Sterically constrained tricyclic phosphine: Redox behaviour, reductive and oxidative cleavage of P-C bonds, generation of a dilithium phosphaindole as a promising synthon in phosphine chemistry

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1 Electrochemical and spectroelectrochemical data

1.1 General electrochemical procedures

All electrochemical (EC) and in situ UV-vis spectroelectrochemical (in situ SEC) measurements were performed in a Glovebox Pure Lab HE GP-1 SR (Innovative Technology, USA) within an atmosphere of purified nitrogen (<0.1ppm O₂; <0.1ppm H₂O). The glovebox was equipped with military grade BNC feedthroughs in a homemade gas tight flange for low noise electrical connection of electrochemical and spectroelectrochemical cells inside. UV-vis-NIR spectroscopy inside the glovebox was performed via another homemade, gas tight flange containing four light-tight chambers with optical grade fused silica windows and four 74-UV (Ocean Optics Inc., USA) collimating lenses with SMA 905 connectors for optical fibers. EC and SEC cells were connected to a PGSTAT302 (Metrohm Autolab, Utrecht, The Netherlands) \( E = \pm 10 \text{ V}, \quad U = \pm 35 \text{ V} \) with an auxiliary voltage monitor (BK Precision 2831E, Yorba Linda, CA USA). NOVA Software (Metrohm Autolab) Version 1.11.2 was used to control the potentiostat, magnetic stirring and to trigger the spectrometer. UV-vis spectra recorded by OceanView software (Version 1.4.1, Ocean Optics) were triggered by a DG1032Z arbitrary waveform function generator (Rigol, Beijing, China) controlled by the Nova Software (1.10.4, Fa Metrohm Autolab) using a DAC164 analog/digital converter. Data analysis of the spectral and electrochemical data was carried out using OriginPro 2019 (OriginLab Cooperation, Northampton, MA, USA).

Solvent preparation / supporting electrolyte preparation

THF was dried by refluxing with potassium and benzophenone as an indicator until a midnight blue color was established, CH₃CN and PhF were dried by heating with CaH₂ to reflux conditions for at least 6 h and distillation under Argon onto vacuum activated molecular sieves (CH₃CN: 3 Å; PhF: 4 Å, \( 1 \cdot 10^{-3} \text{ mbar}, 350 \degree \text{C}, 12 \text{ h} \)). Additionally, all solvents were stored over vacuum activated molecular sieves for at least 14 days. \([\text{Bu}_4\text{N}]\text{[OTf]}\) was pre-dried at least 5 times by dissolving in CH₂Cl₂ and evaporating the solvent to high vacuum at 80 °C. Final drying and removal of HOTf traces was achieved by dissolving in dry benzene and refluxing this solution in a soxleth apparatus for 5 days with vacuum activated molecular sieves in the extraction thimble renewed every day. Prior to each measurement the solvent is passed through a Pasteur pipette with an activated (\( 1 \cdot 10^{-3} \text{ mbar}, 350 \degree \text{C}, 24 \text{ h} \)) aluminum oxide bed (\( D = 5 \text{ mm}; \ L = 70 \text{ mm} \)) in the glove box before the supporting electrolyte is added.
1.2 Cyclic voltammetry data of 3a in PhF, CH$_3$CN and THF

![Cyclic voltammograms](image)

Figure SI.1. Cyclic voltammograms (2nd cycle; $v = 0.1$ V/s) of phosphine 3a (3.94 mM) in PhF / 0.1 M ["Bu$_4$N][OTf] at a $D = 3$ mm platinum disc electrode.

In PhF as a solvent a substrate-based non-reversible reduction I at $E_{P(red)} = -2.62$ V (vs. $E_{1/2}(Cp_2Fe(Cp_2Fe^+))$ and an non-reversible oxidation II at $E_{P(ox)} = 1.12$ V were observed as broad peaks in the CV (Figure SI.1.). Square wave voltammetry revealed half-wave potentials according to the CV at $E_{1/2}(red) = -2.75$ V for the reduction and $E_{1/2}(red) = 0.72$ V for the oxidation reaction. Follow-up reactions are observed after the oxidation reaction III in the second cycle as non-reversible re-reduction peaks III' and III'' at $E_{P(re-red)} = -1.07$ V and $E_{P(re-red)} = -1.55$ V. Therefore, PhF is not usable as solvent for further spectroelectrochemical investigations due to a low diffusion coefficient of 3a in the reduction reaction I and the follow-up reactions III' and III'' after the substrate oxidation III.

![Cyclic voltammogram](image)

Figure SI 2. Cyclic voltammogram of 3a (3.05 mM) in CH$_3$CN / 0.1 M ["Bu$_4$N][OTf] at a Pt disc electrode ($D = 3$ mm; 0.1 V/s) with separated reduction and oxidations cycles. Asterisks mark minor impurities.

In CH$_3$CN as a solvent phosphine 3a showed a reasonable sharp non-reversible reduction I peak $E_{P(red)} = -2.36$ V (vs. $E_{1/2}(Cp_2Fe(Cp_2Fe^+)$; Figure SI.2. dotted curve) attributed to the two-electron reduction mechanism of 3a to [3a]$^{2-}$. The non-reversible oxidation III was observed at $E_{P(ox)} = 1.28$ V.
(dashed line). Additionally, extended CV measurements of the reduction reaction I show the known two-electron re-oxidation II (solid line) of dianion \([3a'\text{II}']^2-\) to \(3a'\) and back to \(3a\) \(\text{vid infra}\) at \(E_{\text{P(Re-ox)}} = -0.7 \text{ V}\). SWV measurements allow an assignment of the half-wave potentials \(E_{1/2(\text{SWV})} = -2.38 \text{ V}\) to the substrate-based reduction I and \(E_{1/2(\text{SWV})} = 1.15 \text{ V}\) to substrate-based oxidation II.

Further investigation of the substrate based reduction I and the substrate based oxidation reaction II were conducted by a comparison of the full potential window CVs (dashed line) versus the partial CV scan for the oxidation follow-up processes (Figure SI.3., solid line), as well as for the reduction follow-up processes (Figure SI.4., solid line).

**Figure SI.3.** Different potential (oxidation) scans of the CV (2nd cycle; \(v = 0.1 \text{ V/s}\)) of phosphine \(3a\) (3.05 mM) in \(\text{CH}_3\text{CN} / 0.1 \text{ M \[n\text{Bu}_4\text{N}\]OTf}\) at a \(D = 3 \text{ mm platinum disc electrode}\) to assign processes of the full potential window cycle to follow-up reduction processes III'-III'' of the substrate oxidation process III.

**Figure SI.4.** Different potential (reduction) scans of the CV (2nd cycle; \(v = 0.1 \text{ V/s}\)) of phosphine \(3a\) (3.05 mM) in \(\text{CH}_3\text{CN} / 0.1 \text{ M \[n\text{Bu}_4\text{N}\]OTf}\) at a \(D = 3 \text{ mm platinum disc electrode}\) to assign processes of the full potential window cycle to follow-up oxidation processes II and I' of the substrate reduction process I.
Unfortunately, the oxidation **III** of phosphine **3a** leads to three follow-up reduction reactions **III’ / III’’ / III’’’**. $E_{\text{P(red)}} = -0.79 / -1.44 / -1.81 \text{ V}$ indicating unwanted reactivity of the oxidation product in acetonitrile (Figure SI.3.). In acetonitrile an additional re-oxidation reaction **I’** $E_{\text{P(ox)}} = 0.55 \text{ V}$ (Figure SI.4.) after the already assigned re-oxidation reaction **II** is also found, rendering acetonitrile as not suitable solvent to handle the two-electron reduction (**I**) product [**3a’**]$^2$ due to further reactions. Based on this detailed peak assignment acetonitrile is not suitable for the reduction of phosphine **3a** although the potential range of CH$_3$CN (in blank measurements) lead to another prediction.

![Figure SI.5](image1.png)

**Figure SI.5.** CV measurement of the reduction only (**1** to **4** cycle; $v = 0.1 \text{ V/s}$) of phosphine **3a** (2.32 mM) in THF / 0.1 M [**nBu4N**][OTf] at a $D = 3 \text{ mm}$ platinum disc electrode. $iR$ Compensated by $R = 4750 \ \Omega$.

![Figure SI.6](image2.png)

**Figure SI.6.** CV measurement of the reduction **I** in the first cycle and following potential cycling around the reoxidation **II** range [-1.33 – 0.27 V] (**2** to **4** cycle; $v = 0.1 \text{ V/s}$) of phosphine **3a** (2.32 mM) in THF / 0.1 M [**nBu4N**][OTf] at a $D = 3 \text{ mm}$ platinum disc electrode. $iR$ Compensated by $R = 4750 \ \Omega$. 
CV measurements in THF do not allow for the observation of the oxidation reaction due to the limited oxidative potential window, but the reductive stability avoid side reactions after multiple reduction I cycles (Figure SI.5.). This enables an exhaustive re-oxidation II after the reduction product $[3a']^2$ is formed (Figure SI.6.). Figure SI.5. shows a CV measurement cycling exclusive around the non-reversible reduction peak I. No changes starting from the second cycle are observed is in accordance with the mechanism hypothesis of the two-electron reduction followed by a very fast chemical follow-up reaction forming $[3a']^2$ without the formation of electro-active side products: $3a + 2e^- \rightarrow [3a']^2$ (EEC mechanism, see manuscript). Additionally, the back reaction from dianion $[3a']^2$ to $3a$ via an EEC mechanism with a slower chemical step. Investigation by composited CV cycles (Figure SI.6.). producing the two-electron reduction I product $[3a']^2$ in a first cycle followed multiple cycles to show the exhaustive properties of the re-oxidation II due to limited amounts of $[3a']^2$ in the diffusion layer from the first cycle.

1.3 Additional in situ UV-vis spectroelectrochemical data and mechanistic investigation of the reduction of 3a

Figure SI.7. Spectroelectrochemical CV measurement of the reduction I and reoxidation II ($v = -15$ mV/s) of phosphine $3a$ (0.84 mM) in THF / 0.1 M $[n$Bu$_4$N][OTf] at a platinum grid electrode. Left contour plot: Relative UV-vis spectral changes during 2 cycles of CV; middle vertical plot: time dependent UV-vis absorption; top left: Projected relative UV-vis spectra after reduction I (red line) and after reoxidation II (black line); top right: in-situ CV, bottom right: absorption based CV. Asterisks mark minor impurities.

Spectroelectrochemical in situ UV-vis CV measurement Figure 2. (Manuscript) is performed in a high-concentration regime and allows to acquire suitable UV-vis spectra accompanied with a negative effect on the peak shapes. The used concentration (2.50 mM) was chosen to allow for a half-life time determination (vide infra). Figure SI.7. depicts the UV-vis CV with a concentration of 0.84 mM for phosphine $3a$ leading to peak shapes for reduction I and re-oxidation II in accordance to the CV data (vide supra). The UV-vis spectra detect only traces of the intermediate $3a'$ (black line, top left and black line, bottom right) formed after $[3a']^2$ (red line, bottom right) is re-oxidized (II). The reformation of phosphine $3a$ is observed by its characteristic absorption (green line, bottom right).
Figure S8. Absorbance during the spectroelectrochemical CV measurement (see manuscript Fig. 4) of the characteristic wavelength attributed to intermediate 3a′ and half-life time determination after re-oxidation UV-vis peak II ($v = -10 \text{ mV/s}$). Phosphine 3a (2.50 mM) in THF / 0.1 M $[\text{nBu}_4\text{N}]\text{[OTf]}$ at a platinum grid electrode in a double-compartment cuvette-cell. Half-life time measurement of intermediate 3a′ based on a composed UV-vis CV experiment (Figure 4, manuscript) after reduction I of 3a to $[3a′]^2$ - the time after the re-oxidation peak in the UV-vis experiment is used for a half-life time determination (Figure S8.). Assuming the electrochemical formation of intermediate 3a′ has fully proceed at the maximum of its characteristic UV-vis absorption.

Figure S9. In situ UV-vis multipulse chronoamperometry / potentiometry (in situ UV-vis-MPCACP) of phosphine 3a (2.50 mM) in THF / 0.1 M $[\text{nBu}_4\text{N}]\text{[OTf]}$ at a platinum grid electrode in a double compartment cuvette cell ($d = 0.5 \text{ mm}$). Left, bottom: 2D-Plot of relative in situ UV-vis spectra during the MPCACV measurement; left, top: UV-vis spectra after the reduction pulse (red line) and after the zero-current pulse (black line); middle vertical: Relative UV-vis absorbance during reduction and zero-current pulses; right top to bottom: chronopotentiogramm, chronocoulombgramm, chronoamperogramm.

In addition to the in situ UV-vis MPCA experiment (Figure 5, manuscript) a background experiment was designed in order to differentiate between diffusion and re-oxidation of dianion $[3a′]^2$ to 3a. Therefore, a chronoamperometric pulse to trigger the reduction I reaction $3a \rightarrow [3a′]^2$ was applied, followed by a chronopotentiometric pulse controlling the current to zero. During the
chronopotentiometric pulse no reduction or re-oxidation happened. Only diffusion effect from the thin-layer area to the bulk compartment of the double-compartment cuvette-cell can take place. The losses by diffusion effects during the time with zero current conditions show only slight changes on the concentration of \([3a']^{2-}\) in the cuvette cell. According to this finding, the reduction I and re-oxidation II in the in situ UV-vis MPCA measurement Figure 4 (manuscript) is suitable to proof the stability, spectroscopic and chemical reversibility of the reactions between \(3a\) and \([3a']^{2-}\).

In addition to the half-life time measurement of the intermediate \(3a'\) for the EEC reoxidation-mechanism (\([3a']^{2-} \rightarrow 3a\)) the EEC reduction-mechanism (\(3a \rightarrow [3a']^{2-}\)) was further investigated. The EEC hypothesis of the reduction is given by a CV experiment with an elevated scan rate of \(v = 10\) V/s (Figure SI10). The reduction peak I has significantly broadened but remains up to 10 V/s non-reversible. Separation of the EE and C part of the mechanism was not possible due to the fast chemical follow-up reaction.

**Figure SI10.** CV measurement of the (2nd cycle; \(v = 10\) V/s) of phosphine \(3a\) (4.25 mM) in THF / 0.1 M \([^nBu4N][OTf]\) at a \(D = 3\) mm platinum disc electrode. No \(iR\) compensation.

### 1.4 Preparative electrochemical reduction of phosphine \(3a\)

Preparative electrochemical synthesis was used to gain UV-vis data of the reduction product dianion \([3a']^{2-}\) on a preparative scale. Based on the assumed low diffusion coefficient deduced from the CV data potentiostatic conditions were chosen. Therefore, a solution of 0.28 mmol phosphine \(3a\) in 35 mL THF with 0.1 M \([^nBu4N][OTf]\) as supporting electrolyte was used in the working electrode compartment of a H-type Schlenk electrolysis cell (Fa. HMTC GmbH, Drensteinfurt, Germany) divided by two D4 glass sinter plates. A platinum sheet metal (25*25 mm) is used as a working electrode together with 3 mm Pt disc electrode for in situ CV measurements. The counter electrode is based on a graphite rod (H*D = 35*15 mm) in 15 mL THF electrolyte, separated by another 5 mL electrolyte in the ion bridge compartment.

Electrolyses was performed potentiostatic with \(E = -3.00\) V at room temperature insight a nitrogen filled glove box. Figure SI11 shows the current over time and after integration the charge consumption. After 60 min of electrolysis time an in situ CV was measured by switching from the preparative to the analytical Pt disc electrode. The potentiostatic synthesis was stopped after 20 h to avoid contamination from the counter electrode compartment. Due to the low current a conversion of only 34% based on a two-electron process with 100% current yield was achieved.
Figure SI11. Current and charge during the potentiostatic electrolysis of phosphine 3a (8.00 mM) in THF / 0.1 M ["Bu4N][OTf] at a platinum sheet working electrode (25*25 mm) in a separated H-type cell. Samples were taken every 60 min.

In situ CV before the electrolysis (Figure SI12) show a very broad peak I for the reduction process, due to the high concentration of phosphine 3a in the preparative electrolysis cell. The reoxidation peak II also showing a reasonable broadening and low intensity. After 23% conversion and a drastic color change from yellow to deep red (insert figure SI13) the CV show a significant increase of the reoxidation peak II due to the formed bulk concentration of [3a']2- from the preparative reduction. Further low intensity peaks (*) indicate side reactions between decompositions products from the counter electrode compartment caused by the prolonged electrolysis time.

Figure SI12. In situ CV measurement of the (2nd cycle; \( v = 0.1 \) V/s) of phosphine 3a (8.00 mM) in THF / 0.1 M ["Bu4N][OTf] at a D = 3 mm platinum disc electrode during the potentiostatic electrolysis in the beginning (\( Q = 0 \) C; 0% conversion) and after 20 h (\( Q = -11.0 \) C; 22.8% conversion, \( n = 2 \) e ) No \( iR \) compensation. External ferrocen reference of the RE after the electrolysis.
UV-vis NIR spectroscopy (Figure SI12, black line) indicate the comparable vis band to the in situ UV-vis CV experiment (Fig. 2, manuscript) at $\lambda = 485$ nm assigned to dication $[3a']^2\cdot$. While remeasuring the separated solution after storage at -30 °C under inert conditions a significant decomposition is observed in the UV-vis spectrum (Figure SI12, red line).

**Figure SI13.** UV-vis NIR spectra of the working electrode solution (1:10 diluted in 0.1 M ["Bu4N][OTf], $d = 1$ cm) after 34.0% conversion ($Q = -16.0$ C; $n = 2$ e$^-$) and after additional 60 h stored at -30 °C. Insert: Photo of the double separated electrolysis cell (left CE, right WE compartment).

Attempts to isolate and crystalize dianion $[3a']^2\cdot$ as its tetrabutyl ammonium salt ["Bu4N]2[3a’] from the electrolyte failed due to the high supporting electrolyte content or the decomposition taking place. This support the necessity of the use of lithium-based reduction reagents to further stabilize the dianion $[3a']^2\cdot$ be formation of a Li–C bond.
2 \(^1\)H, \(^{13}\)C, \(^{31}\)P and \(^7\)Li NMR spectra

2.1 NMR-Spectra of Compound 5

Figure S14: \(^1\)H-NMR spectrum of \(5\) in d\(_8\)-THF

Figure S15: \(^{13}\)C\(_{\{\text{1}H\}}\)-NMR spectrum of \(5\) in d\(_8\)-THF
Figure S16: $^{31}$P{$^1$H}-NMR spectrum of 5 in d$_8$-THF

Figure S17: $^7$Li-NMR spectrum of 5 in d$_8$-THF
2.2 NMR-Spectra of Compound 6

Figure S18: $^1$H-NMR spectrum of 6 in C$_6$D$_6$

Figure S19: $^{13}$C{${^1}$H}-NMR spectrum of 6 in C$_6$D$_6$
Figure S20: $^{31}\text{P}({}^1\text{H})$-NMR spectrum of 6 in C$_6$D$_6$
2.3 NMR-Spectra of Compound 7

Figure S21: $^1$H-NMR spectrum of 7 CDCl$_3$
Figure S22: $^{13}\text{C}\{^1\text{H}\}$-NMR spectrum of 7 in CDCl$_3$

Figure S23: $^{31}\text{P}\{^1\text{H}\}$-NMR spectrum of 7 in CDCl$_3$
2.4 NMR-Spectra of Compound 8

Figure S24: $^1$H-NMR spectrum of 8 in C$_6$D$_6$

Figure S25: $^{13}$C-{$_1$H}-NMR spectrum of 8 in C$_6$D$_6$ (211.5 ppm = Cr(CO)$_6$)
2.5 NMR-Spectra of Compound 9
Figure S28: $^{13}$C$\{^1\text{H}\}$-NMR spectrum of 9 in C$_6$D$_6$

Figure S29: $^{31}$P$\{^1\text{H}\}$-NMR spectrum of 9 in C$_6$D$_6$
2.6 NMR-Spectra of Compound 10

Figure S30: $^1$H-NMR spectrum of 10 in C$_6$D$_6$

Figure S31: $^{13}$C{$_^1$H}-NMR spectrum of 10 in C$_6$D$_6$
Figure S32: $^{31}\text{P}\{^{1}\text{H}\}$-NMR spectrum of 10 in C$_6$D$_6$
3 Quantum Chemical Calculations

3.1 Optimized Structure of 5 in Gas Phase

!Grid6 FinalGrid7 PBE0 def2-TZVP d3bj opt freq

|          |          |          |          |          |
|----------|----------|----------|----------|----------|
| Total enthalpy | ... | -1925.76324239 Eh |
| Total entropy correction | ... | -0.09088281 Eh | -57.03 kcal/mol |

Final Gibbs free enthalpy | ... | -1925.85412520 Eh |

Coordinates from ORCA-job Input

P 9.49489112184651  5.82429782374990  10.76196696745999
C 9.99803782219421  7.50521026447127  11.01496484029531
C 11.10071454022009  5.27635868669592  11.34083684672251
C 11.33019708561039  7.59364214719745  11.54580105337329
C 9.28013296531750  8.70562187869723  10.75144437919929
C 11.93420803894332  6.32485563453546  11.71258317206986
Si 11.57527894340661  3.52080059244557  11.30608727659307
C 7.22188161460727  7.63646464655367  9.84157936284825
C 7.93686106548223  8.72150550023325  10.15036631179401
C 11.90196345274427  8.84858536408239  11.83186705534302
C 9.89282080617129  9.91703619485633  11.04465340670175
H 12.94805687295079  6.21183083377820  12.09574749263300
C 10.24569484778037  2.38958007860984  12.01891893477602
C 13.18448206029211  3.17815173889752  12.24455746281446
C 11.85726030959059  2.89316776754610  9.52923493442899
Si 5.63813081600642  7.35358222591309  9.08410544689554
H 7.60362534047708  9.76523071897335  9.96719036219484
H 12.91091084589129  8.89788053735327  12.23823211880419
C 11.18691071676219  9.99808889292983  11.58525898440296
H 9.33941329550575  10.83034756343723  10.83158999591780
| H   | 10.11614901667215 | 2.58225458816140 | 13.08776677595352 |
| H   | 10.48105153956784 | 1.32999192067866 | 11.87317934510553 |
| H   | 9.29575191101555  | 2.61267597430854 | 11.52620897845276 |
| H   | 14.00658812989892 | 3.75819440000317 | 11.81682083468862 |
| H   | 13.46309554460172 | 2.1197782570615  | 12.22055822030753 |
| H   | 13.07059473294656 | 3.47735866796819 | 13.29044909072272 |
| C   | 12.54217703143715 | 1.70694845614886 | 9.25564190014157  |
| C   | 11.33742091847746 | 3.60237115478615 | 8.44323791798845  |
| C   | 4.55248140289981  | 8.70644708638051 | 8.23837950193830  |
| C   | 4.43606619567036  | 6.55762275869453 | 10.32446546142365 |
| C   | 5.90473384020914  | 6.0553977776603  | 7.70923384444787  |
| H   | 11.62327566096245 | 10.97182107663217| 11.79937453011884 |
| H   | 12.96155256739978 | 1.12831999138915 | 10.07540185766010 |
| C   | 12.70516057934707 | 1.24049939928088 | 7.95760115990405  |
| C   | 11.48924554883234 | 3.13994875059123 | 7.14263419961244  |
| H   | 10.79566944939672 | 4.52633003696935 | 8.64047287157433  |
| H   | 4.33811247866111 | 9.49908014670319 | 8.96368949083261  |
| H   | 3.59093260732460 | 8.33037958698613 | 7.86378139827399  |
| H   | 5.0894568569409  | 9.16116798947785 | 7.39982689481427  |
| H   | 4.93959406381000 | 5.73314826529736 | 10.83440726480745 |
| H   | 3.53544840536884 | 6.17403525613616 | 9.83190182072900  |
| H   | 4.13221576471298 | 7.28900445204866 | 11.08087572203000 |
| C   | 7.06735688794342 | 5.27574372136411 | 7.74013084455514  |
| C   | 4.99612559080160 | 5.81250357593911 | 6.67600852460614  |
| H   | 13.24391191334314 | 0.31466573763147 | 7.77461106969255  |
| C   | 12.17453004909662 | 1.95838478834490 | 6.89429742265137  |
| H   | 11.06606040843438 | 3.70804980587180 | 6.31990518296556  |
| H   | 7.78165336159736 | 5.45797020538349 | 8.54225293673938  |
| C   | 7.30682272377130 | 4.30168155351086 | 6.77953332704264  |
| C   | 5.22723457975963 | 4.83847304948150 | 5.71142109208389  |
| H   | 4.08431908010419 | 6.40214124276500 | 6.61699246509082  |
### 3.2 Structure of 5 with Dummy Atom for NICS(0) Calculation

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| P    | 6.02801 | 4.24972 | 8.85059 |
| C    | 6.53116 | 5.93063 | 9.10358 |
| C    | 7.63383 | 3.70178 | 9.42946 |
| C    | 7.86332 | 6.01906 | 9.63442 |
| C    | 5.81325 | 7.13104 | 8.84006 |
| C    | 8.46733 | 4.75028 | 9.80120 |
| Si   | 8.10840 | 1.94622 | 9.39471 |
| C    | 3.75500 | 6.06188 | 7.93020 |
| C    | 4.46998 | 7.14693 | 8.23899 |
| C    | 8.43508 | 7.27401 | 9.92049 |
| C    | 6.42594 | 8.34246 | 9.13327 |
| H    | 9.48118 | 4.63725 | 10.18437 |
| C    | 6.77881 | 0.81500 | 10.10754 |
| C    | 9.71760 | 1.60357 | 10.33318 |
| C    | 8.39038 | 1.31859 | 7.61785 |
| Si   | 2.17125 | 5.77900 | 7.17273 |
| H    | 4.13675 | 8.19065 | 8.05581 |
| H    | 9.44403 | 7.32330 | 10.32685 |
| C    | 7.72003 | 8.42351 | 9.67388 |
| H    | 5.87253 | 9.25577 | 8.92021 |
| H    | 6.64927 | 1.00767 | 11.17639 |
| H    | 7.01417 | -0.24459 | 9.96180 |
| H    | 5.82887 | 1.03810 | 9.61483 |
3.3 Optimized Structure of 7 (S,R) with Solvent-Correction

IGrid7 NoFinalgrid PBE0 def2-TZVP d3bj CPCM(Chloroform) tightopt verytightscf numfreq normalprint

Total enthalpy ... -2498.47281911 Eh
Total entropy correction ... -0.10154194 Eh -63.72 kcal/mol
Final Gibbs free enthalpy ... -2498.57436105 Eh

Coordinates from ORCA-job Input

|  |  |  |  |
|---|---|---|---|
| C | 1.84166512864063 | 6.22165832192701 | 4.97216186095459 |
| C | 0.47687267357810 | 6.22790528435134 | 7.13619664498095 |
| C | 2.31409843171028 | 9.00298424648067 | 4.05766689083700 |
| C | 1.97803033246095 | 5.04181059219980 | 5.71061511966885 |
| C | 2.66061808575330 | 6.53293728292888 | 3.89407625601186 |
| Si | -0.56969380868668 | 6.65739013262125 | 8.61980654147862 |
| C | 1.17600913121717 | 5.0804973256286 | 6.92117398098502 |
| C | 2.65340450680753 | 7.89543324744385 | 3.36130044524659 |
| Si | 2.62596795410298 | 10.69000716449204 | 3.25952304120720 |
| C | 2.87233790533232 | 4.06671470079678 | 5.25938303609998 |
| C | 3.54834335552597 | 5.54995115294734 | 3.46008882727105 |
| C | -0.72287788281576 | 5.12644273582571 | 9.69157961469667 |
| C | -2.25149161607122 | 7.22446559303237 | 8.02947506029772 |
| C | 0.27014718236262 | 8.04037975604470 | 9.55624891485197 |
| H | 1.15849498005189 | 4.24307380564818 | 7.61380383860227 |
| Atoms | x | y | z |
|-------|---|---|---|
| H     | 3.0445319645748 | 8.01314865834126 | 2.35299875907686 |
| C     | 3.58113639342012 | 10.37636025110172 | 1.67192449043012 |
| C     | 3.6824442276745 | 11.71513120639564 | 4.41454642660357 |
| C     | 1.05010829573672 | 11.60220147631699 | 2.83809741826955 |
| H     | 2.98941580690282 | 3.13227163700990 | 5.79714005496530 |
| C     | 3.62881908130856 | 4.32516327607014 | 4.12556835047634 |
| H     | 4.20510531273298 | 5.75227345263850 | 2.62045174451081 |
| C     | -0.14188176795077 | 5.05009418141122 | 10.95874357760158 |
| C     | -1.42011100726446 | 4.00820268429402 | 9.22358685179313 |
| H     | -2.87634276677124 | 7.51452164611354 | 8.87827525090939 |
| H     | -2.76537118251036 | 6.43483185845817 | 7.47607203215137 |
| H     | -2.15070128367429 | 8.08999429012424 | 7.36793466970377 |
| H     | -0.30252986677472 | 8.31540055547111 | 10.44613721370775 |
| H     | 0.34706590451694 | 8.92574717652790 | 8.91865492970958 |
| H     | 1.28003690359587 | 7.75993637096716 | 9.86454544160784 |
| C     | 4.95184012786412 | 10.10369252577521 | 1.70483855395743 |
| C     | 2.94840981820350 | 10.38382066333538 | 0.42711127171185 |
| H     | 3.14016915801873 | 11.9634250498832 | 5.32910312039567 |
| H     | 3.96199917647725 | 12.65018286410711 | 3.92128932286567 |
| H     | 4.59745275335699 | 11.18808152582905 | 4.69477561580686 |
| H     | 0.55502717285852 | 11.96436534147471 | 3.73983691763861 |
| H     | 0.34601739028791 | 10.96511870260951 | 2.29784905440275 |
| H     | 1.29009772829232 | 12.46293361369229 | 2.20723763137285 |
| H     | 4.32664799737072 | 3.57622018692879 | 3.76850320189999 |
| H     | 0.40754099671489 | 5.89896440971862 | 11.35294725312894 |
| C     | -0.25211797819587 | 3.90193175046339 | 11.73301765977782 |
| H     | -1.88108526246934 | 4.03196287492852 | 8.24025524725301 |
| C     | -1.53414305208891 | 2.85815920091577 | 9.99060794571195 |
| H     | 5.47604356414221 | 10.08466109879281 | 2.65551425655877 |
| C     | 5.66431441355527 | 9.84996036379618 | 0.54191325656531 |
| H     | 1.88497279374630 | 10.59115482453376 | 0.36324386693958 |
3.4  Optimized Structure of 7 (S,S) with Solvent-Correction

|atom  | x      | y      | z      |
|-------|--------|--------|--------|
|       | 3.6541 | 10.1289| -0.7418|
|       | 0.2068 | 3.8646 | 12.7149|
|       | -0.9488| 2.8037 | 11.2497|
|       | -2.0796| 2.0025 | 9.6077 |
|       | 0.0146 | 9.8615 | -0.6858|
|       | 6.7277 | 9.6429 | 0.5917 |
|       | 3.1413 | 10.1398| -1.6974|
|       | -1.0363| 1.9061 | 11.8515|
|       | 5.5687 | 9.6635 | -1.5966|
|       | 0.7416 | 10.2904| 6.1571 |
|       | 1.1159 | 11.2630| 7.4093 |
|       | -0.5238| 10.3645| 5.5755 |
|       | 0.2517 | 12.2997| 7.8210 |
|       | 2.0914 | 11.2038| 7.5544 |
|       | -1.0023| 12.3658| 6.8210 |
|       | 0.5574 | 13.0503| 8.1291 |
|       | -1.3895| 11.3942| 5.9053 |
|       | -0.8328| 9.6111 | 4.8595 |
|       | -2.3699| 11.4413| 5.4447 |
|       | -1.6819| 13.1703| 7.0784 |

Total enthalpy: ... -2498.47645196 Eh
Total entropy correction: ... -0.10043130 Eh, -63.02 kcal/mol

Final Gibbs free enthalpy: ... -2498.57688326 Eh
## Coordinates from ORCA-job Input

| Element | X            | Y            | Z            | X            | Y            | Z            |
|---------|--------------|--------------|--------------|--------------|--------------|--------------|
| P       | 0.15013060884002 | 7.08422699775960 | 5.68009265306768 |
| P       | 1.73201554625871  | 8.40733112103678  | 6.47223010469050  |
| C       | 1.22186148375471  | 6.16930284430282  | 4.59187103670539  |
| C       | -0.1627061077340  | 5.59806859753781  | 6.66732080862156  |
| C       | 2.32537699714715  | 8.92170239199035  | 4.80132623984722  |
| C       | 1.14358878765612  | 4.79422434805576  | 4.83649176135885  |
| C       | 2.10439642771597  | 6.71043924987689  | 3.66578665242080  |
| C       | 0.33444542111167  | 4.51570322696540  | 6.00904294660553  |
| C       | 2.40134250698535  | 8.13780900949395  | 3.70529235567168  |
| C       | 2.93386909442583  | 10.69976271372889 | 4.77611398005635  |
| C       | 1.86033818965634  | 3.92141316597909  | 4.0169747461520   |
| C       | 2.80558769932432  | 5.82409709605867  | 2.84772541192963  |
| C       | -0.46767069104528 | 6.53855089074499  | 9.52676819002356  |
| C       | -1.47276866402405 | 3.75324619262517  | 8.70526627317646  |
| C       | -2.92659545541685 | 6.29323608471953  | 7.73024877504586  |
| H       | 0.14599276750704  | 3.49445590268390  | 6.32934944588689  |
| H       | 2.82599602906619  | 8.56269097019508  | 2.79627098860902  |
| C       | 3.80778634878501  | 10.99960805665356 | 3.14304761875223  |
| C       | 4.13891806079057  | 10.91430630745289 | 6.19237238737449  |
| C       | 1.48351384304984  | 11.86132858038968 | 4.97210768046261  |
| H       | 1.80499034055544  | 2.84889646171574  | 4.16916586500777  |
| C       | 2.66310157073667  | 4.44736313353091  | 3.01279157421742  |
| H       | 3.49942655183855  | 6.21124146884599  | 2.10863375888843  |
| C       | -0.47265061024915 | 7.93509250861629  | 9.47179046680399  |
| C       | 0.22337447935531  | 5.92966787224467  | 10.57680724167163 |
| H       | -2.08167896010779 | 3.69863120770336  | 9.61154307312172  |
| H       | -0.50940887387648 | 3.28108042902427  | 8.91245706447914  |
| H       | -1.97353882551468 | 3.17354135933756  | 7.92559293515765  |
| H       | -3.59171640183027 | 6.28887599358544  | 8.59788578247195  |
| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| H       | -3.4036542470505478 | 5.73152145148837 | 6.92295781550884 |
| H       | -2.809663867668611  | 7.32680220885511  | 7.39465751431316  |
| C       | 5.05601949270445    | 10.42002432995561  | 2.89467953256361 |
| C       | 3.23417922908042    | 11.77079062651455  | 2.13022785629843 |
| H       | 3.66119643689496    | 10.68569672589382  | 7.1489139871728  |
| H       | 4.49414765743265    | 11.94764250549840  | 6.22833972907215 |
| H       | 5.00448496721227    | 10.25677437968812  | 6.08252052553368 |
| H       | 0.9753398128939     | 11.65952231740372  | 5.91870020477006 |
| H       | 0.75785168945688    | 11.73174912442401  | 4.16564500071522 |
| H       | 1.81571359762785    | 12.90297636428621  | 4.97733432938101 |
| H       | 3.22125637948890    | 3.77673074622435   | 2.36945746070231 |
| H       | -0.99646195476455   | 8.4465307793997    | 8.66934354670815 |
| C       | 0.19686055549498    | 8.69589729096566   | 10.41970559200103 |
| H       | 0.25242530214047    | 4.84724024375531  | 10.64885747634072 |
| C       | 0.89171680606879    | 6.6837889476310    | 11.53178139883204 |
| H       | 5.53071852193236    | 9.81078699437159   | 3.65840775270855 |
| C       | 5.70725881703160    | 10.60268028979040  | 1.68371409990773 |
| H       | 2.6595215806595     | 12.23501883070401  | 2.28774040181215 |
| C       | 3.8046053868955     | 11.9594109377280   | 0.91516275801369 |
| H       | 0.18880313163877    | 9.7778880650073    | 10.34948127635370 |
| C       | 0.88312605490354    | 8.06989778269686   | 11.45178556273772 |
| H       | 1.42562218247269    | 6.18965506588324   | 12.33614933142342 |
| C       | 5.11860390081450    | 11.37472927921784  | 0.69004467855348 |
| H       | 6.67496273171607    | 10.14362719269747  | 1.51345683147065 |
| H       | 3.41651093851302    | 12.56328642947529  | 0.14297891681402 |
| H       | 1.41102047942101    | 8.66124091566193   | 12.19157524136766 |
| H       | 5.62516174952806    | 11.51988126224319  | -0.25767756906790 |
| C       | 3.05825677541393    | 7.29108034947845   | 7.05091144599662 |
| C       | 2.93704741899390    | 6.81454449476320   | 8.3579206065144 |
| C       | 4.16922078231762    | 6.91890102751932   | 6.29690170531827 |
| C       | 3.89298407668285    | 5.96487954007560   | 8.88995700752043 |
3.5 Optimized Structure of Phosphoric Acid as Reference for NMR Calculations

!Grid5 FinalGrid6 PBE0 def2-TZVP CPCM(Chloroform) d3bj tightopt verytightscf numfreq

Total enthalpy  ...  -643.86969595 Eh
Total entropy correction  ...  -0.03619163 Eh  -22.71 kcal/mol

Final Gibbs free energy  ...  -643.90588758 Eh

8
Coordinates from ORCA-job Input

P  -4.69063350796895  0.49877921247310  0.11272864873468
O  -3.30888648012770  0.41668613837400  0.86578249507568
O  -4.6173228364226  -0.74848122551954  -0.85217256151414
O  -4.60004488459736  1.70920714709684  -0.90891543168871
H  -4.90711125267117  2.54032512028118  -0.52524640184670
H  -2.53282255636921  0.44290985413306  0.29234482338187
H  -5.42766505354080  -0.89620081784504  -1.35588247685023
O  -5.81269338108252  0.56370209554300  1.04942090470754
3.6 Optimized Structure of 7 (S,R) in Gas Phase

Grid6 FinalGrid7 PBE0 def2-TZVP d3bj tightopt numfreq

Total enthalpy ... -2498.45825960 Eh
Total entropy correction ... -0.10119126 Eh -63.50 kcal/mol

Final Gibbs free enthalpy ... -2498.55945086 Eh

68
Coordinates from ORCA-job Input

|   |   |   |   |
|---|---|---|---|
| P | 0.53132088138187 | 7.25974055893180 | 5.67010675381841 |
| P | 1.93395398970768 | 8.93742209269745 | 5.83826615463572 |
| C | 1.80963474156187 | 6.22611223001559 | 4.95989989541249 |
| C | 0.51741819246797 | 6.24438664708376 | 7.16473026066693 |
| C | 2.26140421582495 | 9.00328399869579 | 4.02621448502185 |
| C | 1.96345440988276 | 5.04679794392264 | 5.69482106480510 |
| C | 2.59535860020165 | 6.53196969949875 | 3.85652768926448 |
| Si | -0.46275600411243 | 6.68472998500968 | 8.6858516217497 |
| C | 1.20152034823286 | 5.09224276318846 | 6.92956808110860 |
| C | 2.57812911050382 | 7.89332116623601 | 3.3234628944374 |
| Si | 2.54809543989602 | 10.67957847042075 | 3.20454930931670 |
| C | 2.83776428284686 | 4.06791337081739 | 5.21558152754466 |
| C | 3.46414728506725 | 5.54522934816092 | 3.39670576758541 |
| C | -0.68448147868334 | 5.13307244624478 | 9.71437529178814 |
| C | -2.11971347024867 | 7.37822107646926 | 8.16172510639995 |
| C | 0.47968275426487 | 7.98419290878611 | 9.64677947294237 |
| H | 1.19823956402641 | 4.25757558745610 | 7.62590395025779 |
| H | 2.94380011013853 | 8.00942497974062 | 2.30528274512845 |
| C | 3.58589359436606 | 10.36801137768648 | 1.66942193279189 |
| C | 3.51099615488820 | 11.78226811574966 | 4.37152626050869 |
3.7 Optimized Structure of 7 (S,S) in Gas Phase

!Grid4 FinalGrid5 PBE0 def2-TZVP d3bj tightopt freq

|        |        |                |                |
|--------|--------|----------------|----------------|
| H      | -2.10796196505574 | 2.04660816654455 | 9.50415226495824 |
| C      | 5.15442477410030  | 9.85680561654138  | -0.59989880417626 |
| H      | 6.76950884857173  | 9.54811396214583  | 0.78109224900289 |
| H      | 3.36471730787168  | 10.22350782857402 | -1.72489392125908 |
| H      | -1.15785702710663 | 1.87466782072136  | 11.78316185439493 |
| H      | 5.76075738984208  | 9.65946727475026  | -1.47675050801158 |
| C      | 0.72899150546548  | 10.28870884679003 | 6.14602467449295 |
| C      | 1.07068266306451  | 11.23160864573178 | 7.11316371086657 |
| C      | -0.52156256725931 | 10.37642675414785 | 5.53543328443619 |
| C      | 0.19063540563004  | 12.24918382302937 | 7.4551206821044 |
| H      | 2.03626670385838  | 11.16062431130531 | 7.6035725349342  |
| C      | -1.04663781017541 | 12.32954409045836 | 6.83607660915961 |
| H      | 0.47115405215161  | 12.97497174852024 | 8.20974607948357 |
| C      | -1.40169001398888 | 11.38964872699120 | 5.87654752814724 |
| H      | -0.80653564175919 | 9.63971257041645  | 4.79258679272746 |
| H      | -2.37020834154043 | 11.44694983422607 | 5.3926389566390 |
| H      | -1.73838403285323 | 13.12005557058556 | 7.10352748817486 |

Total enthalpy        ... -2498.46215026 Eh

Total entropy correction  ... -0.10085220 Eh  -63.29 kcal/mol

Final Gibbs free enthalpy ... -2498.56300246 Eh

Coordinates from ORCA-job Input

P  0.09812794081455  7.07478996063122  5.67778509408559
P  1.68173746625078  8.40556528683055  6.46010671719353
| Atom | X         | Y         | Z         | 2x   | 2y   | 2z   |
|------|-----------|-----------|-----------|------|------|------|
| C    | 1.141169  | 4.537900  | 2.956042  |
| C    | -0.150712 | 6.651851  | 2.952610  |
| C    | 2.277030  | 4.794436  | 2.726913  |
| C    | 1.085051  | 4.755434  | 2.726913  |
| C    | 1.987424  | 3.593838  | 2.726913  |
| Si   | -1.19885  | 8.189241  | 2.726913  |
| C    | 0.331471  | 5.955397  | 2.726913  |
| C    | 2.307297  | 3.887508  | 2.726913  |
| Si   | 2.939603  | 4.806844  | 2.726913  |
| C    | 1.772323  | 3.887508  | 2.726913  |
| C    | 2.657554  | 2.726913  | 2.726913  |
| C    | -0.434711 | 9.506850  | 2.726913  |
| C    | -1.242188 | 8.776847  | 2.726913  |
| C    | -2.920897 | 7.802351  | 2.726913  |
| C    | 0.172114  | 6.268427  | 2.726913  |
| C    | 2.727165  | 2.769650  | 2.726913  |
| C    | 3.856884  | 3.196881  | 2.726913  |
| C    | 4.118373  | 6.251451  | 2.726913  |
| C    | 1.521371  | 4.989284  | 2.726913  |
| C    | 1.731043  | 4.018066  | 2.726913  |
| C    | 2.527839  | 2.863013  | 2.726913  |
| C    | 3.322284  | 1.973297  | 2.726913  |
| C    | -0.494841 | 9.388386  | 2.726913  |
| C    | 0.260202  | 10.594560 | 2.726913  |
| C    | -1.800004 | 9.713046  | 2.726913  |
| C    | -0.237838 | 8.943490  | 2.726913  |
| C    | -1.736626 | 8.038467  | 2.726913  |
| C    | -3.552310 | 8.694144  | 2.726913  |
| C    | -3.386692 | 7.032230  | 2.726913  |
| C    | -2.895004 | 7.427744  | 2.726913  |
| C    | 5.075595  | 2.956042  | 2.726913  |
C  3.34732710698831  11.80403574913718  2.19400973840591
H  3.60865163383898  10.64464565006586  7.19588186483323
H  4.51940282727081  11.86754759787543  6.29678105251150
H  4.95687476397959  10.15703773340756  6.16804453048950
H  0.99308005361784  11.68976188708200  5.92492805072447
H  0.80160111554608  11.78836370074700  4.17384047384370
H  1.87705132530572  12.92291393082161  5.01284793659971
H  3.06142017710670  3.86420221799181  2.18111370281904
H  -1.02149854432026  8.39625372754106  8.55328533814895
C  0.12477409426072  8.77379041009820  10.31094221333869
H  0.33120223453411  4.94695074601317  10.71594104026893
C  0.87703166898948  6.84570396067974  11.52590165993376
H  5.49929431237498  9.68505381577725  3.7137853738239
C  5.75871882701788  10.51335464955875  1.76304115336255
H  2.40352670947228  12.31721461492675  2.34687878576193
C  4.02583882034346  11.98591332874553  0.99669756526319
H  0.07764609481112  9.84968341566334  10.18795660609783
C  0.81376257460156  8.22430604175105  11.38267800452907
H  1.41289796279764  6.41117482701350  12.36258086982840
C  5.23302243399049  11.33989698767508  0.77933428341020
H  6.70348940603868  10.00698921339785  1.5900394834450
C  3.61097804990687  12.63306344492275  0.23193852815628
H  1.30256337439128  8.86962836631525  12.10362619332144
H  5.76505737169002  11.48003540273248  -0.15486166498398
C  3.01515241043730  7.30216352771195  7.0453889397360
C  2.96760922936948  6.94566839685661  8.39394575482253
C  4.05375361967761  6.81649004494067  6.25402852589128
C  3.92351286326906  6.10081328692641  8.93244805205254
H  2.17563510059920  7.33269268454936  9.02409304710323
C  4.95170989797810  5.61645139713138  8.13612785453694
H  3.86665160488171  5.82907426066764  9.98050174515899
### 3.8 Transition-State of Configurational Inversion of 7 at P-Ph in Gas Phase

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
|     |     |     |     |     |     |     |
| C   | 5.01648652695335 | 5.98078103983985 | 6.79904771917061 |
| H   | 4.10857037627440  | 7.09122750671332  | 5.20888017408324  |
| H   | 5.81892179305649  | 5.60783744889887  | 6.17239282690612  |
| H   | 5.70487939201415  | 4.96059807866961  | 8.55794388346570  |

Total enthalpy ... -2498.41755467 Eh
Total entropy correction ... -0.09905821 Eh -62.16 kcal/mol

Final Gibbs free enthalpy ... -2498.51661288 Eh

Coordinates from ORCA-job Input

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| P   | 5.00985148684332 | 4.38201250598389 | 13.17227882038468 |
| C   | 4.21298666743295 | 4.19967499061516 | 14.79309757814461 |
| P   | 5.34285104535168 | 6.45935420259634 | 13.66890582337721 |
| C   | 6.36308861745800 | 3.29312467724023 | 13.70017221043982 |
| C   | 3.19872113349338 | 4.97369027512444 | 15.36468068099170 |
| C   | 4.76097112324461 | 3.09224301292712 | 15.46078653064078 |
| C   | 3.86194881214940 | 7.12660541232952 | 14.31404659735021 |
| C   | 6.79824954183970 | 7.44520758689608 | 13.4368369823582 |
| C   | 7.60328255193699 | 7.27073494661391 | 12.30687245618771 |
| C   | 5.96596119364746 | 2.61932673907514 | 14.80941816366484 |
| Si  | 7.89683049920972 | 2.95818429496983 | 12.70076965928658 |
| C   | 2.93767728392721 | 6.32540302070162 | 14.92774306069173 |
| C   | 2.60031274240452 | 4.46405903928429 | 16.52659476444340 |
| C   | 4.16072246955661 | 2.62098244442370 | 16.62384507399010 |
| Si  | 3.41306615802275 | 8.93949674133919 | 14.0204849288464 |

S37
| X | Y | Z |
|---|---|---|
| 7.15274195140549 | 8.41106023780386 | 14.38269358374507 |
| 6.57194576041357 | 8.50604327357104 | 15.29155244849746 |
| 8.72723688161608 | 8.05386579206663 | 12.12652458214135 |
| 7.33902613873981 | 6.52447326604213 | 11.56722178970297 |
| 6.51802987972487 | 1.77325124236822 | 15.21194730990099 |
| 7.49854625243294 | 3.09753897006310 | 10.87761299843849 |
| 8.55714676680438 | 1.25280403759198 | 13.09870791361067 |
| 9.17447124443082 | 4.24815544603620 | 13.17307598583538 |
| 1.99606746988160 | 6.76985806275079 | 15.23768006101221 |
| 3.05421373281284 | 3.29782309450971 | 17.12395819953842 |
| 1.80085207552880 | 5.03084804564107 | 16.99224789304034 |
| 4.55074323551338 | 1.74556769630604 | 17.13073385644575 |
| 4.16184810286754 | 9.56231558514535 | 12.42654137095429 |
| 3.94444857140244 | 10.01097822692457 | 15.46155557016263 |
| 1.54095065820333 | 8.99688221976772 | 13.88262114860006 |
| 8.25349657073724 | 9.22410692914098 | 14.16794195933153 |
| 9.04722646178841 | 9.04636389888823 | 13.04451886105557 |
| 9.35266987710279 | 7.89611323380776 | 11.25605668468435 |
| 8.3936473709794 | 2.96514837308835 | 10.26466142546890 |
| 7.07066837731645 | 4.07444607106744 | 10.63892497758648 |
| 6.77247871327732 | 2.33595215111677 | 10.58326812180396 |
| 7.83525754192614 | 0.47509253401767 | 12.83746886898713 |
| 8.79546977793554 | 1.16137544528466 | 14.16112805223491 |
| 9.47812113828653 | 1.06584124529469 | 12.54021695622387 |
| 9.06966788270420 | 4.96487376745588 | 14.36629038512049 |
| 10.27755863469058 | 4.49970274891729 | 12.3541858965786 |
| 2.56727625592614 | 2.93833061715164 | 18.02319530017505 |
| 3.81840531922498 | 10.58215406345956 | 12.23384665481193 |
| 3.85649337730003 | 8.93699794368631 | 11.58455974619906 |
| 5.25279582519958 | 9.56755691630892 | 12.46370482349882 |
| 5.03045137294312 | 10.11086982467564 | 15.49375518983880 |
### 3.9 Transition-State of Configurational Inversion of 7 at PC₄ in Gas Phase

| Atom | X (Å) | Y (Å) | Z (Å) | Total energy (Eh) | Total entropy correction (Eh) | Final Gibbs free enthalpy (Eh) |
|------|-------|-------|-------|-------------------|-------------------------------|-------------------------------|
| H    | 3.612 | 3.528 | 8.56  | -2499.42595950    | -0.10038288 Eh               | -2499.5263083 Eh             |
| C    | -0.480| -0.634| 7.80  |                   |                               |                               |
| C    | -1.250| -2.329|      |                   |                               |                               |
| C    | -1.230| 11.179| 6.129 |                   |                               |                               |
| C    | 10.029| 11.241| 5.428 |                   |                               |                               |
| C    | 10.389| 1.485 | 3.964 |                   |                               |                               |
| H    | 1.117 | 12.089| 5.610 |                   |                               |                               |
| H    | -0.957| 7.807 | 11.899|                   |                               |                               |
| C    | -1.250| 10.298| 12.061|                   |                               |                               |
| H    | 1.117 | 12.089| 5.610 |                   |                               |                               |
| H    | -0.957| 7.807 | 11.899|                   |                               |                               |
| C    | -1.250| 10.298| 12.061|                   |                               |                               |
| H    | 1.117 | 12.089| 5.610 |                   |                               |                               |
| H    | -0.957| 7.807 | 11.899|                   |                               |                               |

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Transition-State of Configurational Inversion of 7 at PC₄ in Gas Phase

The transition-state of configurational inversion of 7 at PC₄ in the gas phase was calculated using grid optimization methods. The total enthalpy and entropy correction, along with the final Gibbs free enthalpy, are presented in the table above. The calculations were performed using the PBE0 def2-TZVP d3bj optts numfreq method.
## Coordinates from ORCA-job Input

| Atom | X           | Y           | Z           | X2  | Y2  | Z2  | X3  | Y3  | Z3  |
|------|-------------|-------------|-------------|-----|-----|-----|-----|-----|-----|
| P    | 6.07831248508092 | 5.02423403435716 | 14.04891990884296 |    |     |     |     |     |     |
| C    | 4.57538386858753 | 4.34970179115253 | 14.47977239401771 |    |     |     |     |     |     |
| P    | 6.04559250266479 | 7.14769024544912 | 13.76677995254079 |    |     |     |     |     |     |
| C    | 7.02019498382661 | 3.55544548486513 | 14.12959413715592 |    |     |     |     |     |     |
| C    | 3.36782034559198 | 5.02028872743597 | 14.6928444110834  |    |     |     |     |     |     |
| C    | 4.75745907934297 | 2.9601628476529  | 14.66884611185067 |    |     |     |     |     |     |
| C    | 4.29020358097905 | 7.35117175902789 | 14.26372671942259 |    |     |     |     |     |     |
| C    | 5.89962544823348 | 7.28286760781455 | 11.93926458451611 |    |     |     |     |     |     |
| C    | 4.78648002210022 | 6.84207580944277 | 11.22861887818333 |    |     |     |     |     |     |
| C    | 6.11533785246703 | 2.55871017361302 | 14.46059527764854 |    |     |     |     |     |     |
| Si   | 8.83396203844196 | 3.40524227417998 | 13.74885216527902 |    |     |     |     |     |     |
| C    | 3.31621781255788 | 6.46438923977286 | 14.57901606186927 |    |     |     |     |     |     |
| C    | 2.28053623345203 | 4.24438982574492 | 15.06438651789487 |    |     |     |     |     |     |
| C    | 3.62750897512797 | 2.21774350122133 | 15.0465956534252  |    |     |     |     |     |     |
| Si   | 8.83756933521575 | 9.18871425704498 | 14.4349853689715  |    |     |     |     |     |     |
| C    | 6.96442263153329 | 7.86062986042726 | 11.25580137133293 |    |     |     |     |     |     |
| H    | 7.82744127757923 | 8.21486422235061 | 11.81114459097766 |    |     |     |     |     |     |
| C    | 4.74116614589055 | 6.98177955235546 | 9.85211637910179  |    |     |     |     |     |     |
| H    | 3.95806915672350 | 6.38776534183834 | 11.76105758397719 |    |     |     |     |     |     |
| H    | 6.42705180363073 | 1.52370759051303 | 14.55033198278196 |    |     |     |     |     |     |
| C    | 9.14824791178469 | 4.21552214808274 | 12.09108490114200 |    |     |     |     |     |     |
| C    | 9.30523442564986 | 1.59732557874913 | 13.72121008433639 |    |     |     |     |     |     |
| C    | 9.81042635682166 | 4.32030197471881 | 15.06444783418052 |    |     |     |     |     |     |
| H    | 2.33927105836814 | 6.88893778737285 | 14.81160661030630 |    |     |     |     |     |     |
| C    | 2.41514480016504 | 2.85687235891284 | 15.2264240635253  |    |     |     |     |     |     |
| H    | 1.32024309705114 | 4.71739648166300 | 15.24265810353492 |    |     |     |     |     |     |
| H    | 3.70705814669462 | 1.14794923862870 | 15.20941782029170 |    |     |     |     |     |     |
| C    | 4.76873141415831 | 10.21705840907164 | 13.15097216866763 |    |     |     |     |     |     |
| C    | 4.38431671602783 | 9.74675760769904 | 16.14595498465568 |    |     |     |     |     |     |
| Atom | X          | Y          | Z          | Coordinates |
|------|------------|------------|------------|-------------|
| C    | 2.0267189063348 | 9.37272443157687 | 14.18988075431784 | 14.18988075431784 |
| C    | 6.92360325874311 | 7.99076278220555 | 9.87464113060036 | 9.87464113060036 |
| C    | 5.81031872251758 | 7.55496260839872 | 9.17328632346105 | 9.17328632346105 |
| H    | 3.8717846885208  | 6.63837218608110 | 9.30287373428146 | 9.30287373428146 |
| H    | 10.20603933883531 | 4.16049764224628 | 11.82194228364749 | 11.82194228364749 |
| H    | 8.86319518879224  | 5.27110889376408 | 12.11204597671098 | 12.11204597671098 |
| H    | 8.56115780903055 | 3.73283560198798 | 11.30605234871902 | 11.30605234871902 |
| H    | 8.73571104362431 | 1.06982828213738 | 12.95229043393597 | 12.95229043393597 |
| H    | 9.10559079211576 | 1.11461529830456 | 14.68085497669916 | 14.68085497669916 |
| H    | 10.36713368600077 | 1.47421618370164 | 13.49410859287336 | 13.49410859287336 |
| C    | 10.74913624549019 | 3.67826209058687 | 15.87192104989100 | 15.87192104989100 |
| C    | 9.60685630442913 | 5.68820243391961 | 15.26464453365880 | 15.26464453365880 |
| H    | 1.54783220473330 | 2.27639562140005 | 15.51834738327247 | 15.51834738327247 |
| H    | 4.49796258785007 | 11.26742322896715 | 13.28969982928096 | 13.28969982928096 |
| H    | 4.49852618838085 | 9.92663621603833 | 12.13406095707164 | 12.13406095707164 |
| H    | 5.85413945008342 | 10.13447010056115 | 13.24645673457921 | 13.24645673457921 |
| H    | 5.45782385592013 | 9.58983851538671 | 16.27943257462394 | 16.27943257462394 |
| H    | 3.86785003880905 | 9.1750058063279 | 16.92022229913807 | 16.92022229913807 |
| H    | 4.17710391351745 | 10.80916742051433 | 16.29896184817436 | 16.29896184817436 |
| C    | 1.46209642542376 | 9.08767177302105 | 12.94339760160250 | 12.94339760160250 |
| C    | 1.17395118720184 | 9.77787920928373 | 15.21637947825433 | 15.21637947825433 |
| H    | 7.75858277925364 | 8.43846299002008 | 9.34805276945514 | 9.34805276945514 |
| H    | 5.7294713947532  | 7.66111764040671 | 8.09518900239724 | 8.09518900239724 |
| H    | 10.93192561889974 | 2.61584309247182 | 15.74719263379886 | 15.74719263379886 |
| C    | 11.45922717955437 | 4.37203081739442 | 16.84232652545370 | 16.84232652545370 |
| C    | 10.30977746690911 | 6.38742507274011 | 16.23226953757502 | 16.23226953757502 |
| H    | 8.88054457057143 | 6.22776065231886 | 14.66251745028666 | 14.66251745028666 |
| H    | 2.09935796282271 | 8.76194781844532 | 12.12605657322273 | 12.12605657322273 |
| C    | 0.09831890288947 | 9.20401534171600 | 12.72949360846172 | 12.72949360846172 |
| C    | -0.19385400140431 | 9.89686458942604 | 15.00916560809709 | 15.00916560809709 |
| H    | 1.58011733737684 | 10.00494475446198 | 16.19671830878861 | 16.19671830878861 |
3.10 Input Line for NMR Calculation of NICS(0) of 5
!Grid5 FinalGrid6 HF def2-TZVP AutoAux d3bj NMR

3.11 Input Line for NMR Calculation of Phosphoric Acid
!Grid7 NoFinalgrid PBE0 def2-TZVP d3bj CPCM(Chloroform) AutoAux NMR

3.12 Input Line for NMR Calculation of 7 (S,R)
!Grid7 NoFinalgrid PBE0 def2-TZVP d3bj CPCM(Chloroform) AutoAux NMR

3.13 Input Line for NMR Calculation of 7 (S,S)
!Grid7 NoFinalgrid PBE0 def2-TZVP d3bj CPCM(Chloroform) AutoAux NMR
