Supporting Information

Calix[4]pyrrolato Aluminate Catalyzes the Dehydrocoupling of Phenylphosphine Borane to High Molar Weight Polymers

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Author Contributions

F.S., L.G., and I.M. devised the project. F.S. performed the catalytic reactions and analyzed the polymeric materials. L.M.S. prepared the catalysts, performed the stoichiometric experiments, prepared the DOSY samples and did all computations together with Fr. S. D.H. evaluated the DOSY NMR spectra. M.A.W. provided input on characterization and through discussions. F.S., L.M.S., I.M., and L.G. wrote the manuscript.
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1 General Information

Storage and manipulations of all compounds were performed under an inert atmosphere in a dry nitrogen-filled MBraun 200B glovebox equipped with a cold-well; or using a nitrogen Schlenk line using standard techniques. Hexanes, toluene, diethyl ether, and THF were dried and purified using a MBraun Grubbs/Dow solvent purification system and stored over activated 4 Å molecular sieves. C6D6, and Tol-d8 were dried over sodium/benzophenone ketyl, degassed and vacuum distilled prior to use. All other solvents (chloroform-d, o-DCB, α-DCB-d4) were dried by storing over activated molecular sieves (4 Å) for at least one week prior to degassing with three freeze-pump-thaw cycles. If not stated otherwise, all reagents were purchased from Sigma-Aldrich and used as received. BH3·THF (1 M in THF) was trap-to-trap vacuum transferred prior to use. PhPH2·BH3, meso-octaethylcalix[4]pyrrole (EtC4H4)2, [Li(thf)]4[MeC4Al(thf)]3 and [PPh4]2[EtC4Al]4 were synthesized according to published procedures. 1H and 13C NMR chemical shifts were referenced to residual proteo-solvent resonances and naturally abundant 13C resonances for all deuterated solvents. All heteronuclear NMR spectra were referenced externally to IUPAC standards. Chemical shift assignments are based on NMR experiments performed on Bruker Avance NEO 500 MHz, AV II 360 MHz, or AV III 300 MHz spectrometers. Analytical gel-permeation chromatography (GPC) was performed on a Malvern RI max Gel Permeation Chromatograph, equipped with an automatic sampler, a pump, an injector, and inline degasser. The columns (styrene/divinyl benzene gel, 1xT5000 and 1xT3000) were maintained at 35 °C. Sample elution was detected by means of a differential refractometer. THF (VWR), containing 0.1 wt% [nBu4N]Br, was used as the eluent at a flow rate of 1.0 ml min⁻¹. Samples were dissolved in THF (1 mg/mL), filtered through a 0.2 μm PTFE syringe filter before injection (100 μL). Calibration was conducted using commercially available monodisperse polystyrene standards (Aldrich, Mn = 1,200 – 4,200,000 Da). Data for low molar mass components (i.e. Mn < 1,200 Da) is estimated. Preparative gel-permeation chromatography was performed on a Malvern LC-20AP Preparative Liquid Chromatograph, equipped with an automatic sampler, a pump, an injector, and inline degasser. The column (Shodex KF-2003) was maintained at 40 °C. Sample elution was detected by means of a differential UV/VIS spectrometer. THF (VWR) was used as the eluent at a flow rate of 3 ml min⁻¹. Samples were dissolved in THF (15 mg/mL), filtered through a 0.2 μm PTFE syringe filter before injection (500 μL).
$^{31}\text{P}[^1\text{H}]$ diffusion ordered spectroscopy (DOSY) NMR

Diffusion ordered spectroscopy (DOSY) NMR experiments were performed on a BRUKER Avance III 600 FT NMR spectrometer, operating at $^{31}\text{P}$ resonance frequency of 243 MHz. The instrument was equipped with a 5-mm BBFO z-axis gradient helium-cooled cryogenic probe. The temperature unit of the instrument was calibrated according to the manual of the manufacturer of the instrument using the temperature dependence of the proton chemical shift difference of MeOH.

Diffusion NMR experiments have been performed using the *ledbpgp2sig* pulse sequence delivered by the manufacturer. Phosphorus diffusion data have been collected with 16k data points and a spectral width of 29297 Hz. The relaxation delay was set to 4 s (for monomeric PhPH$_2$:BH$_3$) or 5 s (for the oligomeric mixture). The diffusion delay time (big Delta, $\Delta$) was set to 80 ms and the gradient duration time (little delta, $\delta$/2) was set to 2500 µs. The gradient strength within the diffusion experiments was incremented linearly using 16 (for the oligomeric mixture) or 24 (for monomeric PhPH$_2$:BH$_3$) steps. After Fourier transformation and phase correction, the diffusion dimension of the 2D DOSY spectra were processed by means of the Bruker Topspin software package (version 4.0.8) and analyzed with the Bruker Dynamics Center (version 2.6).

The hydrodynamic radii have been calculated by the Stokes-Einstein equation:

$$D = \frac{k_B T}{6 \pi \eta r_H} \quad \text{(eq. 1)}$$

*D* = diffusion constant  
*T* = temperature  
*$r_H$ = hydrodynamic radius

$k_B$ = Boltzmann constant  
*$\eta$ = viscosity of the solvent
The relation between volume and radius of a sphere is given by:

\[ V = \frac{4}{3} \pi r^3 \]  

(eq. 2)

**Figure S1**: \( \eta(T) \) plot and fitting function for the solvent o-DCB. Values taken from ref 5.

Fitting function (red line):  \[ \eta(T) = 7.57333 \times 10^{-12} \cdot T^4 - 1.08293 \times 10^{-6} \cdot T^3 + 5.85981 \times 10^{-6} \cdot T^2 - 0.00143 \cdot T + 0.1333 \]

The viscosity for the experiment temperature has been calculated as \( \eta_{o-DCB}(295 \text{ K}) = 0.001386 \text{ Pa s} \).
2 Experimental Procedures

2.1.1 Synthesis of $[\text{Li}(\text{thf})_4][\text{EtC}_x\text{Al}(\text{thf})_2]$

**Procedure.** To a flame dried Schlenk flask under nitrogen atmosphere, meso-octaethylcalix[4]pyrrole (1.00 g, 1.85 mmol, 1 eq) was added along with THF (10 mL). Lithium aluminum hydride powder (LiAlH$_4$, 73.7 mg, 1.94 mmol, 1.05 eq) and subsequently additional THF (5 mL) were added. A slightly brown and turbid mixture was obtained. It was stirred for 16 h at 70 °C. It was cooled down to room temperature, and the solvent was removed under reduced pressure. The crude product was washed with Et$_2$O/THF (15:1 %vol, 5 times 3 mL). A colorless solid was obtained. For further purification, the entire material was dissolved in THF (5 mL) and was filtered through a PTFE syringe filter. The solvent was removed under reduced pressure. The desired product was obtained as colorless solid (565 mg, 0.56 mmol, 30% yield) after drying in vacuo for 30 min (0.2 mbar). The yield may be increased by further extraction of the product from the Et$_2$O/THF washing solution. $[\text{Li}(\text{thf})_4][\text{EtC}_x\text{Al}(\text{thf})_2]$ was constantly kept under inert conditions.

$^1$H NMR (600.2 MHz, CD$_2$Cl$_2$, 295 K): $\delta = 5.91$ (s, 8H, $\beta$-H), 3.66 (br s, 20H, THF), 3.13 (br s, 4H, THF), 1.83 (br s, THF (24H) and $\alpha$-methylene (16H)), 0.85 (br s, 12H, $\alpha$-Me), 0.60 (br s, 12H, $\alpha$-Me) ppm.

$^{13}$C($^1$H) NMR (151.9 MHz, CD$_2$Cl$_2$, 295 K), $\delta = 144.5$ (C$_q$, C$_q$-pyrrole), 104.3 (CH, $\beta$-CH), 68.7 (CH$_2$, THF), 44.5 (C$_q$, $\alpha$-C), 25.8 (CH$_2$, THF), 10.0 (CH$_3$, $\alpha$-Me) ppm.

With the standard NMR methods, it was not possible to reliably detect $^{13}$C NMR resonances of the $\alpha$-methylene groups. Direct detection and a $^1$H,$^{13}$C HSQC experiment remained unsuccessful. In the $^1$H,$^{13}$C HMBC experiment, several very week signals were detected correlated to the methyl group protons in the $^1$H dimension. They appeared in the expected region between 28 and 46 ppm in the $^{13}$C dimension. Most likely, the highly dynamic character of the compound (THF association/dissociation, ethyl group rotations, ring flipping of the macrocyclic ligand) and the fact that the methylene positions can become diastereotopic upon binding of a substrate to $^{13}$CAl$^-$ are responsible for the nonappearance of the said signal(s) with the applied NMR experimental parameters.

$^7$Li NMR (233.3 MHz, CD$_2$Cl$_2$, 295 K), $\delta = -3.59$ (br s) ppm.

**HR-MS (ESI, negative ion mode):** m/z calculated for C$_{36}$H$_{48}$AlN$_4$ [M]$^-$: 563.3700, found: 563.3692.

The mono or the bis THF adduct were not detected.

**Elemental analysis:** calc. C 71.82, H 9.64, N 5.58, found: C 71.69, H 9.82, N 5.59 (averaged values of two individual measurements)
3 Polymerization and Additional Experiments

3.1 Thermal stability of [Li(thf)$_4$][EtCxAI(thf)$_2$]

Figure S2: $^1$H NMR spectrum (300 MHz, toluene-d$_8$, 298 K) of [Li(thf)$_4$][EtCxAI(thf)$_2$] a) before heating and b) after 24 h at 105 °C.

3.2 Catalytic and Thermal Dehdropolymerization of PhPH$_2$·BH$_3$

**General Procedure for Catalytic Dehdropolymerization**

PhPH$_2$·BH$_3$ (62 mg, 0.50 mmol) was dissolved in o-DCB (0.4 ml) and toluene-d$_8$ (0.1 ml) and transferred to a quartz J. Young NMR tube, charged with the corresponding catalyst (see Table S1). The J. Young tube was transferred to the Schlenk line, opened to the N$_2$ atmosphere, connected to a mercury overpressure valve, and placed in an aluminium block with a temperature of 105 °C. After the desired reaction time, the J. Young tubes were closed under N$_2$ atmosphere and NMR spectra were recorded. $^{11}$B($^1$H) NMR spectroscopy was used to estimate the conversion of PhPH$_2$·BH$_3$. Prior to the GPC measurement, the reaction solution was added dropwise to rapidly stirred hexanes (15 ml) at −78 °C. The formed colourless precipitate was collected by centrifugation and dried for at least 18 h under dynamic vacuum (1 × 10$^{-3}$ mbar). The $^{11}$B and $^{31}$P NMR spectra of the isolated polymer are shown in Figure S15 and Figure S16. The isolation procedure is described in Chapter 3.8.

**Table S1:** Used catalyst and amounts for the catalytic dehdropolymerization reaction.

| catalyst                        | catalyst loading / mol% | moles / mmol | mass / mg |
|--------------------------------|-------------------------|--------------|-----------|
| [Li(thf)$_4$][EtCxAI(thf)$_2$]  | 2.0                     | 0.10         | 8.1       |
| [Li(thf)$_4$][EtCxAI(thf)$_2$]  | 0.3                     | 0.015        | 1.5*      |
| [Li(thf)$_4$][EtCxAI(thf)$_2$]  | 2.0                     | 0.10         | 10        |
| [Li(thf)$_4$][EtCxAI(thf)$_2$]  | 5.0                     | 0.25         | 25        |
| [Li(thf)$_4$][EtCxAI(thf)$_2$]  | 10                      | 0.50         | 50        |
| [PPh$_4$][EtCxAI]               | 2.0                     | 0.10         | 9.4       |
| [PPh$_4$][EtCxAI]               | 5.0                     | 0.25         | 23        |
| EtCxH$_4$                       | 2.0                     | 0.10         | 5.4       |
| EtCxH$_4$                       | 10                      | 0.50         | 27        |

* A stock solution of [Li(thf)$_4$][EtCxAI(thf)$_2$] in THF was used, transferred into the J. Young NMR tube and the solvent was removed in vacuo.
**General Procedure for Thermal Dehydropolymerization**

PhPH$_2$·BH$_3$ (62 mg, 0.50 mmol) was dissolved in o-DCB (0.4 ml) and toluene-d$_8$ (0.1 ml) in a quartz J. Young NMR tube. The J. Young tube was transferred to the Schlenk line, opened to the N$_2$ atmosphere, connected to a mercury overpressure valve, and placed in an aluminium block with a temperature of 105 °C. After the desired reaction time, the J. Young tube was closed under N$_2$ atmosphere and NMR spectra were recorded. $^{11}$B [$^1$H] NMR spectroscopy was used to estimate the conversion of PhPH$_2$·BH$_3$.

Prior to the GPC measurement, the reaction solution was added dropwise to rapidly stirred hexanes (15 ml) at −78 °C. The formed colourless precipitate was collected by centrifugation and dried for at least 18 h under dynamic vacuum ($1 \times 10^{-3}$ mbar). The $^{11}$B and $^{31}$P NMR spectra of the isolated polymer are shown in Figure S15 and Figure S16. The isolation procedure is described in Chapter 3.8.

**Table S2:** Effect of catalysts on the dehydropolymerization of PhPH$_2$·BH$_3$ at 105 °C in a mixture of o-DCB/toluene-d$_8$ 4:1 or o-DCB/THF-d$_8$ 4:1.

| entry | catalyst | catalyst loading / mol% | time / h | Conversion / %$^{[a]}$ | $M_n$ / kDa$^{[b]}$ | $M_W$ / kDa$^{[b]}$ | PD$^{[c]}$ | DP$^{[d]}$ |
|-------|----------|-------------------------|----------|-------------------------|-------------------|-------------------|---------|---------|
| 1     | none$^{[e]}$ | -                        | 24       | 90                      | 2,370             | 10,560            | 4.46    | 19      |
| 2     | none$^{[e]}$ | -                        | 48       | 99                      | 2,770             | 21,960            | 7.93    | 23      |
| 3     | none$^{[e]}$ | -                        | 24       | 91                      | 21,400            | 36,770            | 1.72    | 175     |
| 4     | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 0.3        | 24       | 90                      | 13,580            | 25,920            | 1.91    | 111     |
| 5     | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 2.0        | 24       | 94                      | 17,400            | 32,080            | 1.84    | 143     |
| 6     | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 2.0        | 24       | 95                      | 33,620            | 46,980            | 1.40    | 276     |
| 7     | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 2.0        | 31       | nd                      | 24,570            | 45,510            | 1.85    | 202     |
| 8     | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 2.0        | 48       | 99                      | 34,600            | 62,910            | 1.82    | 284     |
| 9     | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 2.0        | 72       | nd                      | 39,150            | 64,900            | 1.66    | 321     |
| 10    | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 2.0        | 72       | nd                      | 43,010            | 66,360            | 1.54    | 353     |
| 11    | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 5.0        | 24       | 95                      | 15,490            | 28,310            | 1.83    | 127     |
| 12    | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 10         | 24       | 100                     | 9,320             | 18,620            | 2.00    | 76      |
| 13    | [PPh$_3$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 2.0        | 24       | 94                      | 19,940            | 36,540            | 1.83    | 164     |
| 14    | [PPh$_3$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 5.0        | 24       | 94                      | 17,700            | 29,970            | 1.69    | 145     |
| 15    | [Li(thf)$_4$]_2[ECxAl(thf)$_2$]$^{[e]}$ | 2.0        | 24       | 94                      | 18,670            | 36,330            | 1.95    | 153     |
| 16    | ECxH$_4$$^{[e]}$ | 2.0        | 24       | 91                      | 17,320            | 32,180            | 1.86    | 142     |
| 17    | ECxH$_4$$^{[e]}$ | 10        | 24       | 92                      | 18,870            | 34,620            | 1.84    | 155     |

$^{[a]}$ Conversion estimated by $^{11}$B NMR spectroscopy, nd = not determined. $^{[b]}$ Measured using GPC analysis. $^{[c]}$ Polydispersity estimated using GPC analysis. $^{[d]}$ Degree of polymerization estimated by GPC analysis. $^{[e]}$ o-DCB/toluene-d$_8$ 4:1. $^{[f]}$ o-DCB/THF-d$_8$ 4:1. * Isolated material.
3.3 Comparison of the Thermal and the Catalytic Dehydropolymerization

![Conversion vs. reaction time plot with different aluminate catalysts](image)

**Figure S3:** Conversion vs. reaction time plot with different aluminate catalysts. The conversion of the substrate (PhPH₂BH₃) was monitored by $^{11}$B{¹H} NMR spectroscopy (116 MHz, o-DCB/toluene-d₈, 298 K).

![GPC chromatogram](image2)

**Figure S4:** GPC chromatograms of precipitated products with different aluminate catalysts (1 mg ml⁻¹ in THF with 0.1 wt% [¹²Bu₄N]Br in the THF eluent).
3.4 Comparison of Different Catalyst Loadings

**Figure S5:** Conversion vs. reaction time plot of the reaction of PhPH₂·BH₃ with different catalyst loadings of [Li(thf)₄][Et₅CxAI(thf)₂]. The conversion of the substrate (PhPH₂·BH₃) was monitored in situ by ¹¹B(¹H) NMR spectroscopy (116 MHz, o-DCB/toluene-d₈, 298 K).

**Figure S6:** GPC chromatograms of precipitated products obtained with different catalyst loadings of [Li(thf)₄][Et₅CxAI(thf)₂] (1 mg ml⁻¹ in THF with 0.1 wt% [ⁿBu₄N]Br in the THF eluent).
3.5 Blank Experiment: \( \text{EtC}_{x}\text{H}_{4} \) as Catalyst

![Conversion vs. reaction time plot](image)

**Figure S7:** Conversion vs. reaction time plot of the reaction of PhPH\textsubscript{2}·BH\textsubscript{3} with different catalyst loadings of \( \text{EtC}_{x}\text{H}_{4} \) as well as \([\text{Li(thf)}\textsubscript{4}]\text{[EtC}_{x}\text{Al(thf)}\textsubscript{2}]\). The conversion of the substrate (PhPH\textsubscript{2}·BH\textsubscript{3}) was monitored by in situ \(^{11}\text{B}\{^{1}\text{H}\} \) NMR spectroscopy (116 MHz, \( \alpha \)-DCB/toluene-\( d_{8} \), 298 K).

![GPC chromatograms](image)

**Figure 8:** GPC chromatograms of precipitated products obtained with different catalyst loadings of \( \text{EtC}_{x}\text{H}_{4} \) as well as \([\text{Li(thf)}\textsubscript{4}]\text{[EtC}_{x}\text{Al(thf)}\textsubscript{2}]\) (1 mg ml\textsuperscript{-1} in THF with 0.1 wt\% \( \text{[Bu}_4\text{N}]\text{Br} \) in the THF eluent).
3.6  Comparison of Different Reaction Times

**Figure S9**: GPC chromatograms of precipitated products obtained after different reaction times without catalyst (1 mg ml\(^{-1}\) in THF with 0.1 wt% \([nBu][\text{Br}]\) in the THF eluent).

**Figure S10**: GPC chromatograms of precipitated products obtained after different reaction times with 2.0 mol\% [Li(thf)\(_4\)][\(\text{C}_{6}\text{Al(thf)}\)\(_2\)] as catalyst (1 mg ml\(^{-1}\) in THF with 0.1 wt% \([nBu][\text{Br}]\) in the THF eluent).
3.7 Kinetic measurements

The reaction progress of the dehydrogenation reaction of PhPH₂·BH₃ was followed by ¹¹B[¹H] NMR spectroscopy (116 MHz) at 105 °C, using a quartz glass NMR pressure tube (stable up to 100 psi). Solutions of PhPH₂·BH₃ (62.0 mg, 500 μmol) in o-DCB-h₄ (500 μl) with the desired amount of catalyst (none, 1.0, 2.0, and 3.5 mol% [Li(thf)₄][EtCxAl(thf)₂]) were prepared and ¹¹B[¹H] NMR spectra were recorded every 5 min. The sample was allowed to equilibrate to the temperature for 15 min prior to the measurement. The total acquisition time was at least 180 min. The temperature unit of the instrument was calibrated according to the manual of the manufacturer of the instrument using the temperature dependence of the proton chemical shift difference of DMSO. The error of the measurements was calculated by the gaussian error propagation (ΔT = 0.5 K; integration error = 5%). However, the error for the weighting of the catalyst (±0.2 mg) exceeds the error obtained by modelling the linear region of the pseudo first order kinetic plot.

Figure S11: First-order plot of ln(I) vs. time, based on the relative signal intensities from ¹¹B[¹H] NMR integration of PhPH₂·BH₃ and [PhPHBH₃]ₙ at different times without addition of a catalyst.

Figure S12: First-order plot of ln(I) vs. time, based on the relative signal intensities from ¹¹B[¹H] NMR integration of PhPH₂·BH₃ and [PhPHBH₃]ₙ at different times with 2.0 mol% [Li(thf)₄][EtCxAl(thf)₂].
Figure S13: First-order plot of $\ln(I)$ vs. time, based on the relative signal intensities from $^{11}\text{B}[^1\text{H}]$ NMR integration of PhPH$_2$BH$_3$ and [PhPHBH$_2$]$_n$ at different times with 3.5 mol% [Li(thf)$_4$][EtCxAI(thf)$_2$].

### 3.8 Isolation of [PhPH-BH$_2$]$_n$ after Catalytic Dehydropolymerization

**Procedure.** PhPH$_2$BH$_3$ (186 mg, 1.50 mmol) was dissolved in a mixture of o-DCB (1.2 ml) and toluene (0.3 ml) and [Li(thf)$_4$][EtCxAI(thf)$_2$] (30.0 mg, 300 µmol, 2 mol%) was added. The reaction vessel was transferred to the Schlenk line, opened to the N$_2$ atmosphere, connected to a mercury overpressure valve, and heated in an oil bath to 105 °C for 72 h. The reaction solution was added dropwise to rapidly stirred hexanes (45 ml) at −78 °C. The formed precipitate was collected by centrifugation and dried in vacuo. The residue was redissolved in THF (700 µl), precipitated again in hexanes (15 ml) at −78°C, collected by centrifugation and dried in vacuo. This step was repeated three times before the precipitate was dried for at least 18 h under dynamic vacuum ($1 \times 10^{-3}$ mbar) to afford a colourless powder (134 mg, 1.10 mmol, 73%).

**GPC** (relative to polystyrene): $M_n = 43.010$ kDa, $M_w = 66.360$ kDa, PDI = 1.54.

$^1\text{H NMR}$ (360 MHz, 298 K, CDCl$_3$): $\delta = 7.35 - 6.86$ (m, br, Ar), **4.80** (s, br, PH), **3.82** (s, br, PH), **2.62** – **0.35** (BH) ppm.

$^{11}\text{B NMR}$ (116 MHz, 298 K, CDCl$_3$): $\delta = -34.2$ (m, br) ppm.

$^{11}\text{B}[^1\text{H}]$ NMR (116 MHz, 298 K, CDCl$_3$): $\delta = -34.2$ (m, br) ppm.

$^{31}\text{P NMR}$ (146 MHz, 298 K, CDCl$_3$): $\delta = -49.5$ (d, $J_{PH} = 346$ Hz) ppm.

$^{31}\text{P}[^1\text{H}]$ NMR (146 MHz, 298 K, CDCl$_3$): $\delta = -49.4$ (s, br) ppm.
Figure S14: $^1$H NMR (360 MHz, 298 K, CDCl$_3$) spectrum (left) and GPC (1 mg ml$^{-1}$ in THF with 0.1 wt% [$^t$BuN]Br in the THF eluent) chromatogram (right) of isolated [PhPHBH$_2$].

Figure S15: $^{11}$B (left) and $^{11}$B{$^1$H} (right) NMR spectra (116 MHz, 298 K, CDCl$_3$) of isolated [PhPHBH$_2$].

Figure S16: $^{31}$P (left) and $^{31}$P{$^1$H} (right) NMR spectra (146 MHz, 298 K, CDCl$_3$) of isolated [PhPHBH$_2$].
3.9 Exploration of Catalytic Oligomer Coupling

For this test, a mixture of short polymers and oligomers were synthesized by using the thermal dehydroplymerization reaction:

**Procedure.** PhPH₂·BH₃ (186 mg, 1.50 mmol) was dissolved in o-DCB (1.2 ml) and toluene (0.3 ml) in a J. Young tube. The J. Young tube was transferred to the Schlenk line, opened to the N₂ Atmosphere, connected to a mercury overpressure valve, and heated to 105 °C for 24 h. The reaction solution was added dropwise to rapidly stirred hexanes (45 ml) at −78 °C. The formed precipitate was collected by centrifugation and dried in vacuo. The residue was redissolved in THF (700 µl), precipitated again in hexanes (15 ml) at −78°C, collected by centrifugation and dried in vacuo. This step was repeated three times to make sure the remaining PhPH₂·BH₃ was rigorously removed before the precipitate was dried for at least 18 h under dynamic vacuum (1 × 10⁻³ mbar) to afford a colourless powder (117 mg, 0.967 mmol, 65 %).

**GPC** (relative to polystyrene): Mₙ = 2.600 kDa, M_W = 17.770 kDa, PDI = 6.83.

**¹¹B NMR** (116 MHz, 298 K, CDCl₃): δ = −33.7 (m, br) ppm.

**¹¹B{¹H} NMR** (116 MHz, 298 K, CDCl₃): δ = −33.7 (m, br) ppm.

**³¹P NMR** (146 MHz, 298 K, CDCl₃): δ = −49.4 (d, J_PH ≈ 310 Hz), −52.5 (t, J_PH ≈ 392 Hz), −75.6 (s, br), −80.1 (s, br) ppm.

**³¹P{¹H} NMR** (146 MHz, 298 K, CDCl₃): δ = −49.3 (s, br), −52.7 (s, br), −55.6 (s, br), −75.5 (s, br), −80.2 (s, br) ppm.

**Figure S17:** ¹¹B (left) and ¹¹B{¹H} (right) NMR spectra (116 MHz, 298 K, CDCl₃) of isolated [PhPHBH₂]ₙ.

**Figure S18:** ³¹P (left) and ³¹P{¹H} (right) NMR spectra (146 MHz, 298 K, CDCl₃) of isolated [PhPHBH₂]ₙ.
After subsequent removing of the starting material (PhPH₂BH₃), the mixture of polymers and oligomers (61 mg, 0.50 mmol) was dissolved in o-DCB (0.4 ml) and toluene-d₈ (0.1 ml) and transferred to a quartz J. Young NMR tube charged with [Li(thf)₄][EtCₓAl(thf)₂] (10 mg, 0.010 mmol 2.0 mol%). The J. Young tube was transferred to the Schlenk line, opened to the N₂ atmosphere, connected to a mercury overpressure valve, and placed in an aluminium block with a temperature of 105 °C. The reaction solution was added dropwise to rapidly stirred hexanes (15 ml) at −78 °C. The formed precipitate was collected by centrifugation and dried for at least 18 h under dynamic vacuum (1 × 10⁻³ mbar) to obtain a colourless powder (39 mg, 0.32 mmol, 64 %).

**GPC** (relative to polystyrene): Mᵣ = 31.960 kDa, Mₓ = 62.910 kDa, PDI = 1.97.

**¹¹B NMR** (116 MHz, 298 K, CDCl₃): δ = −34.8 (m, br) ppm.

**¹¹B{¹H} NMR** (116 MHz, 298 K, CDCl₃): δ = −34.3 (m, br) ppm.

**³¹P NMR** (146 MHz, 298 K, CDCl₃): δ = −49.5 (d, ¹JₚH = 348 Hz) ppm.

**³¹P{¹H} NMR** (146 MHz, 298 K, CDCl₃): δ = −49.4 (s, br) ppm.

**Figure S19:** ¹¹B (left) and ¹¹B{¹H} (right) NMR spectra (116 MHz, 298 K, CDCl₃) of isolated [PhPH-BH₂]ₙ.

**Figure S20:** ³¹P (left) and ³¹P{¹H} (right) NMR spectra (146 MHz, 298 K, CDCl₃) of isolated [PhPH-BH₂]ₙ.
3.10 Further statements on the potential role of THF and the free ligand $^{6}\text{C}_{x}\text{H}_4$ 

Although $[\text{Li(}\text{thf})_4][\text{EtC}_x\text{Al(}\text{thf})_2]$ was proven to be stable under the applied conditions, experiments, using the free ligand $^{6}\text{C}_x\text{H}_4$ with 2.0 and 10 mol% catalyst loadings were performed. No increased conversion of the starting material over time was observed in comparison to the thermal dehydropolymerization reaction. However, an increase of the molecular weight (2.0 mol% $^{6}\text{C}_x\text{H}_4$, $M_n = 17,320$ kDa, Table S2, entry 16) was observed, compared to the catalyst-free, thermal dehydropolymerization. Increasing the $^{6}\text{C}_x\text{H}_4$ loading to 10 mol% did not significantly affect the molecular weight ($M_n = 18,870$ kDa, Table S2, entry 17).

Replacing toluene-$d_8$ in the solvent mixture with THF-$d_8$ ($\alpha$-DCB/THF-$d_8$, 4:1) drastically influenced the polymerization process. With 2.0 mol% $[\text{Li(}\text{thf})_4][^{6}\text{C}_x\text{Al(}\text{thf})_2]$ a significant increase of the molecular weight to $M_n = 33,620$ kDa (Table S2, entry 6) was observed, without affecting the reaction rate of the dehydrogenation as evidenced by $^{11}\text{B}[^1\text{H}]$ NMR spectroscopy. Furthermore, performing the catalyst-free dehydropolymerization in the presence of THF-$d_8$ also led to a significant increase of the molecular weight ($M_n = 21,400$ kDa, Table S2, entry 3) without affecting the general rate of the dehydrogenation reaction. Due to the overlapping of several different processes, there is not a clear mechanistic picture for the polymerization process. Nevertheless, the experiments with the THF-free catalyst $[\text{PPh}_4][^{6}\text{C}_x\text{Al}]$ (Table S2, entry 13 and 14) are clearly demonstrating an improved polymerization process by using the aluminate. These results are showing that the dehydropolymerization process of phenylphosphineborane can be separated into two processes: 1) the dehydrogenation, and 2) the polymerization process which can be easily controlled by adding additives such as $^{6}\text{C}_x\text{H}_4$ or THF. The promoting effect of THF, or nucleophiles, on the polymerization process have been earlier studied for inorganic polymers. Due to this, a comparison of different catalyst systems should not only be based on the estimated molecular weight, but rather by the capability of the dehydrogenation reaction.
3.11 Analysis of intermediates and by-products

3.11.1 $^{31}$P('H) NMR spectroscopy

The in situ recorded $^{31}$P('H) NMR spectra (116 MHz, o-DCB/toluene-d$_8$, 298 K) of the catalyzed (2.0 mol% [Li(thf)$_3$][C$_x$H$_y$Al(thf)$_3$] or C$_x$H$_y$Al) as well as uncatalyzed, thermal dehydropolymerization reaction of PhP(H)$_2$BH$_3$ after 24 h reaction time are very different (see Figure S22a) and are not only showing signals for the desired polymer (for the isolated polymer see Figure S20). Figure S22b divides the $^{31}$P('H) NMR spectrum of the uncatalyzed, thermal dehydropolymerization into three different regions: 1) $\delta = -44.5$ to $-52.7$ ppm (blue); 2) $\delta = -52.7$ to $-62.5$ ppm (green); and 3) $\delta = -72.5$ to $-90.0$ ppm (red). The isolated polymer, as well as the monomer PhP(H)$_2$BH$_3$, are overlapping in the blue region. For a better comparison of the distribution of the reaction products, the blue region was corrected by subtracting remaining PhP(H)$_2$BH$_3$ content (estimated via $^{19}$F('H) NMR integration) from the intensity. The ratios of the three integrated regions after this correction are 37:49:14 for the uncatalyzed, thermal dehydropolymerization (Figure S22a, blue), 49:41:10 for the reaction with 2.0 mol% of the free ligand C$_x$H$_y$Al (Figure S22a, yellow) and 68:29:3 for the aluminate-catalyzed reaction (2.0 mol% [Li(thf)$_3$]C$_x$H$_y$Al(thf)$_3$). Figure S22a, green). As a first deduction, we can see that [Li(thf)$_3$]C$_x$H$_y$Al(thf)$_3$ gives, by far, the biggest portion of polymeric product, but the identification of the side-products appears to be helpful to get a deeper understanding of the performance of the catalyst. The chemical shifts of the linear dimer (H$_2$B·PhP(H)BH$_2$·PPh$_2$)(C$_x$H$_y$Al(thf)$_3$)($^{31}$P('H) NMR (202 MHz, CD$_2$Cl$_2$): $\delta = -51.4$, $-53.4$ ppm)$^9$ as well as the cyclic six-membered ring ($^{31}$P('H) NMR (122 MHz, CDC$_2$): $\delta = -52.5$ ppm, taken from Nicola L. Oldroyd, Ph.D. thesis, University of Bristol, 2020) both lie in the green region. According to this, we suggest short oligomers and cyclic species in this area.

![Figure S22](image)

**Figure S22:** a) in situ $^{31}$P('H) NMR spectra (146 MHz, o-DCB/toluene-d$_8$, 298 K), normalized on the peak at 51 ppm, after 24 h reaction time without catalyst (black), with 2 mol% [Li(thf)$_3$]C$_x$H$_y$Al(thf)$_3$ (purple) and with 2 mol% C$_x$H$_y$Al (yellow); b) in situ recorded $^{31}$P('H) NMR spectrum (146 MHz, o-DCB/toluene-d$_8$, 298 K) of the uncatalyzed, thermal dehydropolymerization after 24 h reaction time, divided into three regions: blue (−45 to −53 ppm), green (−53 to −63 ppm), red (−72 to −90 ppm). In both spectra the peak at −125 ppm, assigned to phenylphosphine, is not shown.

3.11.2 $^{31}$P('H) diffusion ordered spectroscopy (DOSY) NMR

To gain further insight into the nature of the peaks in Figure S22b, $^{31}$P('H) DOSY NMR spectroscopy was conducted (243 MHz, o-DCB, 295 K). First, the diffusion coefficient of monomeric PhP(H)$_2$BH$_3$ was determined separately because the signal ($\delta^{31}$P) = −48.4 ppm, blue region in Figure S22b) overlaps with the signals of the polymer and the oligomeric species. It was determined to be $D = 1.63 \times 10^{-10}$ m$^2$ s$^{-1}$ (entry 2, Table S3), which corresponds to a hydrodynamic volume of $V_d = 3658$ Å$^3$. This value appears much to large, so we determined the volume again by molecular modelling. The $\text{COSMO-Volume}^{10}$ of PhP(H)$_2$BH$_3$ was determined to $V_{\text{calc}} = 164$ Å$^3$ (and a corresponding radius of 3.40 Å), what we consider reasonable. Further calculations showed good agreement between experimentally obtained volumes and calculated COSMO-volumes. Thus, this value was used to estimate the relative size of the oligomeric species from the green region ($V_{\text{rel}} = V_d(\text{n-mer})/V_{\text{calc}}(\text{PhP(H)BH}_3)$). These peaks exhibit different diffusion coefficients in the range of $D = 0.52 – 0.35 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (entries 3 – 5, Table S3), which would correspond to sizes
between \( n = 690 \) – 2209 monomeric units, what apparently does not fit with the values obtained from GPC analysis (see Table S2). Again, the same phenomenon occurs as in the monomeric state – most likely aggregation through polar P-H/B-H H-bonding (which exists in the solid state). Consequently, the obtained values only serve as rough estimates of an increasing molecular weight and not as distinct values. Remarkably, it was not possible to determine rational diffusion coefficients for the polymer (blue region), as well as for the peaks in the red region. We attribute this to the larger size (and therefore very slow diffusion) of the molecules, which inhibits the determination of their diffusion coefficients with standard DOSY techniques.

Table S3: Values of the \(^{31}\text{P}\{^1\text{H}\}\) NMR DOSY spectra (243 MHz, 295 K, o-DCB).

| entry | chemical shift / ppm | \( D \) / \( 10^{-10} \text{m}^2 \text{s}^{-1} \) | Error / \( 10^{-11} \text{m}^2 \text{s}^{-1} \) | Error / \( \% \) | \( n_t \) / Å | \( V_t \) / Å\(^3\) | \( V_{H,rel}^{[a]} \) |
|-------|-------------------|------------------|-----------------|-----------------|----------------|----------------|------------------|
| 1     | -                 | -                | -               | -               | 3.40           | 164            | 1                |
| 2     | -48.4             | 1.63             | 1.05            | 6.4             | 9.56           | 3658           | 22               |
| 3     | -52.5             | 0.52             | 0.36            | 6.9             | 30.1           | 113701         | 690              |
| 4     | -53.3             | 0.41             | 0.25            | 6.1             | 38.1           | 230819         | 1402             |
| 5     | -53.9             | 0.35             | 0.23            | 6.5             | 44.3           | 363788         | 2209             |

\(^{[a]}\) Hydrodynamic volume relative to \( V_{calc} \) (PhPH\(_2\)·BH\(_3\)), \(^{[b]}\) Determined by calculation with COSMO.

3.11.3 Separation with preparative GPC

With the help of preparative GPC, the reaction mixture of the thermal dehydropolymerization reaction after 24 h was separated into three fractions (see Figure S23). According to this, a fraction with high molecular weight (fraction 1, \( M_n = 14.010 \text{ kDa} \)), low molecular weight (fraction 2, \( M_n = 2.420 \text{ kDa} \)) and very low molecular weight (fraction 3, \( M_n = 0.560 \text{ kDa} \)) was obtained. The comparison of the recorded \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra of fractions 1, 2 and 3 (Figure S25, Figure S27 and Figure S29) is in line with the results from the DOSY NMR experiments. With decreasing molecular weight (known from GPC analysis), \(^{31}\text{P}\{^1\text{H}\}\) NMR peak(s) in the blue region are decreasing whereas peak(s) in the green region are increasing. The main product of fraction 3 shows a singlet in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum, whereas the \(^{31}\text{P}\) NMR displays a triplet. The absence of a large end group peak suggests that the product may consist mainly of cyclic oligomers. Peaks in the red region are visible in all three fractions. According to the \(^{31}\text{P}\{^1\text{H}\}\) and \(^{31}\text{P}\) NMR spectra, no proton is directly bound to the phosphorus. Therefore, we suggest the assignment as a PhPX\(_3\) species, belonging to branched oligomers. This is in line with calculated \(^{31}\text{P}\) chemical NMR shifts (see below “Calculations of \(^{31}\text{P}\) NMR chemical shifts”)

S20
Figure S23: Comparison of the GPC chromatogram (unknown concentration in THF with 0.1 wt% [1\textsuperscript{4}Bu\textsubscript{4}N]Br in the THF eluent) of the precipitated product obtained after the thermal dehydropolymerization reaction (24 h reaction time) and the fractions isolated by preparative GPC.

**Fraction 1:**

GPC (relative to polystyrene): $M_n = 14.010$ kDa, $M_W = 21.580$ kDa, PDI = 1.54.

$^{11}$B NMR (116 MHz, 298 K, o-DCB/toluene-$d_8$): $\delta = -35.4$ (m, br), $-38.4$ (shoulder, br) ppm.

$^{11}$B\textsuperscript{1}H NMR (116 MHz, 298 K, o-DCB/toluene-$d_8$): $\delta = -35.2$ (m, br) ppm.

$^{31}$P NMR (203 MHz, 298 K, o-DCB/toluene-$d_8$): $\delta = -49.0$ (d, $^1$J\textsubscript{PH} = 305 Hz), $-53.6$ (t, $^1$J\textsubscript{PH} = 404 Hz), $-79.8$ (s, br), $-83.4$ (s, br) ppm.

$^{31}$P\textsuperscript{1}H NMR (203 MHz, 298 K, o-DCB/toluene-$d_8$): $\delta = -45.1$ (s, br), $-48.8$ (s, br), $-52.0$ (s, br), $-53.5$ (s, br), $-79.1$ (s, br), $-82.6$ (s, br) ppm.

Figure S24: $^{11}$B (left) and $^{11}$B\textsuperscript{1}H (right) NMR spectrum (116 MHz, 298 K, o-DCB/toluene-$d_8$) of fraction 1.
Fraction 2:

GPC (relative to polystyrene): $M_n = 2.420$ kDa, $M_W = 7.460$ kDa, PDI = 2.90.

$^{11}$B NMR (116 MHz, 298 K, o-DCB/toluene-d$_8$): $\delta = -36.0$ (m, br) ppm.

$^{11}$B{$_1^1$H} NMR (116 MHz, 298 K, o-DCB/toluene-d$_8$): $\delta = -35.1$ (m, br), $-38.1$ (shoulder, br) ppm.

$^{31}$P NMR (203 MHz, 298 K, o-DCB/toluene-d$_8$): $\delta = -47.6$ (s, br), $-53.6$ (t, $J_{PH} = 404$ Hz), $-78.1$ (s, br), $-82.9$ (s, br) ppm.

$^{31}$P{$_1^1$H} NMR (203 MHz, 298 K, o-DCB/toluene-d$_8$): $\delta = -48.6$ (t, $J_{PX} = 608$ Hz), $-53.5$ (s, br), $-79.4$ (s, br), $-83.0$ (s, br) ppm.
Fraction 3:

GPC (relative to polystyrene): $M_n = 0.560$ kDa, $M_W = 0.750$ kDa, PDI = 1.08.

$^{11}$B NMR (116 MHz, 298 K, o-DCB/toluene-d$_8$): $\delta = -35.1$ (m, br), $-38.9$ (m, br) ppm.

$^{11}$B{H} NMR (116 MHz, 298 K, o-DCB/toluene-d$_8$): $\delta = -35.2$ (m, br), $-38.1$ (t, $J_{BP} = 70$ Hz), $-40.0$ (d, $J_{BP} = 45$ Hz) ppm.

$^{31}$P NMR (203 MHz, 298 K, o-DCB/toluene-d$_8$): $\delta = -52.7$ (s, br), $-78.8$ (s, br) ppm.

$^{31}$P{H} NMR (203 MHz, 298 K, o-DCB/toluene-d$_8$): $\delta = -52.4$ (t, $J_{PH} = 342$ Hz), $-79.3$ (s, br) ppm.

Figure S28: $^{11}$B (left) and $^{11}$B{H} (right) NMR spectrum (116 MHz, 298 K, o-DCB/toluene-d$_8$) of fraction 3.

Figure S29: $^{31}$P (left) and $^{31}$P{H} (right) NMR spectrum (203 MHz, 298 K, o-DCB/toluene-d$_8$) of fraction 3.
3.12 Substoichiometric reactions

3.12.1 [Li(thf)$_4$][EtCxCxAI(thf)$_2$] + PhPH$_2$BH$_3$

Procedure. In a nitrogen filled glove box, [Li(thf)$_4$][EtCxCxAI(thf)$_2$] (10 mg, 9.97 µmol, 1.0 eq) and PhPH$_2$BH$_3$ (0.8 mg, 6.00 µmol, 0.6 eq) were combined in a J. Young NMR tube. Deuterated tetrahydrofuran (THF-$d_8$) was added as solvent (0.5 mL). The sample was incubated for 1 h at 60 °C in an NMR tube heating block without stirring. The color of the reaction mixture changed to yellow. The sample was analyzed by NMR spectroscopy.

![NMR spectrum of the reaction mixture](image)

**Figure S30:** $^1$H NMR spectrum (600.2 MHz, THF-$d_8$, 295 K) of the mixture obtained by reacting [Li(thf)$_4$][EtCxCxAI(thf)$_2$] with a substoichiometric amount of PhPH$_2$BH$_3$. Relative amounts: H-EtCxCxAI : [EtCxCxAI]$^-$ : PhPH$_2$ : PhPH(BH$_3$)$_2$ 1 : 2.5 : 0.9 : 1.1. PhPH(BH$_3$)$_2$ was identified based on the literature.\(^{12}\)
3.12.2 [Li(thf)]_2[EiC_xAl(thf)]_2 + HNTf

Procedure. In a nitrogen filled glove box, [Li(thf)]_2[EiC_xAl(thf)]_2 (10 mg, 9.97 μmol, 1.0 eq) and bis(trifluoromethane)sulfonimide (2.5 mg, 8.97 μmol, 0.9 eq) were combined in a J. Young NMR tube. Deuterated tetrahydrofuran (THF-d_8) was added as solvent (0.5 mL). The color of the obtained solution was yellow. The sample was analyzed by NMR spectroscopy.

\[ \text{[Li(thf)]}_2[EiC_xAl(thf)]_2 + \text{HNTf} \]

\[
\begin{align*}
\text{H NMR} & \quad (600.2 \text{ MHz, THF-d}_8, 295 \text{ K}), \delta_{\text{H}} [\text{ppm}] = \ \begin{cases} 
7.84 & (d, \ J_{\text{HH}} = 5.4 \text{ Hz}, 1\text{H}, \text{H-2}), \\
6.07 & (d, \ J_{\text{HH}} = 3.2 \text{ Hz}, 1\text{H}, \beta-\text{H}), \\
5.97 & (d, \ J_{\text{HH}} = 3.2 \text{ Hz}, 1\text{H}, \beta-\text{H}), \\
5.95 & (d, \ J_{\text{HH}} = 3.3 \text{ Hz}, 1\text{H}, \beta-\text{H}), \\
5.94 & (d, \ J_{\text{HH}} = 3.3 \text{ Hz}, 1\text{H}, \beta-\text{H}), \\
5.894 & (d, \ J_{\text{HH}} = 3.2 \text{ Hz}, 1\text{H}, \beta-\text{H}), \\
5.890 & (d, \ J_{\text{HH}} = 3.2 \text{ Hz}, 1\text{H}, \beta-\text{H}), \\
5.94 & (s, 1\text{H}, \text{H-1}), \\
2.32 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.986 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.971 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.908 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.830 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.736 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.736 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.705 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.595 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.580 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.564 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.19 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.00 & (qd, 1\text{H}, \alpha-\text{methylene}), \\
1.05 & (t, \ J_{\text{HH}} = 7.5 \text{ Hz}, 3\text{H}, \alpha-\text{Me}), \\
0.88 & (t, \ J_{\text{HH}} = 7.5 \text{ Hz}, 3\text{H}, \alpha-\text{Me}), \\
0.85 & (t, \ J_{\text{HH}} = 7.4 \text{ Hz}, 3\text{H}, \alpha-\text{Me}), \\
0.71 & (t, \ J_{\text{HH}} = 7.3 \text{ Hz}, 3\text{H}, \alpha-\text{Me}), \\
0.68 & (t, \ J_{\text{HH}} = 7.3 \text{ Hz}, 3\text{H}, \alpha-\text{Me}), \\
0.61 & (t, \ J_{\text{HH}} = 7.2 \text{ Hz}, 3\text{H}, \alpha-\text{Me}), \\
0.60 & (t, \ J_{\text{HH}} = 7.4 \text{ Hz}, 3\text{H}, \alpha-\text{Me}), \\
0.58 & (t, \ J_{\text{HH}} = 7.4 \text{ Hz}, 3\text{H}, \alpha-\text{Me}). 
\end{cases}
\]

\[
\begin{align*}
\text{C[1]} \text{ NMR} & \quad (150.9 \text{ MHz, THF-d}_8, 295 \text{ K}), \delta_{\text{C}} [\text{ppm}] = \ \begin{cases} 
191.8 & (C_\alpha, C_4-\text{C}), \\
155.7 & (C_\text{H}, C-2), \\
145.6 & (C_\text{C}, C_\text{C}-\text{pyrrole}), \\
144.3 & (C_\text{C}, C_\text{C}-\text{pyrrole}), \\
143.6 & (C_\text{C}, C_\text{C}-\text{pyrrole}), \\
142.3 & (C_\text{C}, C_\text{C}-\text{pyrrole}), \\
139.3 & (C_\text{C}, C_\text{C}-\text{pyrrole}), \\
134.3 & (C_\text{C}, C_\text{C}-\text{pyrrole}), \\
129.8 & (C_\text{C}, C-3), \\
108.8 & (C_\text{H}, \beta-\text{C}), \\
108.6 & (C_\text{H}, \beta-\text{C}), \\
106.6 & (C_\text{H}, \beta-\text{C}), \\
106.2 & (C_\text{H}, \beta-\text{C}), \\
105.4 & (C_\text{H}, \beta-\text{C}), \\
85.2 & (C_\text{C}, C-1), \\
49.1 & (C_\text{C}, C_\alpha-\text{C}), \\
46.3 & (C_\text{C}, C_\alpha-\text{C}), \\
45.9 & (C_\text{C}, C_\alpha-\text{C}), \\
45.8 & (C_\text{C}, C_\alpha-\text{C}), \\
35.4 & (C_\text{H}, \alpha-\text{C}), \\
37.9 & (C_\text{H}, \alpha-\text{C}), \\
37.7 & (C_\text{H}, \alpha-\text{C}), \\
32.9 & (C_\text{H}, \alpha-\text{C}), \\
27.5 & (C_\text{H}, \alpha-\text{C}), \\
10.5 & (C_\text{H}, \alpha-\text{C}), \\
10.3 & (C_\text{H}, \alpha-\text{C}), \\
10.2 & (C_\text{H}, \alpha-\text{C}), \\
10.0 & (C_\text{H}, \alpha-\text{C}), \\
9.9 & (C_\text{H}, \alpha-\text{C}), \\
9.4 & (C_\text{H}, \alpha-\text{C}), \\
9.2 & (C_\text{H}, \alpha-\text{C}), \\
9.0 & (C_\text{H}, \alpha-\text{C}). 
\end{cases}
\]

S25
Figure S31: $^1$H NMR spectrum (600.2 MHz, THF-$d_8$, 295 K) of the solution obtained by reacting [Li(thf)$_4$][C$_x$Al(thf)$_2$] with a substoichiometric amount of HNTf$_2$. The signal at 5.76 arises from residual [C$_x$Al]$^-$ (relative amount: 0.16).

Figure S32: $^{13}$C($^1$H) NMR spectrum (150.9 MHz, THF-$d_8$, 295 K) of the solution obtained by reacting [Li(thf)$_4$][C$_x$Al(thf)$_2$] with a substoichiometric amount of HNTf$_2$. The signals at 143.3 and 104.2 ppm arise from residual [C$_x$Al]$^-$. It was not possible to assign the two signals at around 120 ppm.
The comparison of the spectrum shown in Figure S30 with that in Figure S31 shows congruence (see Figure S33). The observed patterns in the $^1$H and $^{13}$C($^1$H) NMR spectrum as well as in the two-dimensional $^1$H,$^1$H COSY NMR spectrum are characteristic for the calix[4]pyrrolato ligand with one dearomatized pyrrole ring due to protonation at that pyrrole ring’s 2-position.\textsuperscript{13}

Figure S33: Comparison of the $^1$H NMR spectra shown in Figure S30 and Figure S31. The red boxes mark the exact matching of the signals.
4 Computational Details and results

4.1 General remarks

All quantum chemical calculations were done with the ORCA 5.0.1 program package. Minimum and transition structure optimizations were carried out with the \( r^2 \text{SCAN-3c} \) composite method. The default structural convergence settings were used in all cases. The RIJCOSX approximation was applied. Auxiliary basis functions were generated by invoking the AutoAux keyword. The SCF convergence criteria were set with the VeryTightSCF keyword. The DefGrid2 was used for numerical integrations. All structures for mechanistic considerations were optimized without a solvation model.

For all obtained structures, the harmonic vibrational frequencies were computed. It was ensured that zero imaginary modes were present in the case of minimum structures and one in the case of transition structures. Transition structures were further characterized by visual inspection of the imaginary mode as well as by following the intrinsic reaction coordinate (IRC) along the imaginary mode in both directions. For both, the frequency and the IRC calculations, the same program settings were applied as for the structure optimizations.

Final electronic single point energies of all structures were calculated with the RI-DSD-PBEP86/2013 spin-component-scaled double hybrid functional, including the D3(BJ) correction. The def2-QZVPP set of basis functions was used. Again, the RIJCOSX combined with the AutoAux keywords were included. The VeryTightSCF convergence settings were kept, and the integration grid was changed to DefGrid3.

Enthalpies and Gibbs free energies were calculated with the electronic energies from the double hybrid functional calculations combined with the corrections to enthalpies and Gibb's free energies, respectively, from the frequency calculations obtained at \( T = 378.15 \text{ K} \) (105 °C, temperature at which the polymerization reactions were done) and \( p = 1 \text{ atm} \).

Finally, solvent influences were included implicitly at \( T = 378.15 \text{ K} \) with the conductor like screening model for real solvents (COSMO-RS) as it is implemented in the Amsterdam Modeling suite (ADF 2019.304). The ADF preset parameters were used, except for the maximum number of iterations, which were set to zero. COSMO-RS correction for enthalpies were achieved by calculating \( \Delta G \) corrections at five different temperatures (358.15, 368.15, 378.15, 388.15, 398.15 K) and with help of \( \Delta G = \Delta H - T \Delta S \).

Structures which were used to calculate NMR chemical shifts were optimized with the method described above, but with the inclusion of the SMD solvation model for 1,2-dichlorobenzene. Density functional theory using gauge including atomic orbitals (GIAO-DFT) calculations were done with the PBEO functional and the pcSseg-2 basis set. The RIJK approximation was applied in all parts of the calculations. Auxiliary basis functions were generated by the AutoAux keyword. The SCF convergence criteria were set with VeryTightSCF, DefGrid3 was applied, and the frozen core approximation was turned off (NoFrozenCore). In all calculations, the SMD solvation model for 1,2-dichlorobenzene was included. Initial conformational searching was done with the Conformers program of the Amsterdam Modeling Suite 2019.304.

Gas phase acidities were also calculated at the RI-DSD-PBEP86/2013-D3(BJ)/def2-QZVPP/r\(^2\)SCAN-3c computational level as described above, except for the thermochemical corrections, which were obtained at \( T = 298.15 \text{ K} \) and \( p = 1 \text{ atm} \).

Ball and stick representations were rendered with Chemcraft 1.837 or CYLview2038.

4.1.2 Calculations of 31P NMR chemical shifts

The NMR spectroscopic behavior of a linear and branched oligo(phosphinoborane) (2 and 3, Figure S34) was studied by density functional theory using gauge including atomic orbitals (GIAO-DFT). An initial set of conformers was generated (using carbon instead of boron) with the default setting of the Conformers program of the Amsterdam Modeling Suite. For 2, the number of possible structures was limited to 50, for 3 to 70. All obtained structures were optimized with the \( r^2 \text{SCAN-3c} \) composite method, implicitly including the solvent environment (1,2-dichlorobenzene) by means of the SMD solvation model. Boltzmann population weights were calculated with the relative (to the lowest-energy conformer) molecular Gibbs free energies (obtained with the thermal corrections from harmonic frequency calculations, \( r^2 \text{SCAN-3c} \)).
For structures with a contribution of greater than 1% (16 structures for 2, and 19 for 3), the absolute $^{31}$P isotropic chemical shieldings were calculated on the PBE0/pcSseg-2, SMD: 1,2-dichlorobenzen level of theory (see the Computational details section above for further specifics). The applied method was found to precisely reproduce the experimentally known $^{31}$P chemical shift of phenylphosphine borane (calc: -51.6, exp: -48.7, Figure S34) when using phenylphosphine (absolute chemical shielding: 443.410, experimental $^{31}$P chemical shift in 1,2-dichlorobenzene-h$_2$: -123.6 ppm) as reference for the conversion from the absolute shielding to the relative chemical shift scale. The obtained chemical shifts for the oligomers were Boltzmann-weighted (only considering the 16 and 19 structures, respectively). The results are given in Table S4.

Table S5, and in Figure S34.

The chemical shift of the phosphorus atom at the branching position is significantly upfield-shifted compared to the other positions.

![Chemical structures of phenylphosphine borane and the linear (2) and branched (3) oligo(phosphinoborane) which were investigated with GIAO-DFT calculations. The Boltzmann-weighted $^{31}$P chemical shifts are given for the individual positions in ppm. The structures in the bottom row represent the respective lowest-Gibbs free energy conformers (xyz coordinates are given in the “xyz Coordinates and Molecular Energies” section below).](image)

**Figure S34**

**Table S4**: Calculated Gibbs free energies and relative $^{31}$P chemical shifts of 2.

| Structure | Molecular Gibbs free energy [kJ mol$^{-1}$] | Relative weight | Relative $^{31}$P chemical shift [ppm], atom 1 | Relative $^{31}$P chemical shift [ppm], atom 2 | Relative $^{31}$P chemical shift [ppm], atom 3 |
|-----------|-------------------------------------------|----------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1         | -4724931.28                              | 0.2605         | -50.92                                        | -37.48                                        | -30.19                                        |
| 2         | -4724930.82                              | 0.2166         | -44.40                                        | -46.49                                        | -33.06                                        |
| 3         | -4724929.78                              | 0.1422         | -42.92                                        | -51.07                                        | -33.11                                        |
| 4         | -4724928.81                              | 0.0964         | -45.96                                        | -40.97                                        | -32.05                                        |
| 5         | -4724928.07                              | 0.0714         | -46.19                                        | -40.43                                        | -25.23                                        |
| 6         | -4724927.37                              | 0.0539         | -53.48                                        | -41.02                                        | -44.57                                        |
| 7         | -4724926.74                              | 0.0417         | -44.36                                        | -40.33                                        | -31.67                                        |
| 8         | -4724925.46                              | 0.0249         | -39.35                                        | -37.18                                        | -31.48                                        |
| 9         | -4724924.98                              | 0.0206         | -46.31                                        | -42.77                                        | -26.96                                        |
Table S5: Calculated Gibbs free energies and relative $^{31}$P chemical shifts of 3.

| Structure | Molecular Gibbs free energy [kJ mol$^{-1}$] | relative weight | relative $^{31}$P chemical shift [ppm], atom 1 | relative $^{31}$P chemical shift [ppm], atom 2 | relative $^{31}$P chemical shift [ppm], atom 3 | relative $^{31}$P chemical shift [ppm], atom 4 |
|-----------|------------------------------------------|----------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 10        | -4724924.31                              | 0.0157         | -46.76                                       | -41.31                                        | -34.82                                        |
| 11        | -4724924.18                              | 0.0149         | -48.13                                       | -40.39                                        | -33.03                                        |
| 12        | -4724923.68                              | 0.0121         | -49.81                                       | -37.10                                        | -31.25                                        |
| 13        | -4724923.06                              | 0.0095         | -41.38                                       | -44.03                                        | -41.56                                        |
| 14        | -4724922.49                              | 0.0075         | -43.27                                       | -38.31                                        | -32.51                                        |
| 15        | -4724922.17                              | 0.0066         | -47.67                                       | -36.86                                        | -45.15                                        |
| 16        | -4724921.75                              | 0.0056         | -41.21                                       | -38.37                                        | -31.64                                        |
4.1.3 Mechanistic considerations

At first, the reactivity of the isolated substrate (PhPH₂·BH₃, 1) with respect to H₂ elimination was studied. This was done restricted to monomolecular reactivity. Bimolecular reactions were not considered. It was found that the direct H₂ elimination pathway, as it is possible for example for H₃B·NH₃, is not available for phenylphosphine borane. Instead, a multistep reaction is required (Figure S35). Rate-limiting is the traversal of the first transition state (TS-1, $\Delta G^\ddagger = 181$ kJ mol⁻¹), which transforms the B-P bond to a weak H-B interaction (Int-1). This allows for the proton transfer from the phosphorus to the boron side of the molecule (TS-2), which is followed by H₂ ejection (TS-3).

**Figure S35:** Calculated monomolecular reaction pathway for the elimination of H₂ from phenylphosphine borane (1). The calculations were done on the RI-DSD-PBEP86/2013-D3(BJ)/def2-QZVPP///PSCAN-3c level of theory including the effects of the solvation environment (1,2-dichlorobenzene) with the COSMO-RS scheme. Thermochemical corrections to enthalpies and Gibbs free energies, respectively, were done at $T = 378.15$ K and $p = 1$ atm. The COSMO-RS corrections were done at 378.15 K.

The interaction of [Me₆CxAI]⁻ with phenylphosphine borane was studied. All shown minimum and transition structures are the Gibbs free energetically most favorable ones among a group of different configurations found for the individual points of the reaction pathway.

The shown pathway can be described as follows: initially, the substrate coordinates to the aluminum center (Int-4) followed by aluminum-ligand cooperativity-supported proton transfer from the phosphorus atom of the substrate to the 2-position of one pyrrole ring of the ligand backbone (TS-4). This is more favorable than the equivalent process without the inclusion of the aluminum center (TS-5). However, both pathways end up at Int-7 (Figure S36). For Int-6 also some other reactions were explored: i) cleavage of the boron-hydrogen bond ($\Delta G^\ddagger = 118$ kJ mol⁻¹) to give PhPH-BH₂ and H-Me₆CxAI-H, ii) attack of the P-centered lone pair in Int-6 at another PhPH₂-BH₃ ($\Delta G^\ddagger = 127$ kJ mol⁻¹) to give phenylphosphine and PhBH(BH₃)₂ coordinated to H-Me₆CxAI. They come both with a higher activation barrier compared to the Al-H → Al-P bond metathesis (TS-6, $\Delta G^\ddagger = 68$ kJ mol⁻¹).

H₂ elimination (Figure S37) might proceed by the back transfer of the proton from the ligand to one of the hydrogens attached to the boron atom (TS-7), followed by H₂ release (TS-8) to give Int-9. Comparison of this pathway to the process given in Figure S35 shows a barrier lowering ($\Delta \Delta G^\ddagger = 14$ kJ mol⁻¹) for the elimination of H₂. Moreover, [Me₆CxAI]⁻ stabilizes the dehydrogenated product PhPH-BH₂ by aluminum-ligand cooperative binding ($\Delta \Delta G_R = 63$ kJ mol⁻¹).
Figure S36: Calculated reaction pathway for the initial interaction of $\text{[M}_2\text{C}_x\text{Al}]^{-}$ with phenylphosphine borane (left part: non-AILC proton transfer, right part: AILC-supported proton transfer). The calculations were done on the RI-DSD-PBEP86/2013-D3(BJ)/def2-QZVPP//r$^2$SCAN-3c level of theory including the effects of the solvation environment (1,2-dichlorobenzene) with the COSMO-RS scheme. Thermochemical corrections to enthalpies and Gibbs free energies, respectively, were done at $T = 378.15 \, K$ and $p = 1 \, \text{atm}$. The COSMO-RS corrections were done at 378.15 K.
Figure S37: Calculated reaction pathway for the elimination of H$_2$ from Int-7 (see Figure S36). The calculations were done on the RI-DSD-PBE86/2013-D3(BJ)/def2-QZVPP//r$^2$SCAN-3c level of theory including the effects of the solvation environment (1,2-dichlorobenzene) with the COSMO-RS scheme. Thermochemical corrections to enthalpies and Gibbs free energies, respectively, were done at T = 378.15 K and p = 1 atm. The COSMO-RS corrections were done at 378.15 K.

4.1.4 xyz Coordinates and Molecular Energies

The "Total correction" and the "Entropy term" were obtained on the r$^2$SCAN-3c (T = 378.15 K, p = 1 atm), the "Final single point energy" at the RI-DSD-PBE86/2013-D3(BJ)/def2-QZVPP level of theory without a solvation model. These values were combined with the COSMO-RS corrections to calculate the above stated enthalpies and Gibbs free energies.

PhPH$_2$BH$_3$, 1

|                          | Total correction (378.15 K) | Total correction (298.15 K) | Entropy term (378.15 K) | Final single point energy | COSMO-RS correction (Gibbs free energy) | COSMO-RS correction (Enthalpy) |
|--------------------------|-----------------------------|-----------------------------|-------------------------|----------------------------|----------------------------------------|-------------------------------|
|                          | 401.6446 kJ/mol             | 389.1489 kJ/mol             | 155.8598 kJ/mol         | -1575835.2274 kJ/mol       | -26.7020 kJ/mol                       | -37.9031 kJ/mol               |

xyz, charge: 0, multiplicity: 1

P  -1.974801  -0.670103  0.944409
C  -2.660710  0.760696  0.047358
C  -1.988358  1.337757  -1.034587
C  -3.887634  1.279410  -0.463574
C  -2.543065  2.427070  -1.694201
C  -3.768428  2.944121  -1.277831
C  -4.437940  2.371430  -0.202118
H  -4.405360  0.827695  1.304975
H  -3.392633  2.773655  0.122925
H  -2.019367  2.873688  -2.534163
PhPHBH$_2$, 4

Total correction (378.15 K): 349.3732 kJ/mol  
Entropy term (378.15 K): 151.3426 kJ/mol  
Final single point energy: -1572652.2313 kJ/mol  
COSMO-RS correction (Gibbs free energy): -16.9050 kJ/mol  
COSMO-RS correction (Enthalpy): -25.1467 kJ/mol

xyz, charge: 0, multiplicity: 1
P  -1.887714  -0.462318   1.163475
C  -2.666444   0.828735   0.145815
C  -2.121023   1.190805  -1.087516
C  -3.792717   1.505906   0.626111
C  -2.705079   2.216111  -1.834329
C  -3.833875   2.876872  -1.360366
C  -4.374785   2.516793  -0.128499
H  -4.217917   1.238866  1.590177
H  -5.253262   3.030254   0.251594
H  -2.275171   2.490033  -2.793534
H  -1.242998   0.685535  -1.471837
H  -4.288055   3.670835  -1.945481
H  -0.922430  -1.044089   0.321948
B  -3.021852  -1.751661  1.796421
H  -4.149600  -1.462300  2.082083
H  -2.564768  -2.810427  2.08714

H$_2$

Total correction (378.15 K): 34.7573 kJ/mol  
Entropy term (378.15 K): 51.8629 kJ/mol  
Final single point energy: -3071.6571 kJ/mol  
COSMO-RS correction (Gibbs free energy): 5.6061 kJ/mol  
COSMO-RS correction (Enthalpy): -0.9656 kJ/mol

xyz, charge: 0, multiplicity: 1
H  0.000000  0.000000  0.000745
H  0.000000  0.000000  0.742255

TS-1

Total correction (378.15 K): 395.643 kJ/mol  
Entropy term (378.15 K): 158.8173 kJ/mol  
Final single point energy: -1575645.4495 kJ/mol  
COSMO-RS correction (Gibbs free energy): -26.2733 kJ/mol  
COSMO-RS correction (Enthalpy): -37.7928 kJ/mol

xyz, charge: 0, multiplicity: 1
P  -1.293356  -0.458993   1.583137
C  -1.841434   1.163825   1.031383
C  -2.034149   1.413638  -0.329000
C  -2.023903   2.181520   1.988812
TS-2

Total correction (378.15 K): 394.5305 kJ/mol
Entropy term (378.15 K): 155.5273 kJ/mol
Final single point energy: -1575677.7611 kJ/mol
COSMO-RS correction (Gibbs free energy): -19.5347 kJ/mol
COSMO-RS correction (Enthalpy): -28.5077 kJ/mol

xyz, charge: 0, multiplicity: 1

P 0.545809 0.709245 0.411873
H -0.423674 1.576473 0.968708
H -0.043859 -0.698511 -0.514603
H -1.868636 -0.654845 0.547163
H -0.871549 -1.295149 -1.049269
H -1.563563 0.530429 -1.191540
B -1.233710 -0.290632 -0.390152
C 0.880740 -0.280736 1.925713
C 0.042037 -0.274711 3.045781
C 2.048715 -1.050603 1.958896
C 0.367759 -1.020316 4.172481
C 2.364149 -1.810311 3.081298
C 1.526569 -1.793071 4.191575
H -0.874517 0.309026 3.032190
H 2.721304 -1.048315 1.103850
H -0.288583 -1.002448 5.037891
H 3.271782 -2.406842 3.091467
H 1.776416 -2.377815 5.072083

TS-3

Total correction (378.15 K): 391.6104 kJ/mol
Entropy term (378.15 K): 161.8969 kJ/mol
Final single point energy: -1575706.7159 kJ/mol
COSMO-RS correction (Gibbs free energy): -22.3854 kJ/mol
COSMO-RS correction (Enthalpy): -31.9243 kJ/mol

xyz, charge: 0, multiplicity: 1

P 0.735217 -0.035176 -0.032425
H 1.255146 -0.105691 1.282084
H -1.798139 -1.312947 -0.380940
H -1.505295 -0.573875 1.411746
H -1.943637 -0.726833 -0.853371
H -1.812219 0.962629 0.094751
B -1.133132 0.046527 0.457855
C 1.120221 1.724728 -0.392188
C 2.118937 2.413008 0.317890
### Int-2

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| P    | 0.502934 | 0.742172 | 0.444547 |
| H    | -0.321055 | 1.723362 | 1.055784 |
| H    | -0.347969 | -1.304222 | -0.795440 |
| H    | -1.789200 | -0.871663 | 0.439849 |
| H    | -0.801192 | -0.966605 | -1.402025 |
| H    | -1.614924 | 0.406758 | -1.121140 |
| B    | -1.058112 | -0.237937 | -0.264464 |
| C    | 0.873707 | -0.240628 | 1.966657 |
| C    | 0.049694 | -0.243040 | 3.098043 |
| C    | 2.034095 | -1.021386 | 1.982693 |
| C    | 0.378484 | -1.006255 | 4.212654 |
| C    | 2.354677 | -1.799186 | 3.092576 |
| C    | 1.529611 | -1.790775 | 4.211956 |
| H    | -0.859469 | 0.352841 | 3.109314 |
| H    | 2.699758 | -1.011129 | 1.122259 |
| H    | -0.268957 | -0.991522 | 5.085171 |
| H    | 3.258976 | -2.401380 | 3.086227 |
| H    | 1.783345 | -2.388345 | 5.082809 |

**Total correction (378.15 K):** 399.0853 kJ/mol  
**Entropy term (378.15 K):** 159.2099 kJ/mol  
**Final single point energy:** -1575709.9209 kJ/mol  
**COSMO-RS correction (Gibbs free energy):** -23.6226 kJ/mol  
**COSMO-RS correction (Enthalpy):** -33.9055 kJ/mol

### Int-1

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| P    | 0.777940 | 0.780759 | 0.437683 |
| H    | -0.351414 | 1.513835 | 0.869609 |
| H    | 0.039745 | -0.181804 | -0.397472 |
| H    | -1.870732 | -0.657588 | 0.625221 |
| H    | -1.099565 | -1.406099 | -1.130507 |
| H    | -1.856740 | 0.510474 | -1.080216 |
| B    | -1.495749 | -0.467910 | -0.492731 |
| C    | 1.001735 | -0.256126 | 1.932231 |
| C    | 0.095194 | -0.256126 | 2.998979 |
| C    | 2.162558 | -1.033115 | 2.017748 |
| C    | 0.345363 | -1.038818 | 4.124790 |
| C    | 2.401406 | -1.820816 | 3.138732 |
| C    | 1.495319 | -1.820816 | 4.194521 |
| H    | -0.813132 | 0.329224 | 2.943263 |

**Total correction (378.15 K):** 398.3148 kJ/mol  
**Entropy term (378.15 K):** 161.5791 kJ/mol  
**Final single point energy:** -1575718.5262 kJ/mol  
**COSMO-RS correction (Gibbs free energy):** -20.9382 kJ/mol  
**COSMO-RS correction (Enthalpy):** -29.7432 kJ/mol
xyz, charge: -1, multiplicity: 1
N  1.427422  -1.982759  2.117751
C  2.798749  -1.233830  4.084683
C  3.180162  -1.762475  5.470566
H  3.824845  -2.642340  5.376131
H  2.287679  -2.040007  6.039634
H  3.730478  -0.998656  6.029612
C  4.108530  -0.867254  3.337337
H  4.743982  -1.753467  3.225481
H  4.653585  -0.086616  3.880855
H  3.896689  -0.483915  2.321040
N  1.282651  0.518724  3.114459
C  0.671072  1.693433  3.516655
C  1.940598  -0.000265  4.216005
C  0.933735  1.911298  4.852304
H  0.577543  2.738389  5.450215
C  1.753518  0.835884  5.296090
H  2.157638  0.702387  6.290318
C  -0.226584  2.452499  2.571210
C  -1.561693  1.679283  2.405340
H  -2.055169  1.558283  3.376774
H  -1.391854  0.677381  1.993484
H  -2.227191  2.211570  1.715598
C  -0.552181  3.834659  3.144965
H  -1.224069  4.375542  2.470472
H  0.359900  4.424170  3.279297
H  -1.053221  3.735648  4.113365
N  1.030114  1.500181  0.615322
C  1.448694  1.905908  -0.640221
C  0.435626  2.592482  1.223023
C  1.128840  3.234573  -0.821674
H  1.341418  3.833565  -1.696691
C  0.472260  3.669911  0.363673
H  0.072200  4.656730  0.552700
H  2.238094  0.971322  -1.522947
H  2.339163  1.542318  -2.940309
H  2.839297  2.518901  -2.920597
H  1.345726  1.660312  -3.383664
H  2.931210  0.876047  -3.576236
C  3.678603  0.835148  -0.961595
H  4.265974  0.148273  -1.582174
H  3.670830  0.435017  0.059260
H  4.168873  1.815182  -0.928700
N  1.179973  -1.000966  -0.381744
C  0.725614  -2.265709  -0.713928
C  1.587207  -0.389173  -1.554617
C  0.838392  -2.448513  -2.075768
H  0.549778  -3.330037  -2.631865
xyz, charge: -1, multiplicity: 1
N 0.458886 -2.412664 1.078569
C -0.139481 -3.305664 1.957809
C 0.522262 -3.047507 -0.147439
C -0.492903 -4.456304 1.273602
H -0.935932 -5.344169 1.705509
C -0.057727 -4.299381 -0.066275
H -0.151662 -5.017988 -0.869969
N 0.961453 -0.863852 3.233745
C 1.454591 0.067978 4.128309
C 0.261701 -1.804996 3.980802
C 1.047906 -0.245502 5.408804
C 0.278176 -1.433620 5.310577
H -0.155121 -1.984561 6.135224
N 0.956448 1.403980 1.604258
C 0.610262 2.446928 0.748836
C 1.785437 1.954224 2.571772
C 1.216024 3.612044 1.170184
H 1.118383 4.588283 0.716592
C 1.968795 3.297144 2.327571
H 2.571861 3.979144 2.910815
N 0.279876 -0.139956 -0.523787
C 0.441015 -1.052649 -1.550895
C -0.238083 1.015407 -1.096047
C -0.014818 0.514392 -2.739570
H -0.000649 -0.900478 -3.710258
C -0.454962 0.800898 -2.445412
H -0.835048 1.521521 -3.158822
N 0.021856 -3.447848 -2.837349
C 1.063554 -3.249342 -2.568484
C 2.645725 -2.083356 -1.029409
C 1.149558 -2.358411 -1.323376
H 3.176048 -3.024856 -0.843518
H 1.571319 -4.196950 -2.386832
H 2.764836 -1.450333 -0.144226

Int-4

Total correction (378.15 K): 1951.2546 kJ/mol
Entropy term (378.15 K): 405.1039 kJ/mol
Final single point energy: -5634807.4141 kJ/mol
COSMO-RS correction (Gibbs free energy): -204.6021 kJ/mol
COSMO-RS correction (Enthalpy): -219.8215 kJ/mol
xyz, charge: -1, multiplicity: 1

N 1.191602 -1.859257 1.570007
C 2.015358 -1.788352 3.937931
C 1.959321 -2.656346 5.197051

Int-5

Total correction (378.15 K): 1950.5573 kJ/mol
Entropy term (378.15 K): 411.0876 kJ/mol
Final single point energy: -5634793.8576 kJ/mol
COSMO-RS correction (Gibbs free energy): -187.5704 kJ/mol
COSMO-RS correction (Enthalpy): -203.5728 kJ/mol
xyz, charge: -1, multiplicity: 1
N   0.784745  -2.181066   0.366515
C   0.145645  -3.285138   0.940470
C   1.361787  -2.639661  -0.810848
C   0.303047  -4.383836   0.122500
H   -0.078373  -5.379419  -0.301094
C   1.082265  -3.976953  -0.985103
H   1.398695  -4.598175  -1.810697
N   -0.282773  -0.877850   2.467743
C   -0.076647  -0.259285   3.595996
C   -1.154495  -2.016043   2.716607
C   -0.850802  -0.849102   4.673787
H   -1.519342  -1.891943   4.150214
H   -2.210581  -2.546837   4.664612
N   0.401313   1.464198   1.287626
C   0.197449   2.615721   0.541964
C   0.569110   1.867341   2.597620
C   0.223212   3.715659   1.381147
H   0.094377   4.748554   1.091121
C   0.464658   3.240002   2.692099
H   0.565878   3.838118   3.567582
N   0.912406   0.263487  -1.090052
C   1.658585  -0.459101  -2.001176
C   0.706969   1.519731  -1.642892
C   1.903030   0.311360  -3.119046
H   2.474395   0.021897  -3.990098
C   1.292902   1.569673  -2.892227
H   1.296263   2.412589  -3.569059
H   1.869529   2.747160  -3.531855
C   2.726479  -2.524863   2.888491
C   3.555440  -1.486414  -0.777315
C   2.283393  -1.775260  -1.626169
H   4.029079  -2.428236  -0.467042
H   3.223393  -3.463144  -2.620170
H   3.299797  -0.921181   0.122552
H   -2.227458  -4.372206   1.772282
C  -1.406281  -4.488267  2.486877
C   0.772181  -3.566069  3.322511
C  -0.400151  -3.337682  2.347043
H   1.478922   -2.731218  3.287513
H  -0.916743  -5.447269  2.979677
H   1.310961  -4.468333  3.018138
H   2.413429  -0.192110  2.512530
C   2.322043   0.300181  3.485898
C   0.836954   1.547015  5.064585
C   0.899253   0.881921  3.686427
H   1.101051   0.830981  5.850509
H   2.561908  -0.434906  4.264258
H  -0.161969  -3.566069  -1.94020
C  -1.589152   2.452467  -2.18405
C   0.343512   3.973676  -1.529825
H   1.779236   2.512880  -2.296372
H   1.622911  -0.400151  3.604864
H  -1.960334  -1.487347  -0.875338
H   1.407662   4.165793  -1.363903
H  -2.149403   3.245805  -0.709740
H  -0.239757   4.777247  -1.069525
H   4.267514  -0.892824  -1.360111
H   3.439324  -1.919177  -3.45837
H   0.424102  -3.688886  4.355666
H  -1.816144  -4.526439  3.501778
H   1.552804   2.372522  5.107962
H   3.049562   1.117124  3.525229
H  -0.892864  -0.480636  5.689061
Al  0.201772  -0.343428  0.577081
C  -2.930428   1.832425  3.697105
C  -3.032785   1.352187  2.394658
C  -3.644645   1.227335  4.729588
C  -4.451613   0.128833  4.490868
C  -4.562987  -0.341069  3.141758
C  -3.866849   0.266868  2.880017
H  -2.275858   2.680440  3.891633
H   3.588011   1.606967  5.745889
H  -5.010192  -0.356319  5.246625
H  -5.223852  -1.177421  2.921984
H  -2.454419   1.836620  1.609278
P  -4.137377  -0.318794  0.344229
B  -2.372108  -0.990728  -0.269836
H  -2.035913  -1.956064  2.062545
H  -4.087435   0.983333  -0.224451
H  -2.279022  -0.828872  -1.461430
H  -1.533600  -0.222948  0.306342
H  -2.188102  -2.136120  0.062235

TS-4

Total correction (378.15 K): 1941.1285 kJ/mol
Entropy term (378.15 K): 400.3276 kJ/mol
Final single point energy: -5634731.0824 kJ/mol
COSMO-RS correction (Gibbs free energy): -202.2249 kJ/mol
COSMO-RS correction (Enthalpy): -217.9500 kJ/mol

xyz, charge: -1, multiplicity: 1
N   0.246344  -2.363753  1.286009
C   0.019735  -3.095053  2.207745
C  -0.020053  -2.950023  0.012275
C  -0.326869  -4.539489  1.589304
C  -6.643441 -3.788613 -0.28166  
C  -6.412362 -2.692152 -1.10859  
C  -5.236332 -1.958864 -0.99397  
C  -4.263988 -2.308376 -0.045836  
H  -5.849254 -5.001749  1.311194  
H  -7.564045 -4.358823 -0.831363  
H  -7.156503 -2.399850  1.845849  
H  -5.071182 -1.100520 -1.639518  
H  -3.755128 -3.711283  1.510299  
P  -2.678186  5.001749  1.311194  
P  -2.500611  0.786953  1.933512  
H  -1.240392 -2.481898 -0.19431  
H  -2.863870 -0.371311 -0.631363  
H  -2.573314 -1.766180  2.627549  
H  -3.297187  0.077513  2.197979  
H  -1.363056 -0.269119  2.100650  

Int-3

Total correction (378.15 K):  1950.2866 kJ/mol  
Entropy term (378.15 K):  410.4 kJ/mol  
Final single point energy:  -5634841.1494 kJ/mol  
COSMO-RS correction (Gibbs free energy):  -197.2811 kJ/mol  
COSMO-RS correction (Enthalpy):  -213.9942 kJ/mol  

xyz, charge: -1, multiplicity: 1  
N  0.556202 -1.267177  1.463170  
C  1.267877 -1.332414  3.871098  
C  0.974824 -2.159069  5.126141  
H  1.353480 -3.179332  5.004607  
H  1.473410 -2.206845  5.325256  
H  2.802181 -1.318509  3.650901  
C  3.174241 -2.338957  3.503987  
C  3.306143 -0.862497  4.510763  
H  3.075445 -0.737938  2.761516  
N  0.749462  0.951624  2.972306  
C  0.301748  2.175890  3.40163  
C  0.772647  0.805957  4.048267  
C  0.490257  2.076878  4.791980  
H  1.372137  2.866220  5.433412  
C  0.353697  0.743840  5.181633  
C  0.278319  0.326365  6.176443  
C  0.059230  3.320805  2.485861  
H  1.252769  3.054630  1.701265  
H  2.106278  2.969668  2.383836  
H  1.194911  2.117631  1.133549  
H  1.438381  3.860340  0.982055  
C  0.112713  4.628819  3.263245  
H  0.312023  5.454724  2.573038  
H  0.788620  4.861206  3.838705  
H  0.961140  4.553469  3.950964  
N  1.680702  2.319203  0.850974  
C  2.633725  2.746069 -0.058067  
C  1.204421  3.439329  1.509814  
C  2.762724  4.115741  0.029975  
H  3.438552  4.736134 -0.54261  
C  1.843021  4.559231  1.022145  
H  1.670528  5.582163  1.327677  
C  3.431980  1.744869 -0.858579  
C  4.187652  2.453840 -1.986340  
H  4.867037  3.207181 -1.574483  

S44
xyz, charge: -1, multiplicity: 1
N 0.847025-1.7751692.005690
C 2.169368-1.3312974.038218
C 2.374118-1.8301745.474766
H 2.637878-2.8934805.482985
H 1.475953-1.6746676.082987

Int-7

Total correction (378.15 K): 1956.8753 kJ/mol
Entropy term (378.15 K): 400.5462 kJ/mol
Final single point energy: -563480.8389 kJ/mol
COSMO-RS correction (Gibbs free energy): -204.7180 kJ/mol
COSMO-RS correction (Enthalpy): -222.6116 kJ/mol
H  3.196130  -1.283906  5.944876
C  3.410561  -1.707484  3.206473
H  3.515563  -2.795871  3.105054
H  4.301417  -1.317551  3.709253
H  3.375038  -1.269938  2.204977
C  1.153731   0.759925  3.041878
C  0.984511   1.479033  4.036099
C  1.639553   2.292834  4.638579
C  1.674729   2.078973  5.193959
C  2.226279   1.061803  5.922783
N  1.153731   0.759925  3.041878
C  0.984511   2.078973  3.444075
C  1.907096   0.147903  4.036099
C  1.639553   2.292834  4.638579
H  1.674729   3.219092  5.193959
C  2.226279   1.061803  5.922783
H  2.788003   0.871514  5.227833
C  0.070441   3.029608  2.710786
C  -1.397610  2.601454  2.953540
H  -1.648254  2.729431  4.013522
H  -1.557284  1.549572  2.711263
H  -2.079101  3.202969  2.342022
C  0.219958   4.446019  3.287862
C  -0.474959  5.126609  2.786297
H  1.238345   4.822818  3.153337
H  -0.026623  4.447345  4.354541
N  0.934349   1.950503  0.595338
C  1.351981   2.368370  0.656827
C  0.443826   3.060476  1.246504
C  1.066590   3.710916  1.656493
H  1.286418   4.318732  1.684278
C  0.484736   4.150507  0.397979
H  0.160387  5.156103  0.627242
C  2.197450   1.470382  1.515927
H  2.327632   2.058436  2.924321
H  2.788812   3.049462  2.872262
H  1.348329   2.156785  3.403859
H  2.964151   1.420904  3.546886
C  3.618834   1.392438  0.896574
H  4.257338   0.726493  1.490473
H  3.572374   1.06475  0.126019
H  4.066904   2.392209  0.861189
N  1.408676   0.677141  0.438574
C  0.986752  -1.925943  0.891043
C  1.623342   0.882269  1.581838
H  0.923267  -1.932876  2.269557
H  0.653195  -2.772565  2.897063
H  1.332924  -0.655819  2.701053
C  1.411334  -0.321977  3.734781
C  0.838373  -3.170516  0.053550
C  -0.450462  -3.941979  0.426331
C  -0.460673  -4.137851  1.501182
C  -1.338545  -3.360927  0.164381
H  -0.500489  -4.904105  0.095480
C  2.067970  -4.085017  -0.323734
H  2.095684  -4.326302  -1.392990
H  2.025685  -5.020723  0.248822
H  2.992296  -3.556583  -0.073269
C  0.883071  -2.002287  3.451630
C  0.809815  -2.933500  1.418380
C  0.796663  -3.476288  3.605865
H  0.750402  -3.987494  4.558387
C  0.758699  -4.026937  2.368236
H  0.678432  -0.077012  2.139237
Al  0.724367   0.130142  1.226764
P  -1.671933  -0.331424  0.822997
C  -2.680333  1.107769  0.283638
C  -2.163748  2.048046  0.612980
xyz, charge: -1, multiplicity: 1

N  1.137999 -1.901050  1.553741
C  1.893365 -1.755332  3.944245
C  1.780996 -2.586300  5.225086
H  2.368774 -3.504982  5.132112
H  0.739930 -2.857462  5.426225
H  2.167170 -2.018366  6.077824
C  3.394953 -1.449815  3.704056
C  3.957578 -2.382820  3.585729
C  3.805186 -0.876315  4.543663
C  3.539077 -0.857190  2.79333
N  1.072619  0.443221  3.04136
C  0.315865  1.529358  3.51969
C  1.133671 -0.467411  4.090636
C  0.090387  1.271755  4.803034
H  0.703225  1.913849  5.419204
C  0.437203  0.011322  5.173831
C  0.259777  0.491906  6.119719
C  0.213479  2.854489  2.807551
C  0.984008  3.656229  3.27902
H  0.861847  3.863112  4.394875
H  1.927071  3.122593  3.185752
H  1.053931  4.619257  2.812759
C  1.508798  3.652767  3.098589
H  1.463349  4.647721  2.639640
H  2.384997  3.127074  2.705963
H  1.632738  3.759489  4.181489
N  1.126271  1.830205  0.731756
C  1.645861  2.445384  0.338383
C  0.098860  2.686010  1.275438
H  1.010517  3.684882  0.568398
H  1.219111  4.362314  1.384531
H  0.073940  3.475454  0.431649
H  0.598500  4.858998  0.558248
C  2.824203  1.830525  1.051468
C  3.228211  2.74813  2.262927
H  3.496900  3.68453  1.949555
H  2.414040  2.730661  2.91680

C  -3.958984  1.301646  0.815193
C  -2.916118  3.160806  -0.971467
C  -4.188393  3.351823  -0.438250
C  -4.707831  2.418649  0.450099
H  -4.355908  0.576158  1.519540
H  -5.698498  2.561989  0.879821
H  -2.487740  3.892148  -1.651452
H  -1.157693  1.933803  -1.010192
H  -4.769379  4.229557  -0.711186
H  -1.539498  -0.996298  -0.420413
H  0.007235  -1.514958  3.909392
B  -4.355908  0.576158  1.519540
H  -4.707831  2.418649  0.450099
H  -5.698498  2.561989  0.879821
H  -2.487740  3.892148  -1.651452
H  -1.157693  1.933803  -1.010192
H  -4.769379  4.229557  -0.711186
H  -1.539498  -0.996298  -0.420413
H  0.007235  -1.514958  3.909392

TS-5

Total correction (378.15 K):  1939.2268 kJ/mol
Entropy term (378.15 K):  403.2601 kJ/mol
Final single point energy:  -5634708.3528 kJ/mol
COSMO-RS correction (Gibbs free energy):  -195.0158 kJ/mol
COSMO-RS correction (Enthalpy):  -212.0024 kJ/mol
TS-6

Total correction (378.15 K): 1951.7805 kJ/mol
Entropy term (378.15 K): 397.9239 kJ/mol
Final single point energy: -5634723.5716 kJ/mol
COSMO-RS correction (Gibbs free energy): -209.2931 kJ/mol
COSMO-RS correction (Enthalpy): -226.8951 kJ/mol

xyz, charge: -1, multiplicity: 1

N  0.274861  2.125627  0.201825
C -0.482280  3.004563  0.997280
C  0.050305  2.531759  1.056511
C -1.471994  3.904133  0.976583
H -1.048371  2.814300  3.931838
H  1.048322  2.059768  1.177361
H -2.747395  3.033326  0.178762
### PhPHBH<sup>-</sup>

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 4.393293 | -2.400994 | 0.287875 |
| C    | -3.884030 | -1.312150 | 1.014602 |
| H    | -5.812404 | -1.666879 | 3.805897 |
| H    | -6.704016 | -3.577709 | 2.489277 |
| H    | -5.785558 | -4.032443 | 0.220832 |
| H    | -3.957493 | -2.634400 | -0.681101 |
| H    | -4.043072 | -0.219577 | 2.859445 |
| P    | 2.461464  | -0.373107 | 0.335207 |
| B    | -2.004663 | 1.119639  | 1.530250 |
| H    | -1.580131 | -1.260650 | 2.870632 |
| H    | -3.056968 | 0.194968  | -0.813129 |
| H    | -2.089297 | 0.774491  | 2.690023 |
| H    | -0.787738 | 1.295849  | 1.312037 |
| H    | -2.576471 | 2.162305  | 1.311986 |

Total correction (378.15 K): 369.9335 kJ/mol
Total correction (298.15 K): 357.8131 kJ/mol
Entropy term (378.15 K): 153.9681 kJ/mol
Final single point energy: -1574398.0406 kJ/mol
COSMO-RS correction (Gibbs free energy): -194.4000 kJ/mol
COSMO-RS correction (Enthalpy): -215.1000 kJ/mol

### H<sub>3</sub>AlCx

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| N    | 1.191956 | -2.049026 | 2.181675 |
| C    | 2.740512 | -1.316531 | 4.018577 |
| C    | 3.140181 | -1.773819 | 5.425640 |
| H    | 3.644639 | -2.742806 | 5.377144 |
| H    | 2.261593 | -1.888624 | 6.070416 |
| H    | 3.836493 | -1.068855 | 5.877692 |
| C    | 4.033019 | -1.198805 | 3.164884 |
| H    | 4.545644 | -2.165485 | 3.122959 |

Total correction (378.15 K): 1574.278 kJ/mol
Total correction (298.15 K): 1527.476 kJ/mol
Entropy term (378.15 K): 327.8027 kJ/mol
Final single point energy: -4060218.283 kJ/mol
COSMO-RS correction (Gibbs free energy): -77.8336 kJ/mol
COSMO-RS correction (Enthalpy): -90.1950 kJ/mol

xyz, charge: 0, multiplicity: 1
H  4.704678  -0.444613  3.590480
H  3.801269  -0.907446  2.132783
N  1.372930   0.555048  3.001348
C  0.904215   1.802572  3.392806
C  2.072242   0.030676  4.085160
C  1.324347   2.071594  4.675741
H  1.099477   2.954178  5.257661
C  2.070054   0.946744  5.112131
H  2.541894   0.828796  6.076556
C  -0.151723  2.530487  2.598048
C  -1.817117  1.816151  3.810432
H  -1.455194  0.763692  2.470595
H  -2.294897  2.297230  2.146537
C  -0.297594  3.977497  3.082444
H  -1.081365  4.500236  2.524473
H  -0.588935  3.981940  4.135007
N  0.487888   1.349954  0.537320
C  0.750929  -1.643820  0.883785
C  0.217382  -2.481992  1.144062
C  0.622402  -3.117915  0.976416
H  0.743438  -3.676673  1.895682
C  0.291731  -3.607471  0.232206
H  0.108647  -4.638901  0.498115
C  2.084036  -0.995389  1.412330
C  2.361873  -1.514246  2.825954
H  2.645046  -2.571217  2.811774
H  1.494480  -1.382481  3.481420
H  3.195657   0.954717  3.291117
C  3.259661   3.676673  0.499008
H  3.184057   3.960130  0.906627
H  3.156169   3.993913  0.522617
H  3.369278  -2.480846  0.425955
N  1.244199  -1.078562  0.335186
C  0.914831  -2.378251  0.681949
C  1.816204  -0.480576  1.444612
C  1.290169  -2.598423  1.989967
H  1.159378  -3.514110  2.548965
H  1.863711  -1.390600  2.477765
H  2.250012  -1.221765  3.473304
C  0.103976  -3.234444  0.269472
C  -1.327289  -2.635659  0.380075
H  -1.806065  -2.605233  0.602944
H  -1.302663  -1.608427  0.768854
H  -1.929624  -3.230665  1.068747
C  -0.016932  -4.660341  0.271710
H  -0.515727  -4.657374  1.246019
H  -0.612594  -5.273804  0.411112
H  0.969577  -5.119887  0.382123
C  1.845588  -2.349417  3.568667
C  0.764419  -3.242159  1.624409
C  1.788488  -3.710096  3.573920
H  2.229436  -4.255080  4.396706
C  1.092320  -4.277420  2.468450
H  0.882875  -5.326330  2.312139
Al  1.064660  -0.370139  1.392549
H  -0.054189  1.179032  1.478175

TS-7

Total correction (378.15 K): 1941.2881 kJ/mol
Entropy term (378.15 K): 394.2045 kJ/mol
Final single point energy: -5634725.5722 kJ/mol
COSMO-RS correction (Gibbs free energy): -191.7749 kJ/mol
COSMO-RS correction (Enthalpy): -205.7384 kJ/mol

xyz, charge: -1, multiplicity: 1

N 1.093132 -1.644586 3.066896
C 2.517049 -0.525804 4.757975
C 2.759371 -0.577424 6.270919
H 3.073400 -1.582770 6.571946
H 1.855880 -0.303409 6.824608
H 3.557279 0.116924 6.548023
C 3.841661 -0.917354 4.046985
H 4.143631 -1.937010 4.317705
H 4.630643 -0.214484 4.335888
H 3.725495 -0.874552 2.959745
N 1.459742 1.112821 3.136163
C 1.343124 2.497493 3.054240
C 2.106841 0.856297 4.336129
C 1.909470 3.082532 4.167797
H 1.950253 4.139712 4.838743
C 2.401120 2.037183 4.983683
H 2.909500 2.143660 5.931291
C 0.527361 3.191407 1.994606
C -0.956500 3.114736 2.404012
H -1.118635 3.695692 3.320817
H -1.265163 2.087943 2.619627
H -1.611621 3.505643 1.609530
C 0.892619 4.686754 1.956025
H 0.260740 5.207433 1.230179
H 1.940648 4.828041 1.676373
H 0.716346 5.148521 2.932268
N 1.187085 1.285609 0.427505
C 1.458600 1.153619 0.922760
C 0.797790 2.602417 0.627816
H 1.218287 2.348520 -1.571804
H 1.364021 2.549701 -2.624344
C 0.796302 3.270225 -0.582972
H 0.543336 4.308891 -0.743989
C 2.081017 1.068255 -1.457385
C 2.130631 0.063938 -2.987233
H 2.736496 0.785057 -3.319781
N 1.127024 0.038236 -3.412509
H 2.585167 -0.981602 -3.375298
C 3.536690 -0.217338 -0.936287
H 4.003064 -1.138448 -1.306521
C 3.561725 -0.240241 0.157386
H 4.121756 0.648126 -1.268703
N 1.133826 1.566979 0.353385
C 0.417476 -2.759423 0.427658
C 1.293830 -1.300825 -0.995933
C 0.128476 -3.208512 -0.846710
H -0.395237 -4.120093 -1.102442
C 0.691826 -2.281879 -1.755565
H 0.665582 -2.398988 -2.834749
C 0.193363 -3.568337 1.683330
C -1.141996 -4.327989 1.618417
H -1.157309 -5.011048 0.764668
H -1.986416 -3.638734 1.526032
H -1.285387 -4.928851 2.523126
C 1.347327 -4.612735 1.747798
H 1.366342 -5.203303 0.825613
H 1.223012 -5.281151 2.680321
|   |                   |       |       |       |       |
|---|------------------|-------|-------|-------|-------|
| H | 2.306830         | -4.094337 | 1.844124 |
| C | 1.480054         | -1.536628 | 4.361163 |
| C | 0.276799         | -2.778851 | 2.975571 |
| C | 0.931281         | -2.571455 | 5.129904 |
| H | 1.052823         | -3.372797 | 4.253253 |
| C | -0.344587        | -4.274365 | 4.497887 |
| Al| 0.950103         | -0.147875 | 1.719699 |
| P | -1.547516        | -0.393842 | 1.600315 |
| C | -2.611966        | 0.836516  | 0.761098 |
| C | -3.843205        | 1.241208  | 1.281043 |
| C | -2.141323        | 1.408923  | -0.425555 |
| C | -4.596142        | 2.209319  | 0.622259 |
| C | -4.125877        | 2.777550  | -0.558699 |
| H | -2.899678        | 2.372560  | -1.079890 |
| H | -1.168952        | 1.127070  | -0.825664 |
| H | -2.510604        | 2.823122  | -1.988677 |
| H | -5.550576        | 2.522760  | 1.037428 |
| H | -4.207661        | 0.807543  | 2.07966 |
| H | -4.710335        | 3.540530  | -1.066677 |
| H | -1.663129        | -1.461996 | 0.683390 |
| B | -2.367085        | -0.993896 | 3.272808 |
| H | -3.181694        | -1.874306 | 3.198458 |
| H | -1.413651        | -1.310171 | 4.092339 |
| H | -2.704941        | -0.042728 | 3.936681 |
| H | -1.079015        | -1.975455 | 3.500921 |

**TS-8**

Total correction (378.15 K): 1938.2745 kJ/mol  
Entropy term (378.15 K): 411.256 kJ/mol  
Final single point energy: -563489.6537 kJ/mol  
COSMO-RS correction (Gibbs free energy): -192.3669 kJ/mol  
COSMO-RS correction (Enthalpy): -207.0540 kJ/mol

xyz, charge: -1, multiplicity: 1

N         1.280472   -1.790399   1.834747  
C         2.376403   -1.380240   4.032258  
C         2.533339   -2.063499   5.393195  
H         2.974646   -3.057652   5.263969  
H         1.565996   -2.170523   5.894313  
H         3.195066   -1.476415   6.038216  
C         3.784172   -1.246789   3.998995  
H         4.232727   -2.236847   3.252287  
H         4.430414   -0.645426   4.048756  
H         3.733199   -0.754257   2.422930  
N         1.341946   -0.716202   3.099778  
C         0.848665   1.914226   3.606635  
C         1.754856   -0.226006   4.193667  
C         0.942311   1.904774   4.987364  
H         0.632688   2.695116   5.657224  
C         1.525624   0.674866   5.360805  
C         1.753746   0.343833   6.364233  
C         0.259071   3.044478   2.796257  
C         -1.286754   3.037216   2.920614 
H         -1.581101   3.117889   3.973254  
H         -1.718150   2.113833   2.522451  
H         -1.725427   3.864729   2.350151  
C         0.734706   4.381749   3.419385  
H         0.298806   5.231074   2.885372  
H         1.824175   4.456079   3.366109  
H         0.428027   4.454712   4.467048
N  1.261307  1.965193  0.681943
C  1.586373  2.417457 -0.583832
C  0.684926  3.040397  1.346862
C  1.195503  3.732009 -0.736135
H  1.335059  4.347263 -1.614288
C  0.611641  3.146126 -0.299698
H  1.485439  2.755058 -3.25423
C  2.988229  1.586805 -3.609555
C  3.744096  1.238728 -1.009461
H  4.282612  0.576873 -1.698305
H  3.702634 -0.745528 -0.033336
H  4.303082  2.174429  0.889879
N  1.331387 -0.552887 -0.594160
C  0.628920 -1.663305 -1.057483
C  1.557709  0.248603 -1.695457
C  0.396211 -1.527113 -2.413717
H  -0.094845 -2.247231 -3.054881
C  0.995834 -0.311713 -2.823405
H  1.014080 -3.824052
C  0.493511 -2.954405 -0.286233
H  -0.783872 -3.700909 -0.705194
H  -0.764399 -3.919593 -1.777085
H  -1.681993 -3.109265 -0.499222
H  -0.865551 -4.653886 -0.173588
C  1.713337 -3.838659 -0.692959
C  1.726991 -3.985520 -1.778979
C  1.667849 -4.810465 -0.186943
H  2.640761 -3.337389 -0.398961
C  1.506388 -2.209478  3.133487
C  0.572022 -2.817211  1.214338
C  0.917141 -3.436207  3.357809
C  0.934194 -4.001547  4.279416
C  0.306768 -3.820278  2.134094
H  -0.185293 -4.762854  1.931633
Al  1.115832  0.92068  1.247928
P  -1.343775 -0.202610  1.356551
C  -2.533778  0.800827  0.384648
C  -2.017418  1.735274 -0.517580
C  -3.917673  0.652824  0.513561
C  -2.884817  2.511406 -1.281270
C  -4.261490  2.361830 -1.152333
C  -4.778073  1.429177 -0.254461
H  -4.322375 -0.06790  1.219857
H  -5.853203  1.308086 -0.150488
H  -2.470109  3.238478 -1.973496
H  -0.943021  1.866270 -0.625065
H  -4.935005  2.971763 -1.749022
H  -1.629278 -1.508797  0.908179
H  -1.669099 -2.520091  3.194771
B  -1.942377 -0.322329  3.209046
H  -2.363123 -2.281692  3.396729
H  -1.105477 -0.354819  4.051029
H  -3.097987 -0.169868  3.481104

Int-9

Total correction (378.15 K): 1901.4733 kJ/mol
Entropy term (378.15 K): 389.2675 kJ/mol
S54
Final single point energy:  
-5631759.9419 kJ/mol  
COSMO-RS correction (Gibbs free energy): -190.8025 kJ/mol  
COSMO-RS correction (Enthalpy): -205.8644 kJ/mol  

xyz, charge: -1, multiplicity: 1  
N 1.445638 -1.888637 1.807436  
C 2.439370 -1.148061 4.015145  
C 2.849361 -1.795387 5.342341  
H 3.722707 -2.435600 5.190173  
H 2.040117 -2.408267 5.751862  
H 3.122154 -1.027648 6.074582  
C 3.627276 -0.289399 3.505891  
H 4.499007 -0.935013 3.356992  
H 3.879897 0.500242 4.224998  
H 3.383849 0.184572 2.549894  
N 0.673894 0.330799 3.187113  
C -0.346354 1.263610 3.662874  
C 1.271602 -0.215621 4.211175  
C -0.245230 1.156693 5.128953  
H -0.881816 1.701059 5.815864  
C 0.712604 0.256421 3.106680  
C -1.047328 3.706455 3.543032  
H -1.215545 3.649707 4.623360  
H -1.998562 3.533822 3.036998  
H -0.705962 4.721011 3.314523  
C 1.369910 3.148259 3.703378  
H 1.645969 4.107734 3.254333  
H 2.166217 2.433705 3.477163  
H 1.306269 3.269906 4.791788  
N 0.880272 1.749181 0.870252  
C 1.006792 2.267688 -0.407847  
C 0.152844 2.695902 1.604010  
C 0.381034 3.494125 -0.489845  
C 0.304872 4.121168 -1.366918  
C -0.164633 3.761465 0.784986  
H -0.720566 4.644027 1.069454  
C 1.811552 1.561205 -1.465968  
C 1.745376 2.341045 -2.782299  
H 2.120863 3.359659 -2.638866  
H 0.716411 2.939367 -3.152985  
H 2.368804 1.853346 -3.540023  
C 3.294044 1.506396 -1.010587  
H 3.906594 1.018785 -1.778179  
H 3.388436 0.930971 -0.084868  
H 3.673461 2.519054 -0.826897  
N 1.105092 -0.684371 0.602664  
C 0.868516 -1.950133 -1.116800  
C 1.322217 0.153438 -1.677414  
C 0.896027 -1.892753 -2.498662  
H 0.757484 -2.720561 -3.180519  
C 1.190942 -0.552905 -2.856397  
H 1.323360 -0.167209 -3.857961  
C 0.664285 -3.175814 -0.252320  
C -0.841255 -3.420851 0.020166  
H -1.389968 -3.493652 -0.926550  
H -1.266268 -2.602442 0.599897  
H -0.973477 -4.347845 0.590852  
C 1.185192 -4.409389 -1.012268  
H 0.640525 -4.530629 -1.953209  
H 1.024218 -5.316793 -0.421655  
H 2.252069 -4.312026 -1.233253
Int-8

Total correction (378.15 K): 1949.3962 kJ/mol
Entropy term (378.15 K): 400.1544 kJ/mol
Final single point energy: -5634747.9714 kJ/mol
COSMO-RS correction (Gibbs free energy): -190.7018 kJ/mol
COSMO-RS correction (Enthalpy): -204.8312 kJ/mol

xyz, charge: -1, multiplicity: 1

N 1.199238 -1.800566 1.884239
C 2.258737 -1.333704 4.085861
C 2.324750 -1.947229 5.489397
H 2.880601 -2.981715 5.432051
H 1.342059 -1.933505 5.971089
H 3.024041 -1.386792 6.159033
C 3.687783 -1.370883 3.479045
H 4.041967 -2.405085 3.385588
H 4.374569 -0.805055 4.118464
H 3.696190 -0.918383 2.482905
N 1.223137 0.742295 3.064455
C 0.968094 2.043338 3.492248
C 1.775723 0.086370 4.155996
C 1.361412 2.190103 4.806754
H 1.266631 3.081755 5.406964
C 1.879538 0.944641 5.228959
H 2.529767 0.709445 6.205300
C 0.177768 3.042781 2.688496
C -1.331549 2.755179 2.893722
H -1.602220 2.949528 3.938364
C -1.564347 1.709450 2.691696
H -1.944676 3.379233 2.232993
C 0.426976 4.459996 3.239908
H -0.183333 5.187693 2.699270
H 1.481296 4.739395 3.135555
H 0.146083 4.516675 4.295407
N 1.156451 1.930931 0.598161
C 1.506539 2.349344 -0.670368
C 0.580149 3.025982 1.231666
$^{13}$C 1.128891 - 3.663586 - 0.858695

H 1.293620 - 4.259826 - 1.745726
C 0.536153 - 4.092426 0.353015
H 0.148927 - 5.080166 0.561271
C 2.314449 - 1.460423 - 1.573233
C 2.475937 - 2.109186 - 2.950312
H 3.005354 - 3.063006 - 2.856817
H 1.502670 - 2.295895 - 3.415454
H 3.059128 - 1.456060 - 3.607925
C 3.727949 - 1.265659 - 0.968736
H 4.327726 - 0.609738 - 1.611278
H 3.670786 - 0.808184 - 0.023674
H 4.230322 - 2.234665 - 0.865009

N 1.380169 - 0.644935 - 0.581101
C 0.807116 - 1.824161 - 1.051082
C 1.635415 - 0.127399 - 1.700810
C 0.687490 - 1.767542 - 2.426518
H 0.305799 - 2.549083 - 3.070261
C 1.222300 - 0.525421 - 2.842867
H 1.298377 - 0.160152 - 3.857394
C 0.616289 - 3.075721 - 0.229144
H 0.541378 - 4.094995 - 1.768404
H 1.504012 - 3.311739 - 0.530412
H -0.683612 - 4.821469 - 0.165307
C 1.876305 - 3.962891 - 0.476218
H 1.978020 - 4.175136 - 1.546105
H 1.803025 - 4.903643 0.082374
H 2.771597 - 3.428321 - 0.143724
C 1.609571 - 2.153943 3.206658
C 0.565290 - 2.861613 1.263171
C 0.797672 - 3.398398 3.442265
H 0.780696 - 3.930603 4.383179
C 0.273598 - 3.844138 2.205992
H -0.185593 - 4.803985 2.009916
Al 1.005728 0.083842 1.219979
P -1.446463 - 0.310768 0.951334
C -2.605974 1.001173 0.416619
C -2.133888 1.972772 -0.471714
C -3.915575 1.080234 0.896235
C -2.972818 3.004650 0.878196
C -4.277832 3.081926 -0.397552
C -4.748117 2.118335 0.488973
H -4.281268 0.336826 1.599713
H -5.763582 2.176816 0.872054
H -2.586487 3.763648 -1.552472
H -1.104843 1.946210 -0.825682
H -4.925561 3.897822 -0.710287
H -1.530898 -1.184753 -0.151472
H -1.160910 -1.733855 3.193151
B -2.203782 -1.291543 2.464879
H -1.249036 -2.283755 2.536579
H -2.397865 -0.575191 3.412572
H -3.086987 -2.083102 2.281179

$^{13}$C$_{x}$H$_{y}$

Total correction (298.15 K): 1620.2192 kJ/mol
Final single point energy: -3428842.8193 kJ/mol

xyz, charge: 0, multiplicity: 1
N 0.888871 -2.251340 2.404448

S57
### H$_{3}$NH$_3$XH$_4$

**Total correction (298.15 K):** 1651.6053 kJ/mol

**Final single point energy:** -3429788.562 kJ/mol

| xyz, charge: 1, multiplicity: 1 |  |
|---|---|
| N | 1.013914  -2.485138  2.487377 |
| C | 1.359184  -1.360081  4.773332 |
| C | 0.668383  -1.363953  6.152345 |
| H | 0.612321  -2.374315  6.576443 |
| H | -0.339409  -0.941798  6.104043 |
| C | 2.817795  -1.811495  4.946506 |
| C | 2.860983  -2.806674  5.400802 |
| H | 3.343578  -1.124139  5.612705 |
| H | 3.364392  -1.827884  3.994484 |
| N | 0.173033  0.586724  3.654218 |
| C | 0.395637  1.906625  3.329092 |
| C | 1.321130  0.010828  4.162961 |
| C | 1.712253  2.176743  3.643909 |
| C | 2.293501  0.996625  3.329092 |
| C | -0.603749  2.725217  2.546567 |
| C | -2.047166  2.374764  2.936802 |
| H | -2.200029  2.528955  4.009525 |
| H | -2.308604  1.341773  2.677922 |
| H | -2.747950  3.020771  2.400866 |
| C | -0.362696  4.224522  2.816395 |
| C | -1.082239  4.817567  2.245297 |
| H | 0.639155  4.528823  2.501801 |
| H | -0.478793  4.450286  3.881480 |
| N | 0.881467  2.167297  0.603978 |
| C | 0.875624  1.999679  -0.758755 |
| C | -0.380124  2.434210  1.074706 |
| C | -0.430809  2.179689  -1.174788 |
| H | -0.785418  2.128662  -2.194624 |
| C | -1.220731  2.457603  -0.020384 |
| H | -2.277004  2.685922  -0.09108 |
| C | 2.072336  1.386551  -1.445567 |
| C | 1.875895  1.414047  -2.972051 |
| H | 1.765136  2.445627  -3.321230 |
| H | 0.988135  0.847812  -3.268793 |
| H | 2.742573  0.966674  -3.463000 |
| C | 3.373080  2.123154  -1.081919 |
| H | 4.224915  1.663064  -1.598797 |
| C | 3.579924  2.098827  -0.013333 |
| C | 3.307256  3.167359  -1.406546 |
| N | 0.975233  -0.697398  -0.644534 |
| C | 1.215914  -2.005462  -0.309616 |
| C | 2.139277  -0.054039  -0.970273 |
| C | 2.584644  -2.196960  -0.399665 |
| C | 3.114455  -3.130036  -0.243307 |
| C | 3.163530  -0.969220  -0.819920 |
| H | 4.210291  -0.792883  -1.020526 |
| C | 0.108688  -2.876619  0.214472 |
| C | -1.227959  -2.595254  -0.493770 |
| H | -1.085303  -2.691112  -1.572713 |
| H | -1.811469  -1.590892  -0.284506 |

S59
Lowest-Gibbs free energy conformer of 2 (structural optimization was done with SMD(1,2-dichlorobenzene), T = 298.15 K, p = 1 atm)

xyz, charge: 0, multiplicity: 1

P    -0.172076  -0.578400  0.417458
P     2.675902   0.144694  -0.731911
P    -3.104636  -1.044217  1.612153
B     1.721220  -1.035607  0.461747
B    -1.251441  -1.649171  1.630478
B    -4.364650  -2.141181  2.619184
C    -0.392189   1.211311  0.688456
C    -0.210151   1.739408  1.971350
C    -0.719549   2.062873  0.371315
C    -0.355668   3.105972  2.180041
C    -0.684360   3.952391  1.130447
C    -0.865909   3.429625  -0.147437
H    -0.866967   1.658243 -1.369756
H    -1.125740   4.085027  -0.974079
H    -0.216279   3.509999  3.186854
H     0.039380   1.082811  2.801597
H    -0.801285   5.018575  3.103769
H    -1.202558  -2.791177  1.234780
H    -0.808128  -1.521851  2.748062
H    -0.644848  -0.715840  -0.902380
H     2.193356   0.123724  -2.052720
H     2.536739   1.503726 -0.398435
C     4.462939  -0.146597  0.864028
C     5.228990   0.622121  -1.747254
C     5.064872  -1.133584  -0.081431
C     6.436965  -1.349640  -0.184280
C     7.201011  -0.586715  -1.062141
C     6.597138   0.398254  -1.843040
H     4.758877   1.389980  -2.356514
H     4.470890  -1.731694  0.803534
H     6.906265  -2.117334  0.423930
H     8.270842  -0.758994  -1.140293
H     7.193138   0.993381  -2.526780
H    -3.127267   0.291469  2.064667
C    -3.641951  -0.815074  -0.119004
C    -4.026324   0.440457  -0.598899
C    -3.657948  -1.915857  -0.984088
C    -4.049278  -1.756424  -2.309860
C    -4.417087   0.593618  -1.928444
Lowest-Gibbs free energy conformer of 3 (structural optimization was done with SMD(1,2-dichlorobenzene), T = 298.15 K, p = 1 atm)

xyz, charge: 0, multiplicity: 1

P  0.184984     1.777747     0.572298
P  2.306140     1.136119    -1.743039
P -1.352963    -0.987967     1.052710
P -2.659112     2.974296    -0.532224
B  -2.714173   -1.226758     2.431223
B  0.207542     0.093075     1.565120
B  0.463949    1.590439     1.362586
B  -1.428098    2.851277     0.957604
C  1.604901     2.796409     1.155654
C  1.783841     4.090153     0.648341
C  2.552115     2.279180     2.043167
C  2.888137     4.848136     1.021801
C  3.829285     4.325843     1.908972
C  3.657583     3.042593     2.418265
H  4.318133     1.276236     2.442036
H  4.384831     2.628526     3.111595
H  3.014570     5.850024     0.620176
H  1.056591     4.506261    -0.044871
H  4.691250     4.919342     2.201504
H  1.212517    -0.529602     1.311785
H  0.106871     0.351086     2.744873
H  3.235748     2.073519    -1.264233
H  2.553517     1.35417     -3.128116
C  2.925493    -0.453140    -1.135423
C  3.950851    -0.496464    -0.187724
C  2.325920    -1.634370    -1.583434
C  2.759453    -2.856229    -1.082825
C  3.774127    -2.901838    -0.128155
C  4.368999    -1.724406     0.316941
H  4.414401     0.422362     0.161745
H  1.524452    -1.602382    -2.317801
H  2.295321    -3.774043    -1.430735
H  4.101192    -3.859062     0.268225
H  5.161638    -1.758569     1.058817
H  -1.920055   -0.467669    -0.129161
C  -0.816771   -2.626606     0.444237
C  -0.098561   -3.473888     1.296214
C  -1.163478   -3.075658     0.833693
C  -0.802621   -4.355575    -1.250282
C  0.257391    -4.752167     0.870992
C  -0.096024   -5.197206    -0.395012
H  -1.719848   -2.425298    -1.505022
H  -1.076681   -4.694720    -2.245770
H  0.813090    -5.402518     1.548922
H  0.182227    -6.196095    -0.720012
H  0.180602   -3.134047     2.291115
| Atoms | x    | y    | z    |
|-------|------|------|------|
| H     | -2.134232 | -1.780351 | 3.347736 |
| H     | -3.611276  | -1.909357 | 1.974771 |
| H     | -3.089106  | -0.114146 | 2.750140 |
| H     | -0.222400  | 0.699895  | -1.806865 |
| H     | 0.290559   | 2.646419  | -1.929013 |
| H     | -2.051704  | 2.370661  | 1.873352 |
| H     | -1.118560  | 4.003179  | 1.154048 |
| H     | -3.649666  | 3.930718  | -0.247574 |
| C     | -3.572420  | 1.492110  | -1.035977 |
| C     | -3.33769   | 0.899769  | -2.279661 |
| C     | -4.467043  | 0.908374  | -0.133540 |
| C     | -5.122239  | -0.268409 | -0.478238 |
| C     | -3.992626  | -0.282588 | -2.612393 |
| C     | -4.880740  | -0.867601 | -1.712947 |
| H     | -5.387421  | -1.792278 | -1.974860 |
| H     | -5.814248  | -0.723134 | 0.224251 |
| H     | -2.642672  | 1.352857  | -2.981355 |
| H     | -3.806840  | -0.746582 | -3.576840 |
| H     | -4.643778  | 1.361924  | 0.838584 |
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