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**Title:** Remarkable Aggregation Behavior of a Six-membered Cyclic Frustrated Phosphane/Borane Lewis Pair: Formation of a Supramolecular Cyclooctameric Macrocyclic Ring System

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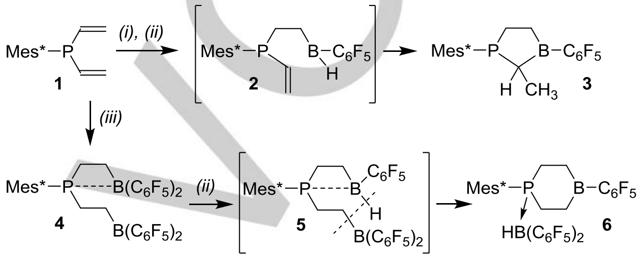
# Remarkable Aggregation Behavior of a Six-membered Cyclic Frustrated Phosphane/Borane Lewis Pair: Formation of a Supramolecular Cyclooctameric Macrocyclic Ring System

Xiaoming Jie,[a] Constantin G. Daniliuc,[a] Robert Knitsch,[b] Michael Ryan Hansen,[b] Hellmut Eckert,[b,c] Sebastian Ehlert,[d] Stefan Grimme,[d] Gerald Kehr,[a] and Gerhard Erker*[a]

Dedication ((optional))

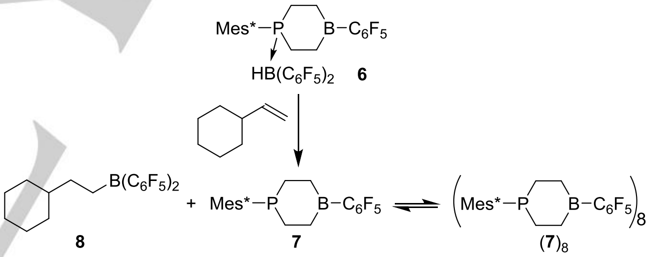
**Abstract:** The six-membered cyclic frustrated phosphane/borane Lewis pair **7** was liberated from its $HB(C_6F_5)_2$ adduct **6** by treatment with vinylcyclohexane. The system **7** is an active FLP that undergoes cycloaddition reactions with suitable π-reagents and it splits dihydrogen. At r.t. in solution compound **7** is a monomer, however, in the crystal and in solution at low temperature it aggregates to a thermodynamically favored supramolecular macrocyclic cyclooctamer.

Frustrated Lewis pair (FLP) chemistry has taken quite some development in the recent years. So far, a manifold of inter- as well as intramolecular FLP systems have been developed and used e.g. in small molecule activation.[1] By far the majority of intramolecular examples are open-chain systems, featuring just a single hydrocarbyl chain between the FLP functional groups.[2] Cyclic systems, where the phosphorus base and the boron Lewis acid are part of a ring structure are rare.[3] We have quite recently described the active five-membered cyclic P/B FLP **3**, which was formed starting from Mes*P(vinyl)$_2$ **1** by means of a sequence of hydroboration reactions, and reported about its specific chemical features.[3a] We also reported about the synthesis of the six-membered P/B system **6** (Scheme 1).[4] This compound was obtained by two-fold hydroboration of **1** with Piers' borane,[5] followed by $C_6F_5$/hydride exchange by treatment with 9-BBN (with formation of $C_6F_5$-BBN)[6] and rearrangement. We have now used the $HB(C_6F_5)_2$ adduct **6** to generate the free six-membered ring P/B FLP system **7** and found that it exhibits some quite remarkable behaviour. This will be described in this account.



Mes*: 2,4,6-tri-tert-butylphenyl; 9-BBN: 9-borabicyclo(3.3.1)nonane; *(i)* + $HB(C_6F_5)_2$; *(ii)* + 9-BBN, - $C_6F_5$-BBN; *(iii)* + 2 $HB(C_6F_5)_2$.

**Scheme 1.** Cyclization reactions derived from the divinyl phosphane derivative **1**.



Mes*: 2,4,6-tri-tert-butylphenyl

**Scheme 2.** Preparation of compound **7**.

Removal of $HB(C_6F_5)_2$ from the adduct **6** was achieved by treatment with a twofold excess of vinylcyclohexane in pentane solution. Stirring this mixture overnight at r.t. gave the six-membered P/B FLP **7** plus the hydroboration product **8** (Scheme 2). Compound **7** was precipitated at -35 $^{o}$C and obtained as a white solid in 80% yield. Single crystals for the structural characterization of the cyclic P/B FLP **7** were obtained by slow solvent evaporation from a dichloromethane/pentane (1:6, v/v) solution at r.t.. The X-ray crystal structure analysis furnished a surprising result. In the crystal, the cyclic P/B FLP exhibits a supramolecular macrocyclic ring structure, which has been formed by association of eight monomeric six-membered ring FLPs. The cyclooctameric structure is constructed by combining four symmetry-equivalent dimers with their counterparts by means of P-B [$P1\cdots B2^{***}$: 2.148(10)Å] and B-P [$B1\cdots P2$: 2.113(10)Å] interactions to form the macrocyclic ring structure. The diameter of the macrocyclic ring structure amounts to ca. 12.5 Å. The crystallographically independent dimeric subunit shows two six-membered P/B FLP rings that exhibit very different

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conformeric arrangements. The P1/B1 containing unit (Figure 1) shows a chair conformation with both the large substitutents, namely the $C_6F_5$ group at boron and the Mes* moiety at phosphorus, in axial positions. The adjacent P2/B2 containing ring in contrast is found in a boat conformation.[7] Again, we found the bulky $C_6F_5$ and Mes* groups oriented in pseudo-axial positions. The equatorial binding sites at both the P1/B1 as well as P2/B2 pair are used for making the connection to the adjacent six-membered P/B FLP subunits of the cyclooctameric structure (**7**)$_8$. We note that the very bulky Mes* substituents show a bent structure at the connecting carbon atoms C21 and C51, respectively.[8]

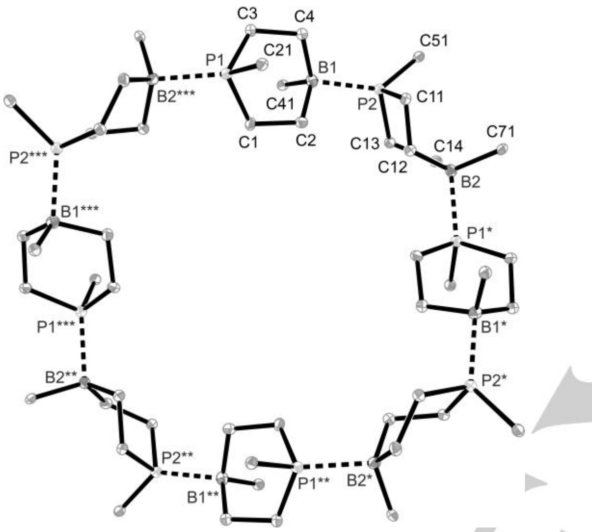

**Figure 1.** A view of the cyclooctameric ring structure (**7**)$_8$ (thermal ellipsoids are shown at 15% probability). Hydrogen atoms are omitted and only the connecting carbon atoms of the bulky $C_6F_5$ and Mes* substituents are shown for clarity. Characteristic structural parameters (Å): P1⋯B1 3.416, P1⋯B2*** 2.148(10), B1⋯P2 2.113(10), P2⋯B2 3.423 B1⋯B1** 12.269, P1⋯P1** 11.425, P2⋯P2** 13.455, B2⋯B2** 12.664. For a space filling view of compound **7** see the Supporting Information.

The cyclooctameric ring (**7**)$_8$ was characterized as a powder by $^{31}$P and $^{11}$B solid-state MAS NMR spectroscopy.[9] The $^{31}$P{$^1$H} CP/MAS NMR spectrum (Figure 2b) includes two $^{31}$P signals at δ 20.0 and 17.7 ppm. Accordingly, the $^{11}$B MAS NMR spectrum (Figure 2a) also contains a pair of $^{11}$B resonances at δ -3.7 and -5.4 ppm. The strong overlap of their second-order quadrupolar powder patterns can be removed by 2D $^{11}$B 3QMAS NMR correlation spectroscopy (Figure S53). We ascribe the pairs of $^{31}$P and $^{11}$B signals to the independent asymmetric dimeric subunits, leading to different chemical environments for P1 and P2 as well as for B1 and B2. While most of the $^{31}$P NMR parameters are very similar for the P1 and P2 signals, the $^{31}$P chemical shift anisotropies differ significantly and therefore allow an assignment (cf. Figure S47). Based on DFT calculations, we assign the $^{31}$P signal at 20.0 ppm to P2 in the boat conformation and the signal at 17.7 ppm to P1 in the chair conformation. Furthermore, using a $^{11}$B{$^{31}$P} refocused-INEPT MAS NMR correlation experiment (cf. Figure S52) the boron species at -3.7 and -5.4 ppm were assigned to B2 and B1, respectively. To gain further evidence for the cyclooctameric structure, we acquired a 2D $^{31}$P double-quantum single-quantum correlation spectrum (Figure S49), showing only the expected cross correlations between the two non-equivalent phosphorus species. As autocorrelation peaks are missing, chemically equivalent $^{31}$P nuclei are distant from each other, whereas P1 and P2 are in close proximity. Finally, the B-P distance geometry was characterized by $^{31}$P{$^{11}$B} REAPDOR and $^{11}$B{$^{31}$P} REDOR NMR experiments (Figure S51 and S50). The resulting experimental REDOR/REAPDOR curves are well reproduced using simulations based on three-spin systems (e.g. $^{11}$B-$^{31}$P-$^{11}$B) that include the respective angles and distances from the crystal structure of (**7**)$_8$. Based on these results, we conclude that the structure of the powdered material investigated is also based on the octameric motif.

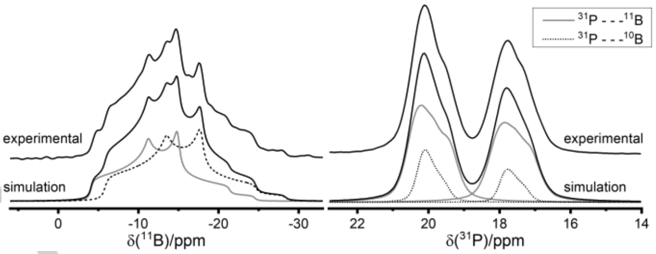

**Figure 2.** [a] $^{11}$B MAS NMR spectrum and [b] $^{31}$P {$^1$H} CP/MAS NMR spectrum for (**7**)$_8$ acquired at 7.05 T and a MAS frequency of 12.5 kHz using SWFTPPM proton decoupling. The simulations in [b] consider the different magnitudes for $^{31}$P species with J-couplings to $^{10}$B/$^{11}$B.

In contrast, we have monitored the NMR spectra of the monomeric P/B FLP **7** in solution ($CD_2Cl_2$) at 299 K. It is characterized by a single $^{31}$P NMR signal at δ -16.5 and a broad $^{11}$B NMR resonance at δ 74, which is typical for a trigonal planar Lewis acidic boron.[10] Consequently, we observed three $^{19}$F NMR resonances with a large $\Delta\delta^{19}F_{m,p}$ chemical shift difference of 10.0 ppm. The $^1$H NMR spectrum shows the typical resonance of the Mes* substituent at phosphorus and four signals of ring methylene groups (the spectra are depicted in the Supporting Information).

The NMR spectra change drastically with decreasing the monitoring temperature. Below 278 K we see the $^{31}$P NMR signals of a new species grow in at the expense of the $^{31}$P NMR resonance of the monomer **7**. Below ca. 243 K it is by far the major compound present. Its $^{31}$P (δ 18.9, δ 17.6) and $^{11}$B (δ -4.9, δ -9.1) NMR signals (193 K) correlate well with the respective solid state NMR features of the cyclooctamer (**7**)$_8$. In accord with the interpretation of the presence of the strongly temperature dependent 8 × **7** ⇌ (**7**)$_8$ equilibrium we monitored a total of four *o*-, two *p*- and four *m*-$C_6F_5$ $^{19}$F NMR signals of the preferred cyclooctameric compound (**7**)$_8$ at 233 K (see the Supporting Information for details).

The equilibrium situation concerning the cyclooctameric ring was further supported by the DFT analysis of the system.[11] We searched for possible oligomeric and cyclooligomeric structures, conducted full geometry optimizations (including possible conformations), and determined their free energy content relative to that of the monomer **7**. The cyclooctamer (**7**)$_8$ was the only

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cyclic supramolecular structure that we could locate as a minimum structure on this hypersurface. We found no other macrocyclic supra-structure of significant stability, but there were several open-chain structures that represented thermally accessible local minima (Figure 3). According to our DFT analysis, the monomer **7** is the energetically favored structure in $CH_2Cl_2$ solution at 298 K. The oligomers fall in a small free energy window of about 2 kcal/mol and thus, lowering the temperature leads to increasingly favoring the aggregated structure. This is attributed to a decrease of the entropic penalty for cyclic aggregation. At a threshold temperature of 268 K (Figure 3), the monomer and the calculated aggregated open dimer and tetramer come very close in Gibbs free energy. At 233 K the associated structures are all more favorable than the monomer and the entropically favored cyclooctamer has become by far preferred.[12]

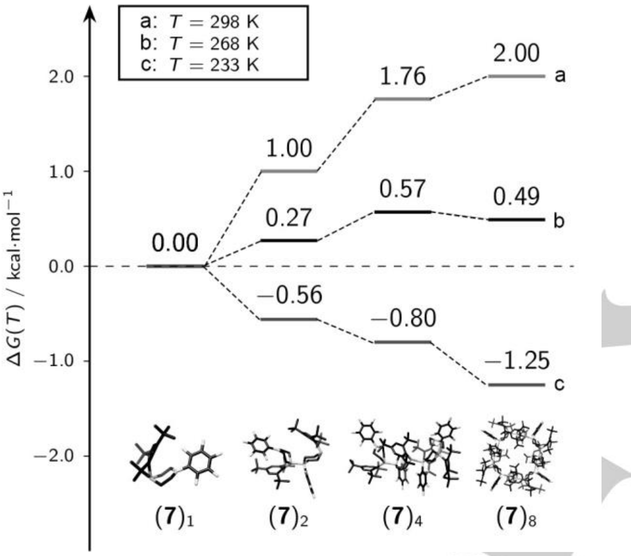
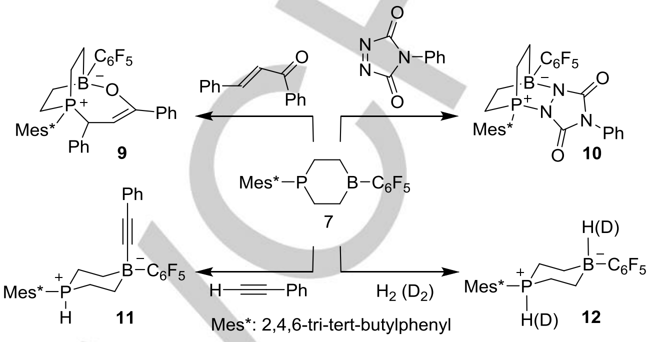


**Figure 3.** DFT calculated relative free energies ΔG in kcal/mol (B97-3c+COSMO-RS($CH_2Cl_2$)//GFN-xTB+GBSA($CH_2Cl_2$) level, see SI for details) of the six-membered monomeric P/B FLP **7** and some of its aggregated oligomers, including the macrocyclic cyclooctamer $(\mathbf{7})_8$, that we have experimentally found in the crystal and at low temperature in solution. The values given always refer to one monomer unit.

The six-membered ring system **7** is an active frustrated Lewis pair. It undergoes a variety of typical P/B FLP reactions under mild conditions.[1] Intramolecular P/B FLPs often undergo selective 1,4-addition reactions to conjugated π-systems[13] and so does the cyclic FLP **7**. (Scheme 3) The reaction of **7** with chalcone (dichloromethane, 6 h, r.t.) gave the 1,4-P/B addition product **9**, that was isolated in 75% yield. It shows the heteroatom NMR resonances at δ 37.2 ($^{31}$P) and δ 0.3 ($^{11}$B), respectively. ($\Delta\delta^{19}F_{m,p}$ = 3.1 ppm), and the $^1$H NMR features of the chalcone derived moiety at δ 5.63 (-CH=, $^3J_{PH}$ = 18.4 Hz) and δ 4.53 (PCHPh-, $^2J_{PH}$ = 17.4 Hz), respectively (see the Supporting Information for further details and the X-ray crystal structure analysis of compound **9**).

*N*-Phenyltriazolinedione reacts rapidly with **7** ($CH_2Cl_2$, r.t., 1h) to give the product **10** (Scheme 3), which was isolated as a solid in 73% yield. The X-ray crystal structure analysis (Figure 4) shows the presence of the heterobicyclo[2.2.2]octane type framework. The nitrogen atoms N2 and N3 are planar tricoordinate, and the geometry at N1, which is adjacent to the very bulky Mes* substitute at phosphorus, deviated from planarity by ca. 10°. The N1-N2 bond length amounts to 1.429(3) Å.



**Scheme 3.** Reactions of compound **7**.

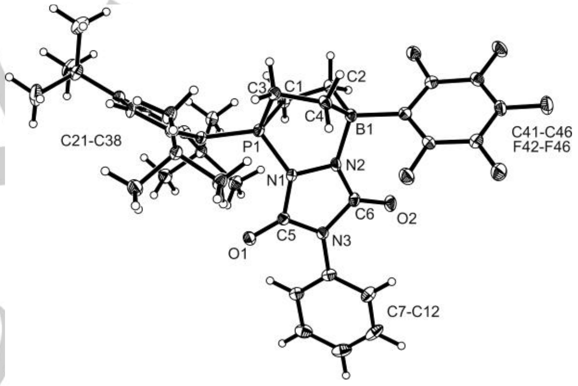


**Figure 4.** A view of the molecular geometry of the P/B FLP adduct **10** (thermal ellipsoids are shown at 30% probability).

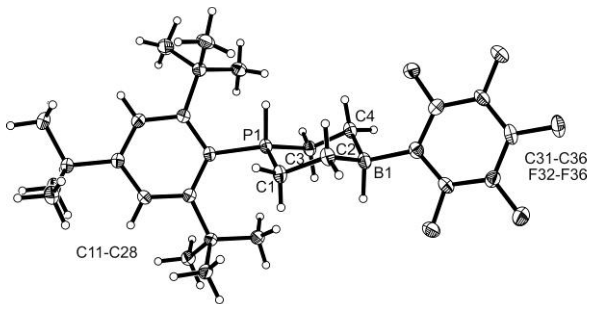


**Figure 5.** A projection of the molecular structure of the FLP dihydrogen splitting product **12** (thermal ellipsoids are shown at 50% probability).

Compound **7** reacts cleanly with phenylacetylene by C-H bond activation[14] to give **11** (isolated in 60% yield), but this reaction requires somewhat forcing conditions (100 °C, 24 h). The X-ray crystal structure analysis (see the Supporting Information for details) revealed the formation of the P-H phosphonium unit and showed that the remaining alkynyl unit had become attached at boron. We note that the Mes* substituent at phosphorus and the $C_6F_5$ group at boron are *trans*-oriented at the six-membered heterocyclic core of compound **11**. Consequently, we conclude that the addition of the components of the phenylacetylene reagent at the cyclic P/B FLP had taken place by means of an intermolecular reaction pathway. In solution ($CD_2Cl_2$) compound **11** shows a $^1H$ NMR [P]-H doublet at δ 6.40 with $^1J_{PH}$ = 454.7 Hz ($^{31}P$: δ 18.0) and a $^{11}B$ NMR feature at δ -19.0. The $\Delta\delta^{19}F_{m,p}$ chemical shift difference in **11** is 2.7 ppm.

The six-membered cyclic P/B FLP **7** is an active dihydrogen splitting agent.[1] Heterolytic H-H cleavage was achieved by exposure of **7** to dihydrogen in $CH_2Cl_2$ solution (2 bar $H_2$, r.t., 5 d) and we isolated the zwitterionic phosphonium/hydridoborate product **12** as a white solid in 74% yield. The reaction of **7** with $D_2$ under similar conditions gave the product **12**-$D_2$ in a similar yield. Compound **12** was characterized by X-ray diffraction (Figure 5). It shows a chair conformation of the six-membered heterocyclic framework with both the bulky Mes* substitutents at phosphorus and the $C_6F_5$ group at boron being in equatorial positions. Consequently, the proton/hydride pair had been *trans*-attached at the phosphorous Lewis base and the boron Lewis acid. Since this cannot be achieved in an intramolecular reaction,[3,15] we conclude that the $H_2$ splitting reaction at the cyclic P/B FLP must have taken place in an intermolecular fashion involving more than one FLP molecule.[16]

In solution ($CD_2Cl_2$) compound **12** shows the typical broad $^1H$ NMR 1:1:1:1 quartet of the [B]-H moiety at δ 1.97 and the $[P]^+$-H resonance at δ 6.50 ($^1J_{PH}$ = 456.0 Hz). The $^{31}P$ NMR signal was located at δ 18.2 and the $^{11}B$ NMR resonance at δ -18.5 as a doublet with a typical $^1J_{BH}$ ~ 85 Hz coupling constant (for further details, see the SI). Both compounds **7** and **12** were used a catalysts for an imine and an enamine hydrogenation, but they both required an elevated reaction temperature (see the Supporting Information for details).

Our study has shown that active cyclic six-membered P/B FLPs can readily be prepared by means of hydroboration sequences, combined with a specific sequence involving formation and removal of a $HB(C_6F_5)_2$ equivalent. The resulting system **7** is an active P/B FLP. It undergoes cycloaddition-type P/B addition reactions to π-systems[3] and it actively cleaves the dihydrogen molecule, although this reaction deviates from the common behavior of intramolecular P/B FLPs in the sense that it produces the respective *trans*-$H^+/H^-$ addition product. More importantly, compound **7** shows a remarkable aggregation behavior. It forms the unique macrocyclic cyclooctameric ring structure [(**7**)$_8$] in the crystal and in solution at low temperature. Cyclic frustrated Lewis pairs have so far rarely been encountered.[3] Their aggregation behavior might open new pathways in FLP chemistry and it might serve to connect FLP chemistry with the important established area of supramolecular chemistry.

## Acknowledgements

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** boranes • phosphanes • frustrated Lewis pairs • macrocycles • self-assembly

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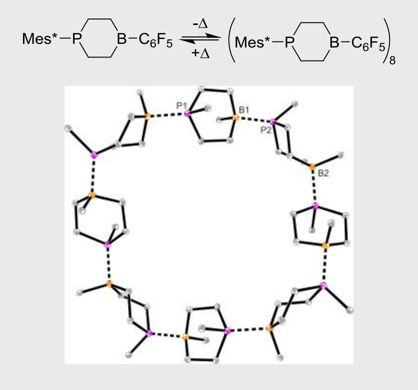
Layout 1:

## COMMUNICATION

The six-membered cyclic frustrated phosphane/borane Lewis pair forms a macrocyclic cyclooctameric structure in the crystal and in solution at low temperature. The supramolecular FLP assembly has an inner diameter of about 12 to 13 Å.



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**Remarkable Aggregation Behavior of a Six-membered Ring Frustrated Phosphane/Borane Lewis Pair: Formation of a Supramolecular Cyclooctameric Macrocyclic Ring System**