2.32. ^1H NMR (500 MHz, CD_2Cl_2 , 299 K): $\delta = 6.82$ (d, $^3J_{\text{HH}} = 17.7$ Hz, 1H, =CH), 6.45 (d, 17.7 Hz, 1H, BCH), 3.64 (m, 1H, CH), 1.83 (dt, $^2J_{\text{HH}} = 16.2$ Hz, $^3J_{\text{PH}} = ^3J_{\text{HH}} = 10.8$ Hz, 1H, CH_2B), 1.61 (m, 1H, CH_2B), 1.14 (dd, $^3J_{\text{PH}} = 20.2$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, 3H, CH_3), 1.08 (s, 9H, tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 299 K): $\delta = 176.3$ (=CH), 128.2 (br, BCH), 36.3 (tBu), 33.1 (br d, $^2J_{\text{PH}} = 20.7$ Hz, CH_2B), 28.5 (tBu), 25.3 (m, CH), 20.1 (d, $^2J_{\text{PH}} =$

25.6 Hz, CH_3), [C_6F_5 not listed]. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 299 K): $\delta = -36.4$ (quin, $^3J_{\text{PF}} = 31.0$ Hz). ^{10}B NMR (54 MHz, CD_2Cl_2 , 299 K): $\delta = 71.5$ ($\nu_{1/2} \sim 600$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2 , 299 K): $\delta = -129.5$ (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -150.3 (tm, $^3J_{\text{FF}} = 20.3$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.1 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.8$]; -129.9 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -150.8 (tm, $^3J_{\text{FF}} = 20.3$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.2 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.5$]; -132.5 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{B}}$), -153.6 (t, $^3J_{\text{FF}} = 20.3$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{B}}$), -162.5 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{B}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{B}} = 8.9$].

Preparation of Compounds **10**_{major} and **10**_{minor}

tert-Butylacetylene (10.5 μL , 0.09 mmol, 3.0 eq) was added to a suspension of compound (**5**)₃ (50.0 mg, 0.03 mmol, 1.0 eq) in dichloromethane (10 mL) and stirred overnight. Then pyridine (7.0 μL , 0.09 mmol, 3.0 eq) was added and the reaction mixture was stirred overnight again. All volatiles were removed *in vacuo* and the remaining residue was dissolved in pentane (ca. 5 mL) and stored at -34 °C. After two days the formed colourless precipitate was isolated and dried *in vacuo* (39.8 mg, 63%). In the CD_2Cl_2 solution of the obtained solid two diastereomers **10**_{major} and **10**_{minor} were observed (major/minor $\sim 5/3$). Crystals suitable for the X-ray single crystal structure analysis were obtained by slow crystallisation from a heptane/dichloromethane solution of **10**. Mp: 259 °C. Anal. calc. for $\text{C}_{32}\text{H}_{22}\text{BF}_{15}\text{NP}$ (747.29 g/mol): C 51.43, H 2.97, N, 1.87; found: C 51.23, H 2.71, N, 1.81. **10**_{major}: ^1H NMR (600 MHz, CD_2Cl_2 , 299 K): $\delta = 8.47$ (m, 2H, *o*-Py), 8.06 (m, 1H, *p*-Py), 7.60 (m, 2H, *m*-Py), 6.21 (dt, $^3J_{\text{HH}} = 17.7$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 1H, BCH), 4.84 (d, $^3J_{\text{HH}} = 17.7$ Hz, 1H, =CH), 3.10 (m, 1H, CH), 1.03 (m, each 2H, CH_2B), 1.00 (dd, $^4J_{\text{PH}} = 21.6$ Hz, $^3J_{\text{HH}} = 6.5$ Hz, 3H, CH_3), 0.92 (s, 9H, tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2 , 299 K): $\delta = 146.8$ (=CH), 146.2 (*o*-Py), 141.3 (*p*-Py), 133.8 (br, BCH), 126.0 (*m*-Py), 34.1 (tBu), 29.7 (tBu), 28.7 (br, CH_2B), 25.3 (br m, CH), 19.2 (d, $^3J_{\text{PC}} = 25.9$ Hz, CH_3), [C_6F_5 not listed]. $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2 , 299 K): $\delta = -37.7$ (quin, $^3J_{\text{PF}} = 29.8$ Hz). ^{10}B NMR (64 MHz, CD_2Cl_2 , 299 K): $\delta = 0.4$ (br, $\nu_{1/2} \sim 200$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2 , 299 K): $\delta = -129.2$ (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -151.2 (tm, $^3J_{\text{FF}} = 20.3$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.9 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 10.7$]; -130.0 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -152.1 (tm, $^3J_{\text{FF}} = 20.3$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.9 (m, 4F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} = 9.8$]; -132.4 (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{B}}$), -159.7 (t, $^3J_{\text{FF}} = 20.2$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{B}}$), -164.9 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{B}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{B}} = 5.2$]. **10**_{minor}: ^1H NMR (600 MHz, CD_2Cl_2 , 299 K): $\delta = 8.47$ (m, 2H, *o*-Py), 8.10 (m, 1H, *p*-Py), 7.60 (m, 2H, *m*-Py), 6.12 (d $^3J_{\text{HH}} = 17.8$ Hz, 1H, BCH), 5.05 (d, $^3J_{\text{HH}} = 17.8$ Hz, 1H, =CH), 2.92 (m, 1H, CH), 1.31, 0.91 (each m, each 1H, CH_2B), 1.00 (dd, $^4J_{\text{PH}} = 21.6$ Hz, $^3J_{\text{HH}} = 6.5$ Hz, 3H, CH_3), 0.95 (s, 9H, tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2 , 299 K): $\delta = 147.9$ (=CH), 146.2 (*o*-Py), 141.3 (*p*-Py), 132.1 (br, BCH), 126.0 (*m*-Py), 34.2 (tBu), 29.7 (tBu), 28.7 (br, CH_2B), 25.3 (br m, CH), 19.2 (d, $^3J_{\text{PC}} = 23.1$ Hz, CH_3), [C_6F_5 not listed]. $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2 , 299 K): $\delta = -35.7$ (quin, $^3J_{\text{PF}} = 28.0$ Hz). ^{10}B NMR (64 MHz, CD_2Cl_2 , 299 K): $\delta = 0.4$ ($\nu_{1/2} \sim 200$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2 , 299 K): $\delta = -129.1$ (m, 2F, *o*- $\text{C}_6\text{F}_5^{\text{P}}$), -151.5 (tm, $^3J_{\text{FF}} = 20.2$ Hz, 1F, *p*- $\text{C}_6\text{F}_5^{\text{P}}$), -161.4 (m, 2F, *m*- $\text{C}_6\text{F}_5^{\text{P}}$), [$\Delta\delta^{19}\text{F}_{\text{pm}}^{\text{P}} =$

9.9]; -129.6 (m, 2F, *o*-C₆F₅^P), -151.8 (tm, ³J_{FF} = 21.0 Hz, 1F, *p*-C₆F₅^P), -161.8 (m, 2F, *m*-C₆F₅^P), [$\Delta\delta^{19}\text{F}_{pm}^P = 10.0$]; -132.2 (m, 2F, *o*-C₆F₅^B), -160.2 (t, ³J_{FF} = 20.2 Hz, 1F, *p*-C₆F₅^B), -165.0 (m, 2F, *m*-C₆F₅^B), [$\Delta\delta^{19}\text{F}_{pm}^B = 4.8$].

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Notes and references

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Graphical Abstract

A unique vicinal Lewis Pair cyclotrimer has been synthesized and characterized with respect to its structure and reactivity.

