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Experimental details

Materials and methods

All reactions were performed using standard Schlenk techniques under a dry argon atmosphere. Sensitive chemicals were stored and weighed in a glove box under argon atmosphere. All solvents were purified and dried by standard methods. [Na(OCP)(dioxane)_{2.5}] and [K(18-crown-6)][PCO] were synthesized by literature methods.¹⁻³ Sodium phosphide was prepared following a slightly modified literature procedure.⁴ All other reagents were used without further purification as received from commercial suppliers. NMR spectra were recorded on BRUKER 250, 300, 400 or 500 MHz spectrometers. Deuterated solvents were further dried and purified prior to use. Chemical shifts are reported in ppm relative to SiMe₄ and 85% H₃PO₄ for ¹H, ¹³C and ³¹P respectively; ¹⁹F chemical shifts are reported relative to CCl₃F. Coupling constants are given in Hz. IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR spectrometer. The IR spectra in solid state were collected using an ATR device under inert atmosphere. The absorption bands are described as follows: very strong (vs), strong (s), medium (m) and weak (w); br stands for broad. Elemental analyses were performed at the microanalysis laboratory of the ETH Zurich. X-ray diffraction measurements were performed on either an Oxford XCalibur, an Oxford Diffraction Supernova or an Enraf-Nonius kappa-CCD diffractometer. UV/Vis spectra were recorded on a UV/VIS Lambda 19 spectrometer. Positive and negative ion mode electrospray ionization mass spectra were recorded on DMF solutions (10–20 μM) on a Waters LCT Time of Flight mass spectrometer with a Z-spray source (150 °C source temperature, 200 °C desolvation temperature, 2.4 kV capillary voltage and 25 V cone voltage). The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe. Samples were introduced directly with a 1 mL SGE syringe and a syringe pump at 0.6 mL h⁻¹.

Experimental procedures

Synthesis of the sodium salt of 1,4,2-diazaphospholidine-3,5-dione Na[4a]

A solution of 2,6-diisopropylphenyl isocyanate (1.25 g, 6.6 mmol) in THF (4 mL) was added dropwise at room temperature to a solution of [Na(OCP)(dioxane)_{2.5}] (1.00 g, 3.3 mmol) in THF

(6 mL). The reaction mixture was stirred for 15 h at 50°C. The solvent was removed under reduced pressure and the obtained orange residue was washed with *n*-hexane to yield an orange-red powder, which was dried *in vacuo*. Yellow-orange crystals suitable for X-ray diffraction were obtained by slow concentration of a THF solution. Yield: 0.89 g (44%) (calculated for {Na(THF)₂[4a]} M = 604.74 g/mol).

³¹P{¹H} NMR (101.28 MHz, D₃C-CN, 25 °C): δ (ppm) = 117.2 (s);

¹³C{¹H} NMR (125.79 MHz, D₃C-CN, 25 °C): δ (ppm) = 195.8 (br d, ¹J_{PC} = 50 Hz, C=O), 153.8 (br s, C=O), 148.3 (s, C_{ipso}), 148.2 (s, C_{ipso}), 128.2 (s, C_{para}), 127.4 (s, C_{para}), 123.4 (s, C_{meta}), 123.1 (s, C_{meta}), 28.8 (s, CH), 28.3 (s, CH), 23.6 (s, CH₃), 23.5 (s, CH₃), 23.5 (s, CH₃), 23.2 (s, CH₃);

¹H NMR (250.20 MHz, D₃C-CN, 25 °C): δ (ppm) = 7.47-7.01 (m, 6H, H_{arom}), 3.74-2.95 (m, 4H, CH), 1.37-0.97 (m, 24H, CH₃);

IR (ATR): 1643 (vs, C=O), 1523 (vs, C=O), 1469 (s), 1446 (s), 1390 (s), 1060 (vs), 800 cm⁻¹ (s).

Reliable data of an elemental analysis could not be obtained, presumably due to the non-stoichiometric amount of coordinated solvent molecules. The purity was checked by ¹³C NMR spectroscopy.

UV (THF) 287 nm, 464 nm

175°C mp. (decompos.)

Reaction of sodium phosphide with two equivalents of 2,6-diisopropylphenyl isocyanate

A solution of 2,6-diisopropylphenyl isocyanate (248 mg, 1.22 mmol) in DME (1 mL) was added drop wise at room temperature to a suspension of sodium phosphide NaPH₂ (50 mg, 0.61 mmol) in DME (1 mL). After refluxing for 5 min the reaction mixture was analyzed by ³¹P NMR spectroscopy.

³¹P NMR (101.27 MHz, DME, 25 °C): δ (ppm) = -150 ppm (t, ¹J_{PH} = 207 Hz, **IM1**), -83 ppm (d, ¹J_{PH} = 240 Hz, **IM2** isomer 1), -70 (d, ¹J_{PH} = 260 Hz, **IM2** isomer 2), -388 (s, Na(OCP)).

Reaction of [K(18-crown-6)][PCO] with 2,6-diisopropylphenyl isocyanate

2,6-Diisopropylphenyl isocyanate (200 μL, 0.936 mmol) was added to a stirring pyridine solution (10 mL) of [K(18-crown-6)][PCO] (84.8 mg, 0.234 mmol). It had been previously determined that this excess was required for the reaction to go to completion. The pale yellow solution was left stirring at room temperature, and gradually turned a darker orange overnight. The solution was

analyzed by ^{31}P and ^{13}C NMR spectroscopy, and showed relatively clean formation of the spiro-phosphoranide $[\text{K}(18\text{-crown})][\mathbf{5a}]$.

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.4 MHz, pyridine, 20 °C, 85% H_3PO_4): δ (ppm) -42.7 (s, $[\text{K}(18\text{-crown-6})][\mathbf{5a}]$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, pyridine, 20 °C): δ (ppm) 179.3 (d, $^1J_{\text{PC}} = 11$ Hz; $\text{PC}(\text{O})$), 156.8 (d, $^3J_{\text{PC}} = 2$ Hz; $\text{PC}(\text{O})\text{NC}(\text{O})$).

The volume of the pyridine solution was reduced to 2 mL *in vacuo*, then diethyl ether (10 mL) was added to precipitate out an off-white solid. Electrospray ionisation mass spectrometry of a DMF solution and ^{31}P NMR spectroscopic analysis of a pyridine solution of this solid showed the presence of the five-membered ring $[\text{K}(18\text{-crown-6})][\mathbf{4a}]$ (ca. 20%) in addition to $[\text{K}(18\text{-crown})][\mathbf{5a}]$ (ca. 80%).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.4 MHz, pyridine, 20 °C, 85% H_3PO_4): δ (ppm) 120.9 (s, $[\text{K}(18\text{-crown-6})][\mathbf{4a}]$), -42.7 (s, $[\text{K}(18\text{-crown-6})][\mathbf{5a}]$).

ESI-MS (–ve ion mode, DMF): m/z 409.3 $[\mathbf{4a-CO}]^-$, 437.0 $[\mathbf{4a}]^-$, 843.2 $[\mathbf{5a}]^-$, 913.2 $\{\text{K}[\mathbf{4a}]_2\}^-$.

ESI-MS (+ve ion mode, DMF): m/z 1044.4 $\{[\text{K}(18\text{-crown-6})]_2[\mathbf{4a}]\}^+$, 1449.4 $\{[\text{K}(18\text{-crown-6})]_2[\mathbf{5a}]\}^+$.

General procedure for the reaction of $[\text{Na}(\text{OCP})(\text{dioxane})_{2.5}]$ with phenyl (2b**), cyclohexyl (**2c**) and *n*-butyl (**2d**) isocyanate in the ratio 1:8**

A solution of isocyanate (8 eq., ca. 2.64 mmol) in THF (2 mL) was added drop-wise at room temperature to a solution of $[\text{Na}(\text{OCP})(\text{dioxane})_{2.5}]$ (0.10 g, 0.33 mmol) in THF (2 mL). The solution was stirred for 1 hour at room temperature and a color change to yellow was observed. Investigation of the reaction solutions by ^{31}P and ^{13}C NMR spectroscopy revealed the formation of compounds $\text{Na}[\mathbf{5}]$, $\text{Na}[\mathbf{6}]$ and **7** and the characteristic data for these compounds are summarized in Table 8.1. In the reaction with **2b** colorless crystals were formed, which were identified by single crystal X-ray diffraction analysis as **7b**. Colorless single crystals of $[(\text{Na}[\mathbf{5c}])(\text{DME})]_{\infty}$ and $[(\text{Na}[\mathbf{5d}])(\text{THF})]_{\infty}$ suitable for X-ray diffraction were obtained by slow evaporation of the solvent at room temperature.

Table SI 1. ^{31}P and ^{13}C (carbonyl carbons) chemical shifts for Na[**5**], Na[**6**] and **7** in THF. Chemical shifts are given in ppm, coupling constants in Hz.

Reaction product	$\delta^{31}\text{P}$	$\delta^{13}\text{C}$
7b		- ^a
7c		146.7
7d		147.1
Na[6b] 15%	-16 (s)	- ^a
Na[6c] 35%	-20 (s)	192.8 (d, $^1J_{\text{PC}} = 50$) 151.6 (d, $^3J_{\text{PC}} = 2$)
Na[6d] 9%	-20 (s)	192.2 (d, $^1J_{\text{PC}} = 54$) 151.8 (d, $^3J_{\text{PC}} = 3$)
Na[5b] 85%	-64 (s)	- ^a
Na[5c] 65%	-86 (s)	175.3 (d, $^1J_{\text{PC}} = 36$) 152.8 (d, $^3J_{\text{PC}} = 6$)
Na[5d] 91%	-85 (s)	174.7 (d, $^1J_{\text{PC}} = 41$) 153.5 (d, $^3J_{\text{PC}} = 7$)

a: Due to the low solubility of the compounds Na[**5b**], Na[**6b**] and **7b** no ^{13}C NMR data is available for the carbonyl groups.

Applying [Na(OCP)(dioxane)_{2.5}] as catalyst for the trimerization of phenyl isocyanate

Phenyl isocyanate (3.90 g, 33 mmol) was added drop-wise at room temperature under vigorous stirring to a solution of [Na(OCP)(dioxane)_{2.5}] (0.10 g, 0.33 mmol) in THF (4 mL). The reaction solution was stirred for 5 min at room temperature. Triphenylisocyanurate (**7b**) was allowed to crystallize at RT over 15 hours and subsequently washed with THF and dried *in vacuo*. Yield: 3.57 g (92%).

Elemental analysis (%) calculated for C₂₁H₁₅N₃O₃: C 70.58, H 4.23, N 11.76; found: C 70.47, H 4.15, N 11.66.

The IR spectrum shows a very strong band in the carbonyl region at 1708 cm^{-1} , which corresponds to that of triphenylisocyanurate (1710 cm^{-1}).⁵ No significant peaks were observed in the ranges $1800\text{-}1720\text{ cm}^{-1}$ and $1650\text{-}1600\text{ cm}^{-1}$. Note that the carbonyl shifts of the diphenyluretdione are at 1780 and 1760 cm^{-1} , while those of diphenylmethyl iminoxadiazinedione are at 1620 , 1680 and 1735 cm^{-1} .^{6,7}

An X-ray diffraction analysis revealed the identity of **7b**. The found cell parameters for **7b** are in agreement with those reported in the literature⁵ (given in parentheses): $a = 11.06$ (11.24) Å, $b = 11.15$ (11.31) Å, $c = 11.18$ (11.49) Å; $\alpha = 91.87$ (91.12)°, $\beta = 113.61$ (115.10)°, $\gamma = 118.65$ (119.09)°.

Variable temperature NMR study on the 2,6-difluorophenyl substituted phosphoranide Na[5f]

A solution of cyclohexyl isocyanate (83 mg, 0.66 mmol) in THF (0.2 mL) was added drop-wise at room temperature to a solution of $[\text{Na}(\text{OCP})(\text{dioxane})_{2.5}]$ (25 mg, 0.08 mmol) in THF (0.3 mL). After 30 min stirring the reaction solution was transferred to an NMR tube and cooled to $-80\text{ }^{\circ}\text{C}$. At this temperature slowly a solution of 2,6-difluorophenyl isocyanate (103 mg, 0.66 mmol) in THF (0.2 mL) was added drop-wise.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, THF, $-40\text{ }^{\circ}\text{C}$): δ (ppm) = -67.4 (t, $J_{\text{PF}} = 126$ Hz);

$^{19}\text{F}\{^1\text{H}\}$ NMR (376.5 MHz, THF, $-40\text{ }^{\circ}\text{C}$): δ (ppm) = -116.53 (s, 2F), -118.65 (d, $J_{\text{PF}} = 126$ Hz, 2F^{A}), -117.39 (s, 2F), -118.95 (s, 2F); F^{B} , F^{C} and F^{D} cannot be assigned unambiguously.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, THF, $10\text{ }^{\circ}\text{C}$): δ (ppm) = -65.8 (q, $J_{\text{PF}} = 61$ Hz);

$^{19}\text{F}\{^1\text{H}\}$ NMR (376.5 MHz, THF, $10\text{ }^{\circ}\text{C}$): δ (ppm) = -118.12 (s, 2F), -118.88 (s, 2F), -119.53 (br s, 4F ($2\text{F}^{\text{A}} + 2\text{F}^{\text{B}}$)); F^{C} and F^{D} cannot be assigned unambiguously.

Isocyanate exchange experiment: Substitution of cyclohexyl isocyanate units of Na[5c] by phenyl isocyanate units to generate Na[5b]

A solution of cyclohexyl isocyanate (100 mg, 0.8 mmol) in THF (0.3 mL) was added at room temperature to a solution of $[\text{Na}(\text{OCP})(\text{dioxane})_{2.5}]$ (30 mg, 0.1 mmol) in THF (0.3 mL). A ^{31}P

NMR spectrum of the reaction mixture was recorded to ensure that the sample contains no Na(OCP). Subsequently, an excess of phenyl isocyanate (0.5 mL, 0.55 g, 4.6 mmol) was added and a ^{31}P NMR spectrum of the sample was recorded. A full conversion of the cyclohexyl-substituted phosphoranide to the phenyl-substituted phosphoranide was observed (^{31}P δ (ppm) = -64 ppm).

Generation of a TDI/Cy-phosphoranide-mixture and subsequent generation of the corresponding polyurethane with 1,4-cyclohexandimethanol. Subsequent catalytic formation of triphenyl isocyanurate (7b)

A solution of cyclohexyl isocyanate (170 mg, 1.36 mmol) in THF (0.5 mL) was added drop-wise at room temperature to a solution of $[\text{Na}(\text{OCP})(\text{dioxane})_{2.5}]$ (50 mg, 0.17 mmol) in THF (0.5 mL). After 10 min stirring at room temperature, a ^{31}P NMR spectrum of the reaction mixture was recorded to ensure that the sample contains no Na(OCP). Then a solution of toluene diisocyanate (TDI) (236 mg, 1.36 mmol) in THF (2 mL) was added drop wise at room temperature. After 5 min stirring a ^{31}P NMR spectrum of the reaction mixture was recorded, showing a broad signal (δ ^{31}P (ppm) = -60 to -75), which is assigned to a mixture of phosphoranides. To form a polyurethane, a solution of 1,4-cyclohexandimethanol (190 mg, 1.6 mmol) in THF (1.0 mL) was added drop-wise at room temperature. Immediately after the addition no change in the ^{31}P NMR spectrum was observed. After 12 h stirring at room temperature the ^{31}P NMR spectrum showed still the broad signal of the TDI/Cy-phosphoranides (δ ^{31}P (ppm) = -60 to -75). Finally an excess (0.5 mL, 0.55 g, 4.6 mmol) of phenyl isocyanate was added to the reaction mixture. After 1 h standing at room temperature a colorless crystalline material was formed which was identified by X-ray diffraction analysis as **7b**.

IR investigation after the final reaction step:

IR (ATR): 3424 (vbr, NH), 2978 (w, CH_{arom}), 2933 (w, CH_{arom}), 2856 (w, CH_{arom}), 1708 (vs, C=O), 1686 (vs, C=O), 1596 (w), 1576 (s), 1535 (w), 1506 (w), 1405 (vs), 1224 (br s, CN), 1535 (w), 1203 (s), 1060 (vs, C-O stretch), 1034 (s), 906 (s), 793 (vs), 753 (vs), 674 cm^{-1} (s).

Additional Experiment:

Reaction of sodium phosphide with phenyl isocyanate in the ratio 2:1

When a solution of phenyl isocyanate (2 eq.) in DME was added to a suspension of sodium phosphide (1 eq.) in DME, the ^{31}P NMR spectrum showed the formation of Na(OCP), Na[**4b**] (104.8 ppm), **7b** (-20.1 ppm) and Na[**5b**] (-67.2 ppm).

X-ray structure analyses

Additional structures

Crystals of both [K(18-crown-6)][**4a**] and [K(18-crown-6)][**5a**] suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a pyridine solution of the mixture of products.

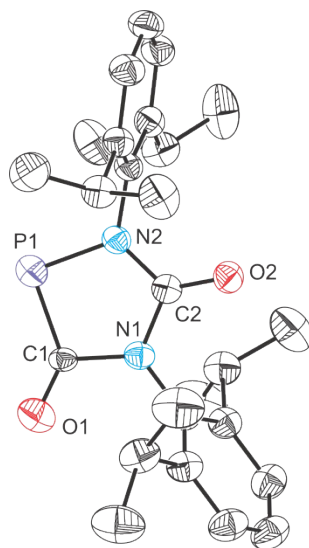


Figure S11: Thermal ellipsoid plot of the anionic moiety isolated in [K(18-crown-6)][**4a**] (thermal ellipsoids are pictured at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1: 1.778(2); P1–N2: 1.767 (2); C1–O1: 1.184(3); C1–N1: 1.501(3); N1–C2: 1.386(3); C2–O2: 1.239(3); C2–N2: 1.348(3); P1–C1–N1: 105.9(1); C1–N1–C2: 117.0(2); N1–C2–N2: 109.7(2); C2–N2–P1: 116.7(2); N2–P1–C1 90.7(1).

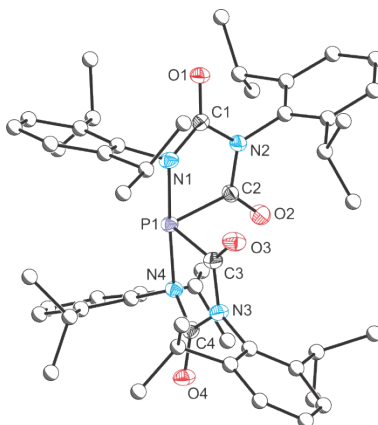


Figure SI2: Thermal ellipsoid plot of the anionic moiety isolated in [K(18-crown-6)][**5a**] (thermal ellipsoids are pictured at 50% probability level). Hydrogen atoms have been omitted for clarity and the carbon atoms from Dipp substituents are pictured as spheres of arbitrary radius Selected bond lengths (Å) and angles (°): P1–N1: 1.933(3); N1–C1: 1.340(4); C1–O1: 1.226(4); C1–N2: 1.416(4); N2–C2: 1.385(4); C2–O2: 1.215(4); C2–P1: 1.901(3); P1–N4: 1.939(3); N4–C4: 1.340(4); C4–O4: 1.233(4); C4–N3: 1.419(4); N3–C3: 1.386(4); C3–O3: 1.206(5); C3–P1: 1.906(4); P1–N1–C1: 115.4(2); N1–C1–N2: 110.2(3); C1–N2–C2: 118.1(3); N2–C2–P1: 111.0(2); C2–P1–N1: 83.15(13); P1–N4–C4: 113.8(2); N4–C4–N3: 110.6(3); C4–N3–C3: 117.8(3); N3–C3–P1: 110.4(3); C3–P1–N4: 83.59(14).

Refinement details

X-ray structure determination of [K(18-crown-6)][**4a**]

Single crystals (yellow blocks) were obtained by slow diffusion of diethyl ether into a pyridine solution of the crude reaction mixture. The X-ray data of a single crystal with the approximate dimensions of 0.10×0.12×0.2 mm was obtained at 150 K using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector (Cu K α radiation). Crystal data and refinement details: $M(\text{C}_{38}\text{H}_{58}\text{KN}_2\text{O}_8\text{P}) = 740.93 \text{ g mol}^{-1}$; crystal system: monoclinic, space group $P2_1/n$, $a = 10.7457(2) \text{ Å}$, $b = 17.6496(3) \text{ Å}$, $c = 21.5074(3) \text{ Å}$, $\beta = 99.870(1)^\circ$; $V = 4018.66(12) \text{ Å}^3$, $Z = 4$, reflections collected: 87300, independent reflections: 8414, $R(\text{int}) = 0.0508$, final R indexes [$I \geq 2\sigma(I)$]: $R_1 = 0.0627$, $wR_2 = 0.1822$, final R indexes [all data]: $R_1 = 0.0663$, $wR_2 = 0.1859$. Summary of all data: **CCDC 1049373**.

X-ray structure determination of $[\text{Na}(\text{THF})_2[\mathbf{4a}]]_\infty$

Single crystals (yellow blocks) were obtained by slow evaporation of the solvent from a solution of the compound in THF. The X-ray data of a single crystal with the approximate dimensions of $0.26 \times 0.21 \times 0.15$ mm was obtained at 120 K using an Oxford XCalibur diffractometer (Mo K_α radiation). Crystal data and refinement details: $M(\text{C}_{34}\text{H}_{50}\text{N}_2\text{NaO}_4\text{P}) = 604.75$ g mol⁻¹; crystal system: monoclinic, space group P21/n, $a = 10.6728(3)$, $b = 15.0865(4)$, $c = 21.8147(6)$ Å, $\alpha = 90.000$, $\beta = 93.643(3)$, $\gamma = 90.000^\circ$; $V = 3505.4(2)$ Å³, $Z = 4$, reflections collected: 29868, independent reflections: 7720, $R(\text{int}) = 0.0668$, final R indexes [$I \geq 2\sigma(I)$]: $R_1 = 0.0772$, $wR_2 = 0.1252$, final R indexes [all data]: $R_1 = 0.1159$, $wR_2 = 0.1396$. Summary of all data: **CCDC 986846**.

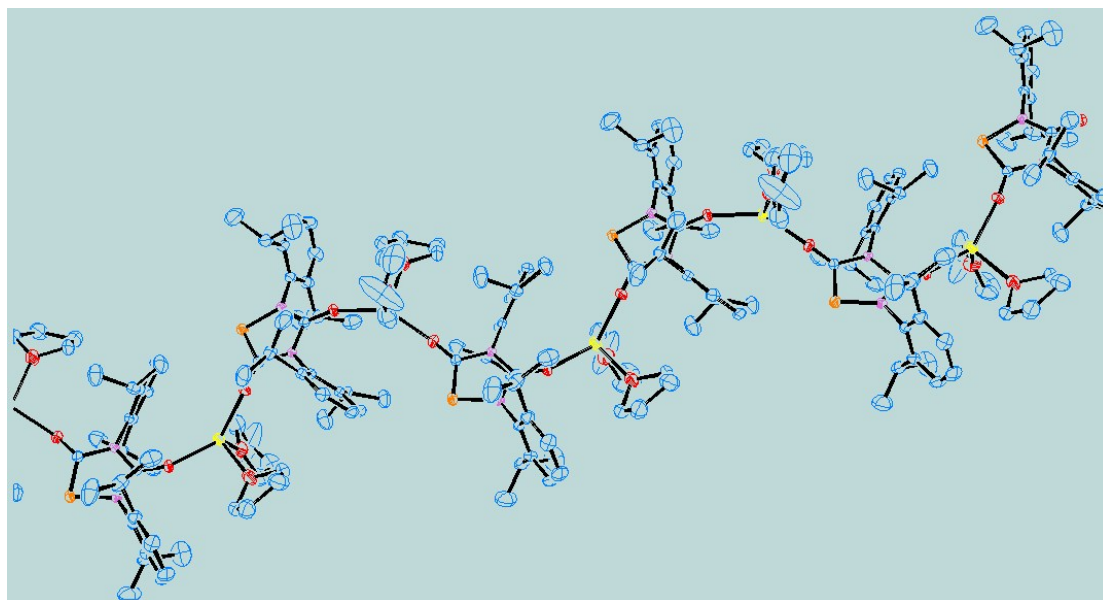


Figure SI3: ORTEP plot of $(\text{Na}(\text{THF})_2[\mathbf{4a}]]_\infty$ showing the polymeric network (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms have been omitted for clarity. P (orange), N (pink), C (blue), Na (yellow), O (red). For data see the paper.

X-ray structure determination of [K(18-crown-6)][5a]

Single crystals (yellow blocks) were obtained by slow diffusion of diethyl ether into a pyridine solution of the crude reaction mixture. The X-ray data of a single crystal with the approximate dimensions of 0.30×0.60×0.70 mm was obtained at 150 K using an Enraf-Nonius kappa-CCD diffractometer equipped with a 95 mm CCD area detector (Mo K α radiation). Crystal data and refinement details: M(C₆₄H₉₂KN₄O₁₀P) = 1147.48 g mol⁻¹; crystal system: monoclinic, space group *P*2₁, *a* = 13.2330(3) Å, *b* = 19.9093(4) Å, *c* = 13.5733(3) Å, β = 115.271(3) °; *V* = 3233.79(14) Å³, *Z* = 2, reflections collected: 19203, independent reflections: 11186, R(int) = 0.0416, final R indexes [*I* ≥ 2σ(*I*): R₁ = 0.0458, wR₂ = 0.1096, final R indexes [all data]: R₁ = 0.0550, wR₂ = 0.1168. Summary of all data: **CCDC 1049374**.

X-ray structure determination of [(Na[5c](DME))_∞]

Single crystals (colourless blocks) were obtained by slow evaporation of the solvent from a solution of the compound in DME. The X-ray data of a single crystal with the approximate dimensions of 0.08×0.05×0.03 mm was obtained at 100 K using a Bruker diffractometer (Cu K α radiation) equipped with a CMOS 100-Bruker Area detector. Crystal data and refinement details: M(C₃₂H₅₄N₄NaO₆P) = 644.75 g mol⁻¹; crystal system: orthorhombic, space group *P*2₁2₁2₁ *a* = 10.4709(3), *b* = 17.4983(5), *c* = 18.6976(5) Å, α = 90.00, β = 90.00, γ = 90.00°; *V* = 3425.8(2) Å³, *Z* = 4, reflections collected: 9948, independent reflections: 1889, R(int) = 0.0390, final R indexes [*I* ≥ 2σ(*I*): R₁ = 0.0409, wR₂ = 0.0926, final R indexes [all data]: R₁ = 0.0460, wR₂ = 0.1001. Summary of all data: **CCDC 986881**.

X-ray structure determination of [(Na[5d](THF))_∞]

Single crystals (colourless prismatic blocks) were obtained by slow evaporation of the solvent from a solution of the compound in THF. The X-ray data of a single crystal with the approximate dimensions of 0.16×0.16×0.08 mm was obtained at 100 K using a Bruker diffractometer (Mo K α radiation) equipped with a CMOS 100-Bruker Area detector. Crystal data and refinement details: M(C₄₈H₈₈N₈Na₂O₁₀P₂) = 1045.18 g mol⁻¹; crystal system: monoclinic, space group *P*21/*n*, *a* = 19.369(1), *b* = 14.674(1), *c* = 21.918(2) Å, α = 90.000, β = 111.339(2), γ = 90.000°; *V* = 5802.7(7) Å³, *Z* = 4, reflections collected: 81997, independent reflections: 8325, R(int) = 0.0740, final R

indexes [$I \geq 2\sigma(I)$]: $R_1 = 0.0503$, $wR_2 = 0.1097$, final R indexes [all data]: $R_1 = 0.0783$, $wR_2 = 0.1234$ Summary of all data: **CCDC 986854**.

Comparison of data for P-spiro anions [5a –d]⁻

5a: R = Dipp; **5b:** R = Ph; **5c:** R = Cy; **5d:** R = ⁿBu.

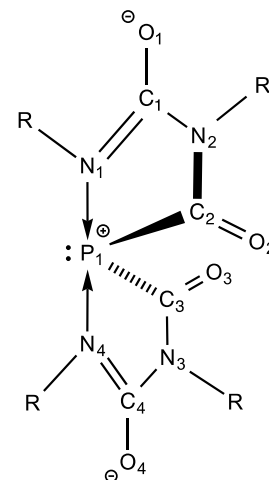
Table SI2. ³¹P and ¹³C NMR chemical shifts and coupling constants.

	δ ³¹ P (ppm)	δ ¹³ C (ppm)
K(18-crown-6)[5a]	-43 (s)	179.3 (d, ¹ J _{PC} = 11 Hz) 156.8 (d, ³ J _{PC} = 2 Hz)
Na[5b]	-64 (s)	-
Na[5c]	-86 (s)	175.3 (d, ¹ J _{PC} = 36 Hz) 152.8 (d, ³ J _{PC} = 6 Hz)
Na[5d]	-85 (s)	174.7 (d, ¹ J _{PC} = 41 Hz) 153.5 (d, ³ J _{PC} = 7 Hz)

The NMR spectrum of K(18-crown-6)[**5a**] was recorded in pyridine, the ones of Na[**5b**], Na[**5c**] and Na[**5d**] in THF. Note the different solvent is not the cause of the difference in NMR because ³¹P NMR of K(18-crown-6) [**5a**] has also been carried out in THF and given the same chemical shift at -43 ppm, though a ¹³C spectrum was not recorded on that sample.

Table SI3. Selected bond lengths (Å) for the structures of different P-spiro anions [**5a**]⁻: R = Dipp; [**5c**]⁻: R = Cy; [**5d**]⁻: R = *n*Bu. Note numbering scheme is as per the diagram below to ease comparison, as all the structures originally had different schemes.

Bond	[K(18-crown-6)][5a]	Na(DME)[5c]	Na(THF)[5d]
P1–C2	1.901(3)	1.860(7)	1.888(3)
P1–C3	1.906(4)	1.870(7)	1.884(3)
C1–O1	1.226(4)	1.255(6)	1.240(3)
C4–O4	1.233(4)	1.252(7)	1.237(3)
N1–C1	1.340(4)	1.305(7)	1.320(4)
N4–C4	1.340(4)	1.318(7)	1.312(4)
P1–N1	1.933(3)	1.941(5)	1.909(2)
P1–N4	1.939(3)	1.917(6)	1.892(2)



There is a reasonable difference in NMR between [**5a**]⁻ and the other P-spiro compounds. The $^1J_{PC}$ and $^3J_{PC}$ coupling constants are significantly lower for [**5a**]⁻ than [**5c**]⁻ and [**5d**]⁻. This can be partly rationalised by looking at the longer bond lengths of the P1–C2 and P1–C3 in [**5a**]⁻, leading to a poorer overlap of the s orbitals and a weaker Fermi contact. This could simply be due to the large steric constraints of the Dipp groups, so the whole core of the molecule is less compact. However this trend does not match the relative size of the coupling constants and bond lengths for [**5c**]⁻ vs. [**5d**]⁻ (although the large standard deviations in the [**5c**]⁻ values mean that the relevant P–C bond lengths are not statistically different between [**5c**]⁻ and [**5d**]⁻, so caution should be used in looking at the absolute values).

A better explanation can be rationalised by looking at the electronics of the system. The major resonance structure deduced in the paper spectroscopically and computationally is the one shown above, with formal negative charges on the O atoms and a positive charge on the P atom. This resonance form would be better stabilised by a smaller cation that can get close to the anionic oxygens, like a mono-solvated Na⁺. The K⁺ is sequestered by 18-crown-6, and this much larger cation cannot get as close to the oxygen atoms, particularly with the sterics of the Dipp groups. The crystal structure of [K(18-crown-6)][**5a**] shows the 18-crown-6 is puckered, with the K⁺ not

in the centre of the sequestering agent and straining to get close to the anionic oxygen, but it is still relatively far away. This means the resonance shown is less favoured. This is supported by the bond lengths in [**5a**]⁻: the C1–O1/C4–O4 are shorter and the C1–N1/C4–N4 are shorter than in [**5c**]⁻ and [**5d**]⁻ (*i.e.* less like the resonance shown).

This means there is less positive charge localised on the P atom, which explains the difference in ³¹P chemical shift and the lower magnitudes of the coupling constants.

Computational details

The computations reported in the paper were carried out with the Gaussian 09 program package.⁸ In order to decrease the computation time, the larger Dipp, Ph, n-Bu and Cy groups were replaced by methyl substituents. All structures were optimized using the B3LYP functional with the 6-31+G* basis set. Single point calculations have been performed using the B3LYP/aug-cc-pVDZ and ωB97XD/aug-cc-pVDZ levels. The difference between the results obtained with the two basis sets is negligible (2-3 kcal/mol). The ωB97XD functional includes empirical dispersion correction, which may be important in case of larger molecules, and these computations reproduced well the results obtained with the B3LYP functional. Previously very similar theoretical methods were found to be suitable for the description of comparable systems (*e.g.* the reaction of Na(OCP) with CO₂)² and it was also confirmed that the inclusion of solvent effects (PCM model with THF as solvent) does not change the energetics of the reaction significantly. The calculations have been performed with Na⁺ counter ions, for the geometrical parameters or Kohn-Sham molecular orbitals in some cases also without counter ions. At each optimized structures vibrational analysis was performed to check that the stationary point located is a minimum or first order saddle point (for transition states) of the potential energy hypersurface. At the optimized structures no instability of the wavefunction was found. The anions were proved to be stable against electron loss. At the saddle points IRC calculations were performed to locate the minima connected by the transition structure. Absolute isotropic shielding values were obtained at the GIAO/B3LYP/aug-cc-pVDZ level and the ³¹P NMR chemical shifts were determined according to a previously reported method.⁹

Total energies and geometries in Cartesian coordinates

[IA]⁻

HF=-825.000479

C	0.035460	0.341537	-0.497423
O	-0.195227	1.363911	0.032249
P	0.318517	-1.143924	-1.205712
C	2.387097	-0.705071	-1.508753
N	2.541867	-0.063036	-2.642607
O	3.108065	-1.157099	-0.641919
Na	0.567329	0.359337	-3.559129
C	3.960319	0.178930	-2.967691
H	4.017678	0.708124	-3.924818
H	4.452983	0.791386	-2.200268
H	4.523782	-0.760092	-3.053791

[IIA]⁻

HF=-1033.011217

C	0.329613	0.471852	-0.738837
O	0.725411	0.236104	0.322478
P	0.034585	0.819979	-2.421058
C	-1.761223	1.384372	-1.995804
N	-2.631981	1.156801	-3.019684
C	-4.068162	1.339174	-2.802927
O	-2.083989	1.827602	-0.901578
C	-2.150764	0.628632	-4.282431
O	-2.712783	-0.437020	-4.709927
N	-1.094393	1.250785	-4.735041
C	-0.478094	0.668777	-5.914190
Na	-1.100115	-1.627575	-3.781140

H	-1.196740	0.526086	-6.732048
H	0.328727	1.323940	-6.255218
H	-0.018490	-0.326609	-5.726386
H	-4.347087	2.390202	-2.941368
H	-4.596049	0.715502	-3.526078
H	-4.329671	1.040595	-1.785175

[III A]⁻

HF=-1241.037970

C	0.035178	-0.350600	-0.196120
P	0.052972	0.618897	1.180668
C	1.744408	0.294675	2.019200
N	2.945171	0.215554	1.357911
C	3.055892	-0.146247	-0.027231
N	3.853553	0.619616	-0.784319
C	4.487578	0.186704	-2.101132
O	5.679798	0.511066	-2.184898
O	-0.256466	-0.942137	-1.170481
O	1.681558	0.379202	3.235197
C	4.151218	0.150943	2.209759
O	2.414075	-1.145395	-0.407759
C	4.379861	1.910964	-0.311690
N	3.686477	-0.402594	-2.963226
C	4.379345	-0.724267	-4.215938
Na	1.757438	-1.426338	-2.490387
H	4.059861	-0.683399	2.910576
H	5.020819	-0.001883	1.570774
H	4.263999	1.076812	2.779659
H	5.400686	1.815462	0.065325
H	3.723712	2.315942	0.459169
H	4.402743	2.593450	-1.163151

H	3.670162	-1.189944	-4.913351
H	4.791839	0.172685	-4.699751
H	5.219973	-1.417145	-4.064095

TS(IIA|6e)

HF=-1033.014346

C	-0.057512	-0.079205	0.020002
O	-0.182677	-0.125625	1.170125
P	0.670024	-0.005866	-1.631876
C	-1.075274	-0.026802	-2.305630
N	-1.193059	0.025720	-3.700742
C	-2.527755	0.001798	-4.297152
O	-2.093781	-0.079187	-1.611617
C	-0.055794	0.033239	-4.524767
O	-0.228516	0.024360	-5.796170
N	1.080353	0.048993	-3.871072
C	2.319013	0.045966	-4.583874
Na	1.260191	-0.006665	-7.243142
H	2.460321	0.944481	-5.225130
H	3.150353	0.052160	-3.870389
H	2.464499	-0.862187	-5.211870
H	-2.511337	0.569578	-5.227582
H	-2.846066	-1.025922	-4.512674
H	-3.226625	0.441057	-3.585365

TS(IIA|4e)

HF=-1033.006848

C	0.065617	-0.112474	0.019589
N	0.008792	-0.013776	1.482706
C	1.311250	0.042091	2.180185
N	1.847635	-1.115861	2.364643

C	3.155769	-1.100487	3.002616
C	-1.179532	0.008583	2.103271
O	-2.285675	0.044779	1.581986
P	-1.251627	0.121366	4.056080
C	-0.226520	-1.161850	4.508722
O	0.312384	-2.056715	5.015121
O	1.726952	1.221823	2.471088
Na	0.881144	2.137970	4.156621
H	3.875360	-0.473288	2.455299
H	3.113221	-0.708316	4.033646
H	3.542618	-2.123092	3.049682
H	0.675628	0.707621	-0.373782
H	0.519950	-1.068273	-0.259741
H	-0.946150	-0.045723	-0.381163

TS(0|IA)

HF=-824.998222

C	0.226867	-0.133085	0.089605
P	0.100857	-0.026095	1.734622
C	2.722094	0.084672	1.848947
O	2.947512	1.234621	2.033504
O	0.308078	-0.197773	-1.091529
N	3.083561	-1.127756	1.711484
C	4.556215	-1.320130	1.806240
Na	1.281182	-2.452201	1.364536
H	4.770536	-2.384808	1.682605
H	5.081804	-0.764152	1.020698
H	4.939796	-0.996572	2.781366

TS(IA|IIA)

HF=-1032.990653

C	0.016152	-0.015336	-0.050955
O	0.011532	-0.085467	1.113185
P	0.129644	0.059840	-1.727029
C	-1.531468	1.201247	-1.901680
N	-2.408214	0.587386	-2.716586
C	-3.605180	1.405689	-2.983236
O	-1.592459	2.261865	-1.310658
C	-1.667476	0.010405	-4.580833
O	-1.760974	-1.207043	-4.562708
N	-1.402201	1.094088	-5.106866
C	-0.920701	1.166684	-6.489458
Na	-2.076661	-1.699897	-2.430482
H	-0.834619	0.182621	-6.968314
H	-1.608517	1.789235	-7.071391
H	0.059485	1.654684	-6.495799
H	-3.345229	2.325834	-3.519476
H	-4.296005	0.820849	-3.599368
H	-4.105715	1.683477	-2.048137

TS(IIA|IIIA)

HF=-1241.019128

C	-0.042893	0.196998	0.274000
P	0.120248	-0.380544	1.845665
C	1.974944	-0.164580	2.274970
N	2.910314	0.476061	1.514935
C	2.764463	0.721288	0.090468
N	2.963983	1.938814	-0.393033
C	3.198615	3.076272	0.488426
O	-0.357796	0.589979	-0.789434
O	2.210190	-0.576383	3.403042
C	4.256243	0.592302	2.105017

O	2.410077	-0.260783	-0.618062
C	4.296677	2.182291	-2.121884
O	5.284305	2.538768	-1.571279
N	3.556039	1.895031	-3.096720
C	4.197709	1.941133	-4.430107
Na	1.590119	1.048428	-2.238346
H	4.663559	-0.402865	2.309121
H	4.901273	1.110491	1.394823
H	4.211635	1.150883	3.043720
H	4.270782	3.268580	0.625547
H	2.739907	2.941791	1.475323
H	2.764417	3.971915	0.029733
H	3.485119	2.364210	-5.144302
H	5.108352	2.551063	-4.439168
H	4.452147	0.925512	-4.755102

TS(IIIa|1+7e)

HF=-1241.009877

C	0.087542	0.001449	0.050288
P	0.193596	0.084327	1.731536
C	2.123991	0.047001	1.562366
N	2.676401	-1.183766	1.259877
C	1.932698	-2.418520	1.363658
N	1.609659	-2.877524	2.564382
C	0.994760	-4.205589	2.651250
O	-0.004545	-0.249507	-1.114210
O	2.777752	1.061691	1.672723
C	4.138295	-1.320663	1.397703
O	1.712485	-3.056534	0.298934
C	1.808567	-2.153468	3.896032
O	2.251337	-2.868508	4.804824

N	1.426245	-0.903891	3.835299
C	1.604518	-0.143864	5.065412
Na	1.082467	-2.212665	-1.553306
H	4.616048	-0.458900	0.929461
H	4.428392	-1.360815	2.454364
H	4.451048	-2.238952	0.894668
H	1.501874	-4.901015	1.978857
H	-0.064364	-4.151441	2.371273
H	1.097037	-4.536826	3.684150
H	1.298562	0.893402	4.888976
H	0.997741	-0.552290	5.887250
H	2.650622	-0.143315	5.405066

[IB]⁻

HF=-1241.079137

C	0.001136	0.024678	0.032107
N	-0.047375	0.038288	1.508862
C	1.124639	-0.148485	2.212590
P	1.189008	0.016934	4.039104
C	-0.598450	0.209668	4.439380
O	-0.911062	0.338380	5.609816
C	-1.354092	0.155593	2.044538
O	-2.299446	0.205315	1.271768
N	-1.564956	0.231563	3.417684
C	-2.981789	0.360274	3.815130
O	2.190730	-0.361001	1.594580
C	1.459527	-1.916430	4.598744
N	2.662659	-2.312293	4.243811
O	0.534305	-2.432463	5.211317
C	2.955274	-3.690472	4.676587

Na	3.883232	-1.257866	2.689192
H	-3.545427	-0.496635	3.441047
H	-3.011822	0.392370	4.901731
H	-3.405003	1.273742	3.391149
H	-0.437080	-0.900949	-0.350274
H	1.044410	0.095192	-0.265475
H	-0.573104	0.867844	-0.352256
H	2.893289	-3.792599	5.768529
H	2.258179	-4.420359	4.241039
H	3.973196	-3.956636	4.365754

[IIB]⁻

HF=-1449.095220

C	0.114012	0.146164	-0.026386
N	0.001077	0.045543	1.445825
C	1.188722	0.327459	2.184436
N	1.244922	0.081790	3.550607
C	2.565092	0.320962	4.169458
C	-1.237222	-0.304245	1.927603
O	-2.131540	-0.577286	1.106409
P	-1.579182	-0.451472	3.764456
C	-2.024307	1.413772	4.088310
O	-1.111131	2.233212	4.075549
C	0.167047	-0.193160	4.396321
O	0.323736	-0.317676	5.600237
O	2.179559	0.720853	1.592488
N	-3.300348	1.705770	4.437823
C	-3.547142	3.047296	4.985706
C	-4.418858	0.812091	4.189550
O	-4.145783	-0.158475	3.383037

N	-5.527104	1.112961	4.770941
C	-6.646610	0.239027	4.476848
Na	-4.237613	-1.070590	1.521826
H	2.800201	1.387995	4.141617
H	2.506877	-0.021874	5.200010
H	3.329149	-0.227554	3.617382
H	-0.595232	0.890544	-0.394807
H	-0.124250	-0.821077	-0.474698
H	1.131001	0.441435	-0.266384
H	-2.727182	3.318810	5.653169
H	-3.601545	3.785791	4.177473
H	-4.495751	3.008794	5.517159
H	-6.473436	-0.794230	4.817537
H	-6.873009	0.188340	3.395553
H	-7.539704	0.617944	4.984486

[III^B]⁻

HF=-1657.109825

N	-0.083177	-0.008783	-0.122757
C	-0.228322	-0.347960	1.220557
N	0.883390	-0.295453	2.107025
C	2.170903	0.115785	1.827246
O	2.948976	0.340992	2.762682
C	0.577340	-0.554626	3.531873
O	-1.320537	-0.676134	1.651252
P	2.743159	0.148876	0.056588
C	3.250468	2.009392	0.002279
O	2.400641	2.854952	-0.195602
C	-1.334943	-0.040287	-0.908924
N	4.596474	2.337616	0.098789
C	4.945288	3.737928	-0.213650

C	5.559769	1.413300	0.545587
O	5.217429	0.236479	0.786625
N	6.836139	1.870412	0.679358
C	7.904556	0.865766	0.646589
Na	5.081996	0.905861	3.132336
C	7.084798	2.963214	1.702603
N	6.242717	2.855113	2.724039
C	6.426139	3.908215	3.725812
O	8.019856	3.734453	1.481750
H	-2.029537	0.714696	-0.533474
H	-1.073677	0.171991	-1.943182
H	-1.796366	-1.024578	-0.816485
H	0.461805	0.390283	4.070700
H	1.404027	-1.115185	3.967775
H	-0.347214	-1.122882	3.581809
H	4.288374	4.080751	-1.012949
H	4.806715	4.369591	0.667200
H	5.986381	3.774790	-0.529577
H	7.767737	0.203662	-0.211295
H	7.936712	0.255594	1.561050
H	8.846078	1.408905	0.546045
H	6.345536	4.914089	3.288628
H	5.655295	3.809476	4.500219
H	7.412500	3.853035	4.210052
C	1.087938	0.405539	-0.767814
O	1.083549	0.769739	-1.929640

[6e]⁻ + 7e

HF=-1657.186390

C	0.402251	1.190918	-0.042479
N	0.334002	0.673721	1.335626

C	1.472698	0.713103	2.135779
P	1.449140	0.264441	3.870999
C	-0.141506	-0.588586	3.984508
O	-0.419438	-1.245784	4.992897
C	-0.915559	0.147265	1.701909
O	-1.843502	0.194567	0.900092
N	-1.090704	-0.464013	2.941762
C	-2.426613	-1.052313	3.146967
O	2.568279	1.090978	1.623181
C	1.828766	-3.915750	4.985566
N	1.707621	-3.456475	6.288297
C	2.537654	-2.506239	6.868044
N	3.584609	-2.041269	6.048259
C	3.726116	-2.387054	4.725615
O	4.578318	-1.847932	3.998500
O	1.070309	-4.735386	4.503168
C	0.513793	-3.889718	7.036158
O	2.400022	-2.106663	8.008537
C	4.456485	-0.989124	6.588063
N	2.910484	-3.388003	4.254553
C	3.056628	-3.803251	2.853496
Na	4.098852	-0.037552	2.780458
H	-2.614671	-1.827628	2.399737
H	-2.443182	-1.478799	4.147298
H	-3.189754	-0.277738	3.042672
H	0.213359	0.385724	-0.757788
H	1.397659	1.603672	-0.189299
H	-0.360234	1.959969	-0.181436
H	-0.357260	-3.347601	6.659055
H	0.378451	-4.961089	6.889489
H	0.677119	-3.657549	8.086259

H	4.405994	-1.042794	7.673611
H	4.107620	-0.004654	6.259532
H	5.475296	-1.159361	6.239817
H	2.528633	-4.746968	2.732749
H	2.613384	-3.055613	2.187236
H	4.116052	-3.920963	2.624429

CO

HF= -113.317323

O	0.000000	0.000000	0.131333
C	0.000000	0.000000	1.268667

TS(0|B)

HF= -1241.072062

C	-0.012107	0.075924	0.003114
N	0.009691	0.019352	1.476694
C	1.300559	-0.037927	2.038346
N	1.476695	-0.084020	3.417611
C	2.886395	-0.118770	3.850752
C	-1.188532	0.060973	2.172993
O	-2.267150	0.192265	1.530926
P	-1.280903	-0.103986	3.968270
C	-1.857709	2.390950	4.709324
O	-0.894122	2.699693	5.321939
C	0.480191	-0.102964	4.423188
O	0.795082	-0.135780	5.606973
O	2.271509	-0.040075	1.290184
N	-3.014770	2.551232	4.223157
C	-3.616718	3.880267	4.523200
Na	-3.840435	0.863928	2.907659
H	3.405033	0.775459	3.497152

H	2.890964	-0.157393	4.937633
H	3.381436	-0.997630	3.431126
H	0.468160	0.994541	-0.343739
H	-1.052461	0.050032	-0.311707
H	0.537500	-0.775681	-0.402053
H	-3.742418	4.023542	5.602756
H	-3.002189	4.697477	4.127899
H	-4.600719	3.925481	4.049395

TS(II_B|II_B)

HF=-1449.072246

C	-0.542961	-0.001793	-0.025518
N	-0.194376	-0.014009	1.411350
C	1.082657	-0.379096	1.778901
P	1.648061	-0.235326	3.527644
C	0.042690	0.056251	4.394161
O	0.050326	0.089662	5.611280
C	-1.283614	0.271996	2.273148
O	-2.374522	0.500597	1.775586
N	-1.125565	0.300877	3.657722
C	-2.364412	0.590543	4.409829
O	1.905406	-0.738930	0.915503
C	1.838984	-2.170599	3.885051
N	3.034588	-2.608786	3.474712
C	4.733759	-1.581278	4.148086
N	4.661752	-1.729814	5.368702
C	5.700926	-1.215699	6.264739
O	0.895611	-2.763575	4.388444
C	3.245714	-4.040455	3.749354
O	5.250833	-1.206351	3.109271
Na	3.853807	-1.701403	1.447916

H	-3.103190	-0.190494	4.217632
H	-2.104905	0.613839	5.465632
H	-2.772280	1.550856	4.088783
H	-1.221578	-0.827656	-0.252840
H	0.379611	-0.108681	-0.590522
H	-1.041188	0.937838	-0.265313
H	3.273832	-4.234454	4.828577
H	2.445490	-4.653311	3.316511
H	4.205046	-4.346219	3.316308
H	5.248767	-0.489921	6.948722
H	6.531797	-0.736076	5.731043
H	6.091256	-2.044054	6.865168

TS(IIIB|IIIB)

HF=-1657.092347

C	-0.006395	0.020408	-0.002464
N	-0.000397	0.014623	1.476808
C	1.246525	0.036874	2.073456
P	1.384867	0.327784	3.908631
C	-0.320530	-0.254301	4.406500
O	-0.524684	-0.451910	5.591320
C	-1.270757	-0.139900	2.098015
O	-2.275140	-0.183992	1.405349
N	-1.373493	-0.253178	3.479258
C	-2.745623	-0.462874	3.984992
O	2.248224	-0.025308	1.345245
C	2.256136	-1.329009	4.374312
N	3.613994	-1.311311	4.577697
C	4.438288	-0.200307	4.209525
N	5.735968	-0.364208	4.344460
C	6.535868	0.832934	4.118263

O	1.584079	-2.334891	4.533726
C	4.204443	-2.538890	5.134575
O	3.837330	0.813087	3.720284
C	6.580692	-1.855310	2.888666
O	7.268266	-2.520700	3.579531
N	6.040090	-1.442283	1.828982
C	6.448013	-2.172740	0.600237
Na	4.438442	0.310845	1.618258
H	-3.131938	-1.421692	3.630943
H	-2.693729	-0.458245	5.071468
H	-3.393396	0.336061	3.620690
H	0.351782	-0.940534	-0.382443
H	0.658921	0.809910	-0.353918
H	-1.025365	0.195714	-0.334945
H	3.546767	-2.919786	5.917889
H	4.303122	-3.307094	4.360521
H	5.186308	-2.289182	5.529963
H	6.200654	1.668846	4.745265
H	6.516585	1.191769	3.072215
H	7.577404	0.605256	4.365732
H	6.966742	-3.112554	0.819470
H	5.553011	-2.399573	0.011867
H	7.111150	-1.540226	-0.001591

TS(III B|6e+7e)

HF=-1657.086988

C	0.572898	0.146371	0.074577
N	0.183574	0.079010	1.500700
C	1.270131	-0.159231	2.383742
N	1.055993	-0.424913	3.736653
C	2.274820	-0.794178	4.489011

C	-1.116068	0.336406	1.841538
O	-1.977751	0.521457	0.964385
P	-1.690372	0.327145	3.616865
C	-1.236389	2.184194	4.003697
O	-0.341088	2.714710	3.367776
C	-0.143376	-0.313543	4.446027
O	-0.214558	-0.584242	5.632744
O	2.395988	-0.206163	1.921399
N	-1.694455	2.655524	5.209037
C	-0.939765	3.762850	5.820428
C	-2.880778	2.227869	5.883703
O	-2.877245	2.127699	7.102664
N	-4.002808	1.975193	5.116409
C	-5.145197	1.461545	5.888328
C	-4.360643	2.763520	3.924306
N	-3.418664	2.791501	2.980780
C	-3.600726	3.850782	1.986430
O	-5.491156	3.276999	3.914563
Na	-4.028677	1.198882	1.467071
H	2.979390	0.040342	4.478701
H	1.971668	-1.024113	5.507807
H	2.745552	-1.660693	4.021281
H	1.172870	1.042653	-0.098386
H	-0.338408	0.181907	-0.516645
H	1.167004	-0.731943	-0.178628
H	0.130241	3.557385	5.752276
H	-1.152654	4.702859	5.299372
H	-1.239317	3.827779	6.865326
H	-5.576521	2.233290	6.532718
H	-4.803193	0.631465	6.508683
H	-5.909717	1.124285	5.187599

H	-3.809739	4.824381	2.449611
H	-2.683222	3.936426	1.392529
H	-4.450390	3.682089	1.290826

[IC]⁻

HF=-1127.758217

C	-0.092115	0.049800	0.002212
N	-0.064080	0.348157	1.443603
C	1.109956	0.112091	2.000041
O	2.188194	-0.279680	1.535528
P	1.063805	0.230200	3.947346
C	0.534639	1.991724	4.197045
N	1.587096	2.731200	4.633908
C	2.843448	2.048380	4.725357
O	3.859489	2.604931	5.114068
N	2.697127	0.744796	4.345921
C	3.834049	-0.177294	4.381294
O	-0.609863	2.457943	4.022783
C	1.476752	4.150159	4.958050
Na	-1.734053	1.511461	2.385867
H	4.720087	0.387584	4.675728
H	3.653977	-0.974453	5.112398
H	3.980396	-0.611625	3.389314
H	0.644983	4.304834	5.649828
H	2.418370	4.453844	5.416115
H	1.299388	4.736349	4.050750
H	-1.106771	0.212481	-0.384179
H	0.599144	0.687356	-0.567109
H	0.188652	-0.992700	-0.202439

[HC]⁻

HF=-1335.786225

C	0.016947	-0.023738	-0.019598
N	-0.007327	0.017932	1.439351
C	1.217498	0.040422	2.195017
O	2.309850	0.055154	1.647032
C	-1.160836	-0.046602	2.144192
O	-2.268756	-0.165132	1.591044
P	-0.786398	-0.034679	4.006314
N	0.937848	-0.017779	3.518569
C	2.030480	0.023620	4.485531
C	-0.873456	1.861367	4.376860
O	0.133219	2.546035	4.253283
N	-2.052532	2.322187	4.895928
C	-2.135639	3.693045	5.407859
C	-3.217674	1.502117	4.897022
O	-3.044663	0.338660	4.333821
N	-4.289645	1.996009	5.416383
C	-5.456985	1.139419	5.386479
Na	-4.163242	-0.364414	2.658971
H	2.308740	1.058547	4.710672
H	1.704961	-0.469850	5.406799
H	2.896676	-0.505475	4.080368
H	-0.555651	0.814325	-0.426207
H	-0.420361	-0.960336	-0.378832
H	1.060607	0.046556	-0.326326
H	-1.125933	4.101712	5.439546
H	-2.766752	4.304129	4.755509
H	-2.585594	3.676852	6.402071
H	-5.287050	0.157942	5.857019
H	-5.825112	0.947456	4.353684

H -6.280536 1.632942 5.912171

[III C]⁻

HF=-1543.798559

C	0.791592	-0.272864	0.356568
N	0.508410	-0.370717	1.787104
C	1.512820	-0.816839	2.707569
O	2.623388	-1.162237	2.342207
C	-0.692121	-0.014102	2.308956
O	-1.621937	0.424256	1.623455
P	-0.672671	-0.331098	4.183924
N	1.009950	-0.824756	3.974313
C	1.863362	-1.234375	5.088822
C	-0.307664	1.501532	4.682331
O	0.843920	1.862224	4.841734
N	-1.385880	2.332116	4.980630
C	-1.098850	3.655948	5.560636
C	-2.688978	1.889296	4.743133
O	-2.857325	0.738407	4.270287
N	-3.711122	2.726033	5.065711
C	-3.793789	4.042200	4.302747
N	-3.411817	3.868881	3.043658
C	-3.454634	5.105478	2.259068
C	-5.025013	2.116253	5.292534
O	-4.229178	5.019033	4.912780
Na	-3.337732	1.749733	2.112130
H	2.398958	-0.372901	5.501177
H	1.239406	-1.679538	5.869938
H	2.585008	-1.974946	4.737208
H	0.737236	0.770583	0.032863
H	0.061934	-0.860147	-0.207013

H	1.797234	-0.662393	0.198532
H	-0.155766	3.588695	6.102356
H	-1.012011	4.405823	4.769931
H	-1.913362	3.931439	6.230041
H	-4.930592	1.263588	5.968711
H	-5.500600	1.774978	4.360703
H	-5.654848	2.880748	5.751833
H	-3.048511	4.913075	1.258540
H	-4.479307	5.490867	2.148962
H	-2.863247	5.909199	2.721028

[5e]⁻

HF=-1335.787210

C	-0.027887	0.024369	0.025548
N	-0.039852	0.100921	1.405812
C	1.201330	0.024523	2.091348
O	1.280436	0.374995	3.303481
O	-1.048510	0.030233	-0.640453
P	1.738879	-0.061018	-0.722749
C	2.197056	1.781174	-0.475496
N	2.067930	2.474093	-1.624629
C	1.484372	1.784346	-2.760319
O	1.371842	2.350419	-3.843793
N	1.157531	0.535659	-2.403344
N	2.179146	-0.355115	1.288347
O	2.585220	2.324166	0.581311
Na	2.524503	2.154909	2.760507
C	-1.309198	0.227365	2.118399
C	3.521552	-0.533076	1.790087
C	0.604704	-0.371398	-3.399317
C	2.426269	3.884498	-1.724423

H	1.045166	-0.177575	-4.382452
H	0.829359	-1.400851	-3.099812
H	-0.483165	-0.259576	-3.463942
H	3.455955	4.032348	-1.387312
H	2.322303	4.168136	-2.771893
H	1.759514	4.494293	-1.105392
H	-1.086325	0.353853	3.177765
H	-1.867577	1.089253	1.741337
H	-1.918383	-0.669455	1.966683
H	4.095220	-1.099308	1.048446
H	4.070980	0.416907	1.940987
H	3.528300	-1.085453	2.737026

TS(0|IB)

HF=-1127.732242

C	-0.336673	-0.166347	0.155746
N	0.353786	-0.014190	1.430908
C	1.530843	-0.008425	1.716299
P	1.264676	0.281411	4.516516
N	-0.316236	-0.468599	4.795400
C	-1.571095	0.266146	4.733869
O	2.743673	-0.021976	1.641481
C	2.003205	-1.311483	4.877644
O	3.234487	-1.626486	4.817430
N	1.040303	-2.238853	5.217043
C	1.360602	-3.613862	5.570324
C	-0.296952	-1.781007	5.179294
O	-1.265021	-2.490916	5.458817
Na	4.194051	-0.621083	3.188439
H	-2.389759	-0.435850	4.905471
H	-1.602844	1.049337	5.502421

H	-1.690692	0.730363	3.748777
H	2.068496	-3.632923	6.404069
H	0.427202	-4.101653	5.854655
H	1.809932	-4.136533	4.718910
H	-1.009939	0.684006	0.014232
H	0.358858	-0.220570	-0.690585
H	-0.941113	-1.077893	0.186340

TS(**IB|IB**)

HF=-1335.751406

C	-0.707097	-0.004578	0.045945
N	-0.286700	0.064506	1.442943
C	1.008108	-0.076776	1.828097
P	1.130702	0.100369	3.679861
C	1.379195	-1.797201	4.044656
N	2.637603	-2.187767	3.794821
C	4.183945	-1.054349	4.715036
N	3.921194	-1.181481	5.911207
C	4.790510	-0.620810	6.949692
C	-1.244115	0.224685	2.495712
N	-0.611042	0.250644	3.709192
C	-1.382746	0.370092	4.947314
O	-2.438428	0.347605	2.280007
O	1.949299	-0.286632	1.043570
O	0.414632	-2.431431	4.466023
C	2.891023	-3.594003	4.150546
O	4.836474	-0.682915	3.756543
Na	3.749037	-1.294811	1.901979
H	-1.422636	-0.595048	5.461389
H	-0.916568	1.115159	5.600465
H	-2.393707	0.693246	4.692941

H	-0.524789	-1.006119	-0.355219
H	-0.145907	0.724109	-0.544537
H	-1.773519	0.219887	0.016011
H	2.786333	-3.755079	5.230842
H	2.190660	-4.267324	3.640928
H	3.914420	-3.857750	3.858295
H	5.681015	-0.123605	6.543716
H	5.105085	-1.427015	7.620510
H	4.216606	0.101618	7.539574

TS(IIIB|IIIB)

HF=-1543.782836

C	0.158079	-0.276742	-0.008043
N	0.129615	-0.194735	1.449462
C	1.264222	-0.198370	2.192599
P	0.818735	-0.015147	4.032496
C	0.892928	-1.889403	4.487987
N	2.087381	-2.376406	4.974543
C	3.242162	-1.555673	4.986684
N	4.363864	-2.081127	5.427605
C	5.460609	-1.142642	5.628293
C	-1.116737	-0.112569	2.157582
N	-0.881101	-0.026522	3.491012
C	-2.005032	0.054263	4.419865
O	-2.190478	-0.087707	1.575331
O	2.391365	-0.279704	1.684361
O	-0.118469	-2.572446	4.436587
C	2.105038	-3.744419	5.509450
O	3.082874	-0.373885	4.513425
C	5.160672	-3.601764	4.029601
O	5.320336	-4.549669	4.716744

N	5.186630	-2.915989	2.972120
C	5.774472	-3.613649	1.799224
Na	4.327332	-0.706164	2.665205
H	-2.326648	-0.947406	4.724094
H	-1.693551	0.616233	5.306182
H	-2.838043	0.572110	3.938516
H	0.617032	-1.218435	-0.323081
H	0.737103	0.555289	-0.418585
H	-0.874405	-0.227434	-0.354117
H	1.182200	-3.915706	6.066902
H	2.161499	-4.475516	4.696503
H	2.978636	-3.845066	6.150605
H	5.155508	-0.288746	6.246061
H	5.878725	-0.729133	4.691333
H	6.275751	-1.668132	6.135321
H	5.175488	-3.377154	0.914062
H	6.799034	-3.260508	1.631726
H	5.796105	-4.702233	1.922681

TS(IIIc|4e+7e)

HF=-1543.757079

C	-1.430777	0.208970	0.504503
N	-0.835640	0.099348	1.832851
C	0.540301	0.434879	2.048144
O	1.286444	0.741679	1.135963
C	-1.543155	-0.226288	2.932948
O	-2.736399	-0.584266	2.916556
P	-0.421745	-0.195427	4.432950
N	0.873857	0.276322	3.366812
C	2.260973	0.488914	3.792662
C	-0.707400	1.457899	5.382157

O	0.345166	1.880135	5.842706
N	-1.939852	1.761496	5.916963
C	-1.981955	2.815436	6.946909
C	-3.160926	1.611802	5.171023
O	-4.002465	0.765318	5.567922
N	-3.373666	2.434104	4.146518
C	-2.370994	3.449087	3.583450
N	-1.176775	2.933825	3.478274
C	-0.140899	3.866071	3.051200
C	-4.688001	2.427710	3.507171
O	-2.871670	4.549337	3.302750
Na	-4.339125	-0.965337	4.340464
H	2.425340	1.532372	4.072674
H	2.466370	-0.143472	4.659619
H	2.925197	0.216676	2.969520
H	-2.074062	1.093104	0.457830
H	-2.021467	-0.685597	0.293774
H	-0.615484	0.308440	-0.212224
H	-1.175915	2.635007	7.659376
H	-1.852752	3.809911	6.503394
H	-2.946209	2.755609	7.457457
H	-5.476603	2.312265	4.255053
H	-4.756444	1.610900	2.773811
H	-4.795375	3.384417	2.995057
H	0.828363	3.515020	3.424291
H	-0.077988	3.921337	1.953585
H	-0.312002	4.886473	3.420993

TS(IIB|5e)

HF=-1335.772152

C	-0.004523	-0.000801	0.003825
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N	-0.001473	-0.000743	1.467908
C	1.186697	-0.000394	2.147748
N	0.948252	0.089088	3.558944
C	2.056796	0.084024	4.510081
P	-1.452273	0.182632	2.421731
C	-1.589098	2.132286	2.361540
N	-2.704994	2.635131	2.916589
C	-2.898181	4.086485	2.964524
C	-0.343767	0.232608	3.936755
O	-0.711366	0.359489	5.117683
O	-0.658368	2.771959	1.883257
O	2.305629	-0.110844	1.679780
C	-3.865704	1.794076	3.301280
O	-4.037738	1.665484	4.568184
N	-4.533958	1.336256	2.300102
C	-5.674483	0.501114	2.651910
Na	-2.624458	1.011575	5.991312
H	1.911770	-0.712546	5.244641
H	2.971411	-0.085379	3.941462
H	2.110859	1.045757	5.028386
H	0.894122	-0.509561	-0.349990
H	-0.889840	-0.534828	-0.352908
H	-0.016483	1.025197	-0.379185
H	-6.376020	1.017697	3.324193
H	-6.206693	0.220846	1.737233
H	-5.363415	-0.423414	3.165564
H	-3.423551	4.429147	2.065034
H	-3.498161	4.325733	3.846215
H	-1.927173	4.582396	3.022384

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