

Electronic Supplementary Information

**Rearrangements and Reductive Cleavage of
3a,6a-Diaza-1,4-diphosphapentalenes**

*Yulia S. Panova, Alexandra V. Khristolyubova, Vyacheslav V. Sushev, Natalia V. Zolotareva,
Evgeny V. Baranov, Georgy K. Fukin, and Alexander N. Kornev**

*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Science 49 Tropinin
str., 603137 Nizhny Novgorod, Russia. E-mail: akornev@iomc.ras.ru*

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Experimental part

General Procedures

All preparations were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen or argon. Solvents were distilled from appropriate drying agents immediately prior to use [1]: dimethoxyethane (DME) and THF were dried and distilled over Na/benzophenone, pyridine was distilled from KOH and kept over CaH₂. Toluene and hexane were thoroughly dried and distilled over sodium prior to use. Diazadiphosphapentalene dichlorides were obtained according to previously described methods [2,3]. NMR spectra were recorded in THF-d₈, CD₂Cl₂, or C₆D₆ solutions using a Bruker AV-400 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer from 4000 to 400 cm⁻¹ in nujol or on a Perkin-Elmer FT-IR Spectrometer System 2000 as KBr mulls. Elemental analysis was performed using an Elementar vario EL cube elemental analyzer.

Table S1. The crystal data and structures refinement details for complexes **2**, **4**, and **9**.

Complex	2	4	9
Empirical formula	C ₁₄ H ₁₈ NNaO ₂ P ₂	C ₆₄ H ₉₂ N ₄ Na ₄ O ₁₂ P ₄	C ₁₆ H ₁₄ N ₂ P ₂
Formula Weight	317.22	1325.25	296.23
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> -1	<i>P</i> 2(1)/ <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	7.1413(5)	16.7757(3)	21.5266(7)
<i>b</i> , Å	10.5119(7)	21.2281(4)	5.1677(2)
<i>c</i> , Å	11.2705(8)	19.6970(4)	12.6369(4)
α , °	106.580(2)	90	90
β , °	107.348(2)	103.9970(10)	97.827(3)
γ , °	90.391(2)	90	90
<i>V</i> , Å ³	770.08(9)	6806.2(2)	1392.67(8)
<i>Z</i>	2	4	4
<i>d</i> _{calc} , Mg/m ³	1.368	1.293	1.413
μ , mm ⁻¹	0.310	0.198	0.302
<i>F</i> ₀₀₀	332	2816	616
Crystal Size, mm	0.140 x 0.050 x 0.020	0.220 x 0.210 x 0.200	0.556 x 0.080 x 0.049
θ Range for Data Collection, °	2.375 - 27.183	2.291 - 28.000	3.255 - 27.991
Index Ranges	-9<= <i>h</i> <=8 -13<= <i>k</i> <=12 0<= <i>l</i> <=14	-22<= <i>h</i> <=22 -28<= <i>k</i> <=28 -26<= <i>l</i> <=26	-28<= <i>h</i> <=28 -6<= <i>k</i> <=6 -16<= <i>l</i> <=16
Reflns Collected / unique	5745 / 5745	79557 / 16394	9820 / 1673
<i>R</i> _{int}	0.1116	0.0324	0.0375
Completeness to θ , %	99.3	99.8	99.0
Data / restraints / parameters	5745 / 84 / 224	16394 / 230 / 935	1673 / 0 / 99
<i>S</i> (<i>F</i> ²)	1.035	1.041	1.047
Final <i>R</i> Indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0770 <i>wR</i> ₂ = 0.1331	<i>R</i> ₁ = 0.0377 <i>wR</i> ₂ = 0.0951	<i>R</i> ₁ = 0.0307 <i>wR</i> ₂ = 0.0721
<i>R</i> Indices (all data)	<i>R</i> ₁ = 0.1434 <i>wR</i> ₂ = 0.1571	<i>R</i> ₁ = 0.0486 <i>wR</i> ₂ = 0.0996	<i>R</i> ₁ = 0.0394 <i>wR</i> ₂ = 0.0744
Largest Diff. Peak and Hole, e/Å ³	0.637 / -0.571	0.605 / -0.498	0.341 / -0.186

Crystal data for 2. Colorless plate-shaped crystal with dimensions 0.14 x 0.05 x 0.02 mm was a twin. Intensities of 23510 reflections were measured with a Bruker D8Quest diffractometer (ω -scans, λ [MoK α] = 0.71073 Å, μ = 0.310 mm⁻¹, $2\theta_{\max}$ = 54.36°). After merging of equivalents and absorption correction, 5745 independent reflections were used for the structure refinement with HKLF5 instruction (BASF is 0.24). Final *R* factors: *R*₁ = 0.0770 [3582 reflections with *I* > 2*s*(*I*)], *wR*₂ = 0.1571 (all reflections), GOF = 1.035.

Crystal data for 4. Brown cube-shaped single crystal with dimensions 0.22 x 0.21 x 0.20 mm was selected and intensities of 79557 reflections were measured using a Bruker D8Quest diffractometer (ω - and ϕ -scans, $\lambda[\text{MoK}\alpha] = 0.71073 \text{ \AA}$, $\mu = 0.198 \text{ mm}^{-1}$, $2\theta_{\text{max}} = 56.00^\circ$). After merging of equivalents and absorption correction, 16394 independent reflections ($R_{\text{int}} = 0.0324$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.0377$ (13699 reflections with $I > 2\sigma(I)$), $wR_2 = 0.0996$ (all reflections), GOF = 1.041.

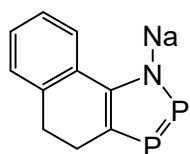
Crystal data for 9. Yellow stick-shaped single crystal with dimensions 0.56 x 0.08 x 0.05 mm was selected and intensities of 9820 reflections were measured using an Agilent Xcalibur E diffractometer (ω -scans, $\lambda[\text{MoK}\alpha] = 0.71073 \text{ \AA}$, $\mu = 0.302 \text{ mm}^{-1}$, $2\theta_{\text{max}} = 56.00^\circ$). After merging of equivalents and absorption correction, 1673 independent reflections ($R_{\text{int}} = 0.0375$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.0307$ (1423 reflections with $I > 2\sigma(I)$), $wR_2 = 0.0744$ (all reflections), GOF = 1.047.

The intensity data were integrated by SAINT [4] (for **2**, **4**) and CrysAlisPro [5] (for **9**) programs. TWINABS [6], SADABS [7] and SCALE3 ABSPACK [8] were used to perform area-detector scaling and absorption corrections for **2**, **4** and **9** respectively. The structures were solved by direct method with a dual-space algorithm using SHELXT program [9] and was refined by the full-matrix technique on F^2 using SHELXTL [10] package. All non-hydrogen atoms were refined anisotropically. The H atoms were placed in the calculated positions and refined in the 'riding model' except for the H(2A) and H(2B) atoms of the methylene group, which were located and refined isotropically from the difference Fourier synthesis of the electron density. Crystal of **4** contains a solvate molecule of DME at the common position per one molecule of Na complex. In complex **2** the carbon fragment of the heterocyclic ligand is disordered over two positions. Also, in complex **4** one carbon fragment in a heterocyclic ligand as well as some DME molecules, both fully and partially, were found to be disordered over two positions. Figures of structures of **2**, **4** and **9** were generated using the Olex2 program [11] CCDC 2090432 (**2**), 2090433 (**4**) and 2090434 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

Computation details

The geometry optimization of the isolated molecules **9-14** was performed by the density functional theory (DFT) calculations at the B3LYP/6-31+G(d) levels of theory using the Gaussian 09 software package [12]. The optimized geometries of **9-14** correspond to energy minima, as indicated by frequency computations. There are no imaginary frequencies in the calculation.

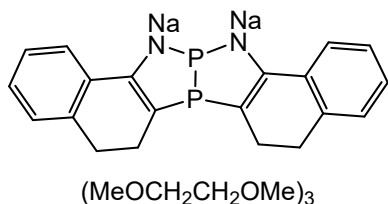
Synthesis



Sodium 4,5-Dihydronaphtho[2,1-*d*][1,2,3]azadiphosphol-1-ide (**2**).

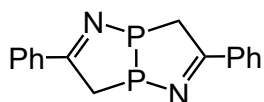
A suspension of dichloride **1** (412 mg, 0.99 mmol) in dimethoxyethane was stirred for 12 h with an excess of sodium at 20 °C. The reaction mixture was filtered, DME was replaced by diethyl ether. The reaction mixture was kept in Et₂O overnight at room temperature for better extraction of the reaction product. NaCl was filtered off, and Et₂O was replaced by toluene. The solution was concentrated and kept at 0 °C over night. The pale yellow crystals of **2** were washed with cold toluene and dried in a vacuum. Yield 0.100 g (32 %). Found (%): C, 51.63; H, 5.29; N, 4.70; P, 20.48. C₁₀H₈NNaP₂·(C₄H₁₀O₂). Calculated (%): C, 51.50; H, 5.32; N, 4.62; P, 20.43. ¹H NMR (400 MHz, THF-d₈, δ , ppm, J/Hz): 2.76-2.83 (m, 2H, 5-dihydronaphtho), 3.10-3.18 (m, 2H, 4-dihydronaphtho), 3.28 (s, 6 H, 2 CH₃O-), 3.44 (s, 4 H, 2 CH₃O-CH₂-), 6.92-6.98 (m, 1 H, Ph), 7.09-7.16 (m, 2 H, Ph), 7.82-7.87 (m, 1 H, Ph). ³¹P {¹H} NMR (162 MHz, THF-d₈, δ , ppm, J/Hz): 254.0 (d, $J = 453$), 312.7 (d, $J = 453$). ³¹P NMR (162 MHz, THF-d₈, δ , ppm, J/Hz): 254.0 (dt, $J = 453.0, 5.6$), 312.6 (d, $J = 453.4$). IR spectrum (liquid

paraffin), ν/cm^{-1} : 1597 w, 1423 m, 1313 w, 1261 w, 1251 w, 1221 w, 1205 w, 1192 w, 1163 w, 1124 m, 1102 m, 1080 w, 1063 s, 1032 m, 1011 m, 975 w, 965 w, 947 w, 938 w, 918 w, 892 w, 857 s, 843 m, 820 s, 770 s, 736 s, 697 s, 656 m, 642 w, 576 m, 511 w, 484 w.



N, N'-disodium salt of annelated 1,6-diaza-3a,6a-diphosphapentalene 4.

To a suspension of dichloride **1** (417 mg, 1.0 mmol) in 15 ml of dimethoxyethane a solution of sodium naphthalene prepared [13] from 143 mg of naphthalene (4 equiv.) in 15 ml of the same solvent was added at 0 °C. After dissolving (reacting) the entire amount of dichloride (~ 10 min), 50 % of the solvent was removed in vacuum. The separated red crystals of the product were dried in a vacuum. Yield 31 mg (5 %) **4**. Found (%): C, 57,94; H, 7,08; N, 4,15, C₄₀H₃₂N₄P₄Na₄·(C₄H₁₀O₂)₆. Calculated (%): C, 58,00; H, 7,00; N, 4,23. ¹H NMR (400 MHz, THF-d₈, δ , ppm, J/Hz): 6.79-8.17 (m, 8H), 3.44 (s, 12H, CH₂, 3DME), 3.28 (s, 18H, CH₃, 3DME), 2.43-3.21 (m, 8H, CH₂CH₂CP). ³¹P {¹H} NMR (162 MHz, THF-d₈, δ , ppm, J/Γ_{C}): 138.8 (d, $J=165$), 20.3 (d, $J=165$). IR spectrum (liquid paraffin), ν/cm^{-1} : 1663 w, 1576 w, 1561w, 1490 w, 1299 m, 1276 w, 1245 w, 1234 w, 1193 m, 1127 m, 1113 m, 1083 s, 1026 m, 979 w, 938 w, 903 w, 859 m, 840 m, 820 w, 777 w, 765 m, 738 s, 689 m, 646 w, 564 w, 517 w, 464 w.



2,5-diphenyl-3H,6H-1,4-diaza-3a,6a-diphosphapentalene (9).

To a solution of dichloride **5** (103 mg, 0.28 mmol) in 15 ml of THF, a solution of sodium-naphthalene prepared [13] from 143 mg of naphthalene (1.12 mmol, 4 equiv) in 15 ml of the same solvent was added at -10 °C. The color of the reaction mixture changed from yellow to dark red. To the resulting solution 20 mg (1.12 mmol, excess) of water (an aliquot of the THF solution) was added. THF was replaced with toluene; the precipitated NaCl was filtered off. Toluene and naphthalene were removed in vacuum at 30 °C for 60 min. Crystalline product **9** (12 mg, 14 %) was isolated from the oily residue, washed with cold THF, dried in vacuum. Found (%): C, 65,28; H, 4,06; N, 9,58; P, 21,10. C₁₆H₁₂N₂P₂. Calculated (%): C, 65,31; H, 4,11; N, 9,52; P, 21,05. ¹H NMR (400 MHz, CD₂Cl₂, δ , ppm, J/Hz): 8.25 – 6.75 (m, 10H, Ph), 3.45 (m, 4H, CH₂). ³¹P {¹H} NMR (162 MHz, THF-d₈, δ , ppm, J/Hz): 98.5 (s). IR spectrum (liquid paraffin), ν/cm^{-1} : 1589 m, 1565 m, 1313 w, 1266 m, 1177 m, 1153 w, 1124 w, 1073 w, 1026 w, 985 m, 925 m, 834 m, 819 w, 804 w, 757 s, 751 s, 739 s, 692 s, 621 w, 553 m, 485 m.

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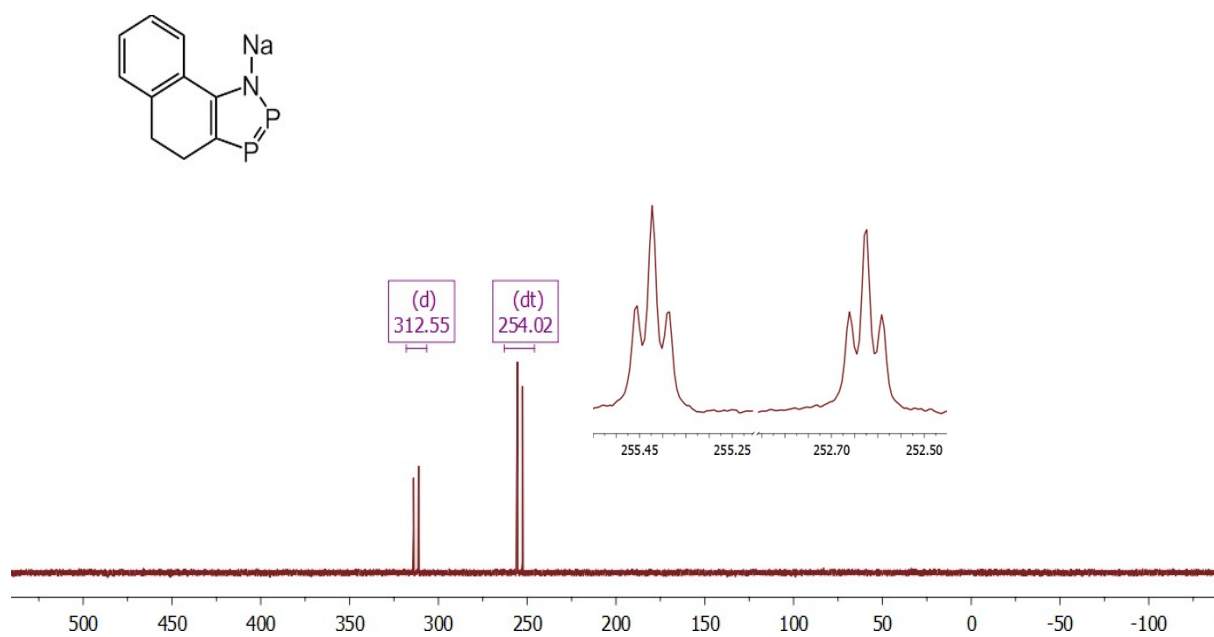


Figure S1. ^{31}P NMR spectrum of **2** in THF- d_8 . δ , ppm: 312.7 (d, $J = 453$ Hz); 254.0 (dt, $J = 453.0, 5.6$ Hz).

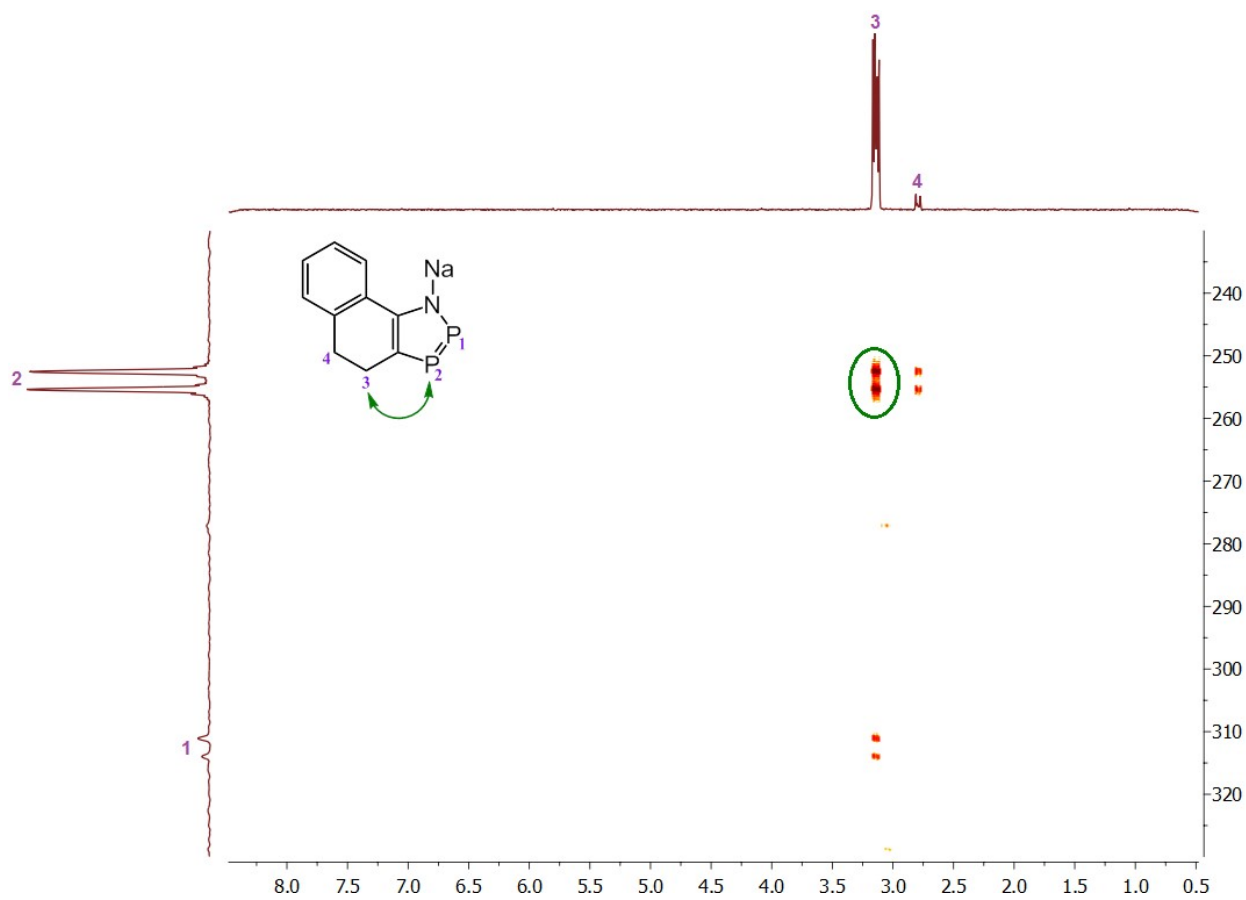


Figure S2. ^1H - ^{31}P correlation for **2**.

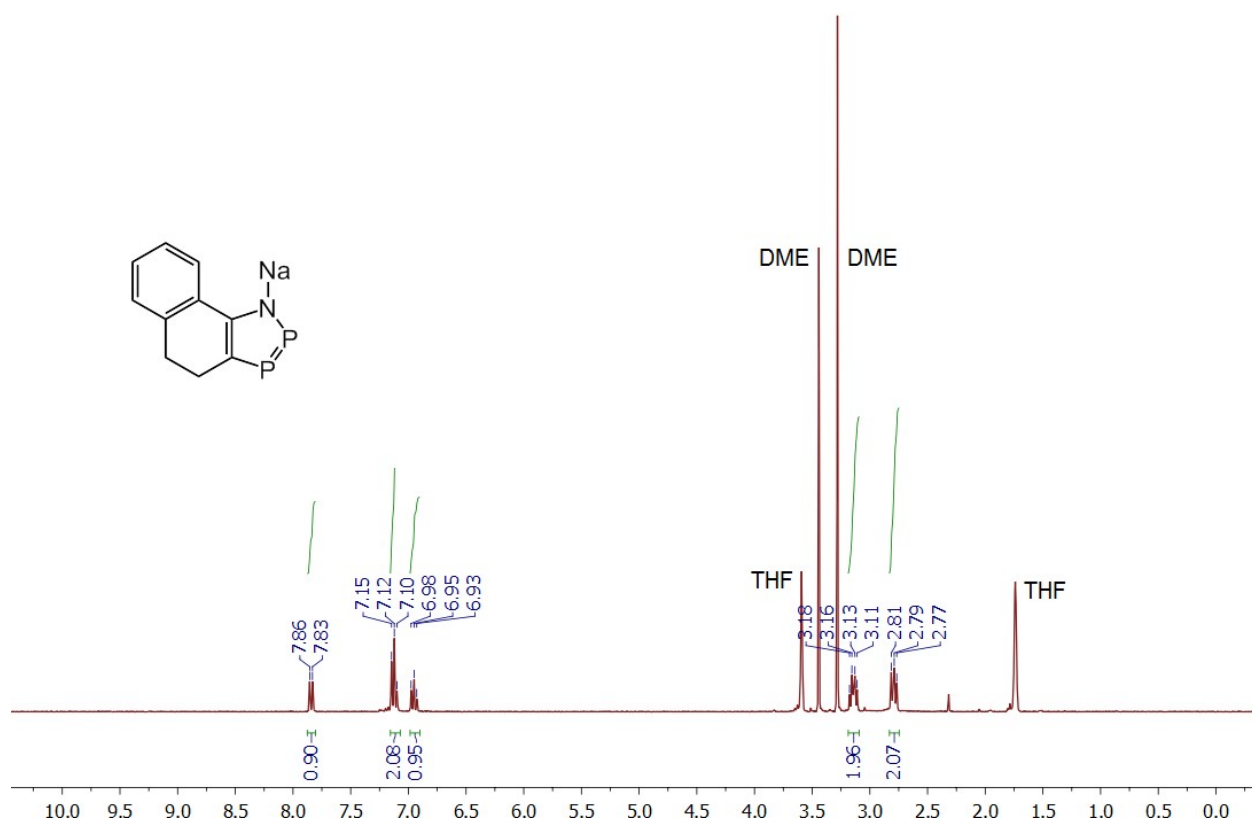


Figure S3. ¹H NMR spectrum of 2 in THF-d₈.

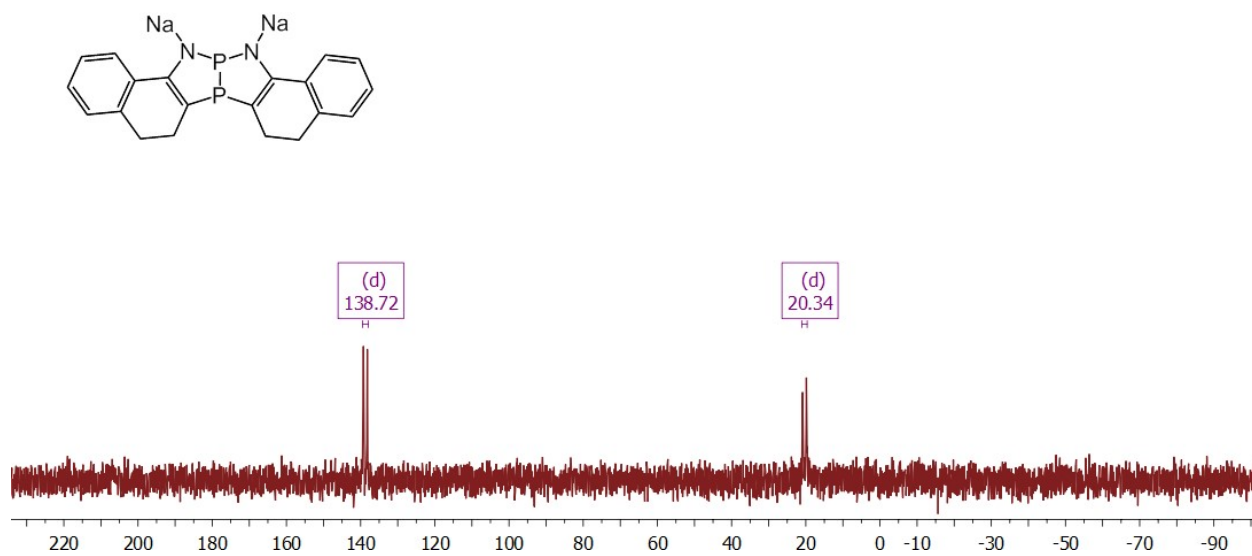


Figure S4. ³¹P{¹H} NMR spectrum of 4. δ , ppm: 138.8 (d, $J=165$ Hz), 20.3 (d, $J = 165$ Hz).

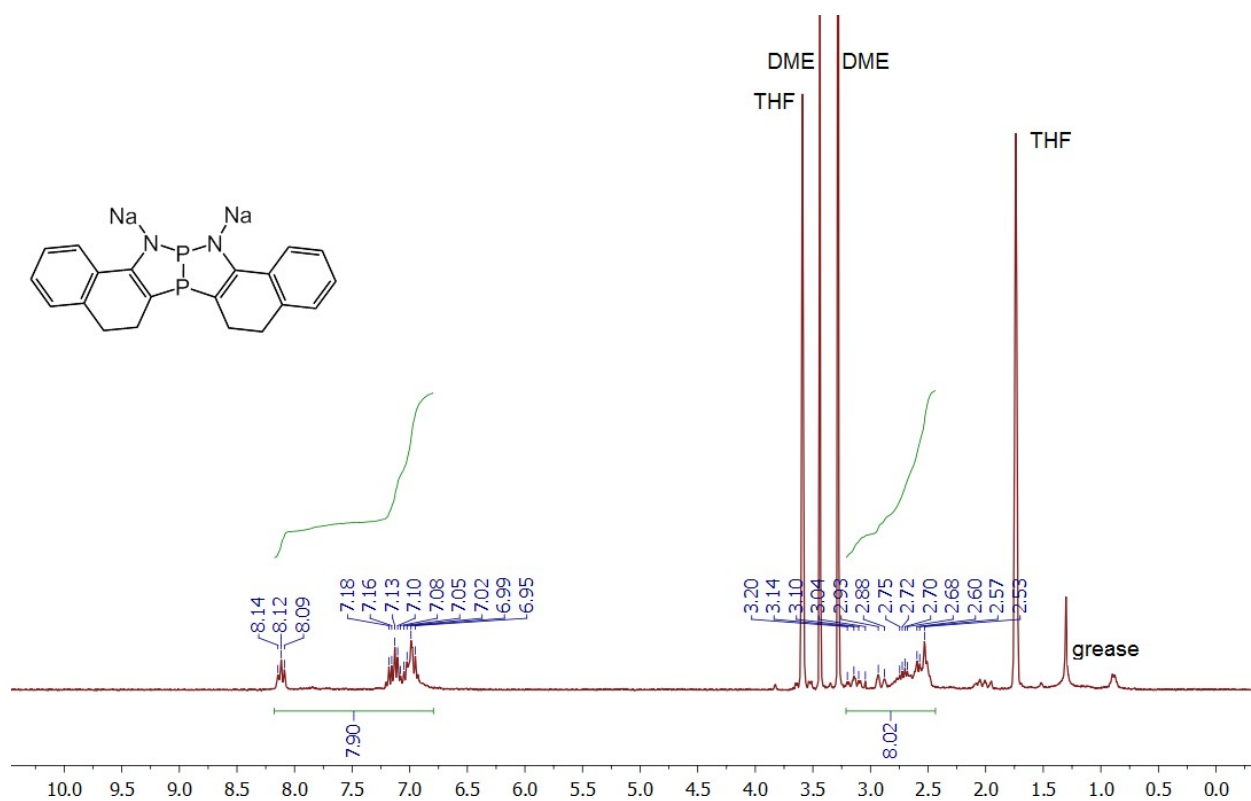


Figure S5. ¹H NMR spectrum of 4.

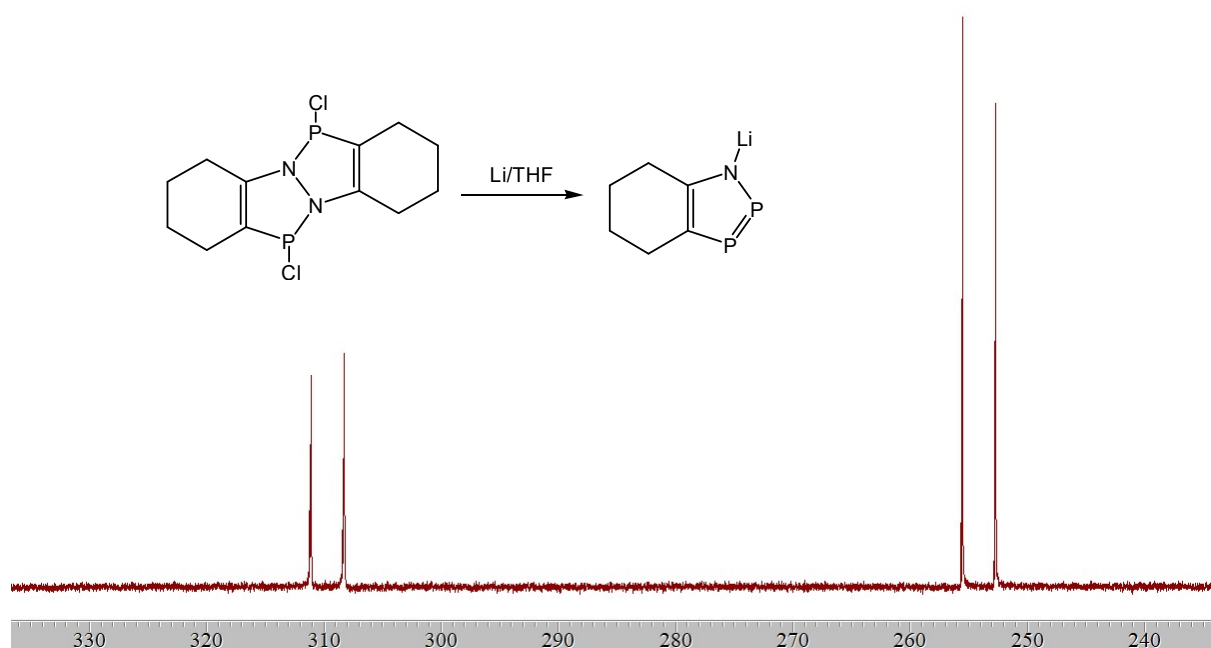


Figure S6. ³¹P{¹H} NMR spectrum of the reaction mixture after 3 h of stirring a solution of cyclohexane-annulated 1,4-dichloro-3a,6a-diaza-1,4-diphosphapentalene in THF with metallic lithium. The product was not characterized as a pure compound. δ , ppm: 309.7 (d, $J_{P,P} = 458$ Hz), 254.3 (d, $J_{P,P} = 458$ Hz).

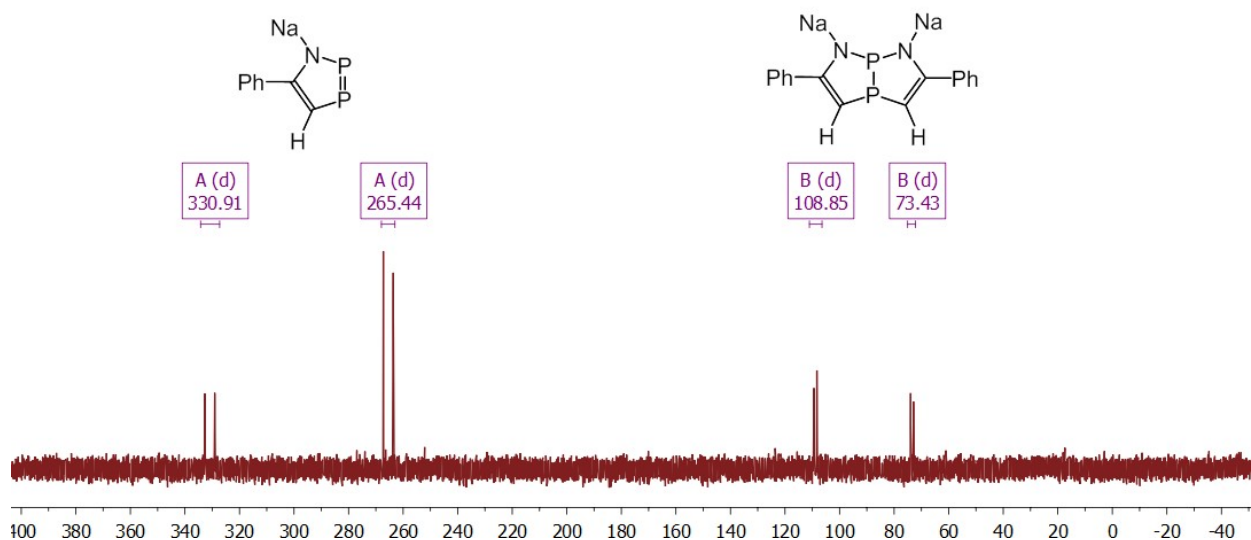


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture **5** + $(\text{Na}/\text{C}_{10}\text{H}_8)/\text{THF}/20\text{ }^\circ\text{C}/3\text{h}$. δ , ppm: 330.9 (d, $J_{\text{P,P}} = 444$ Hz), 265.4 (d, $J_{\text{P,P}} = 444$ Hz); 108.8 (d, $J_{\text{P,P}} = 130$ Hz), 73.4 (d, $J_{\text{P,P}} = 130$ Hz).

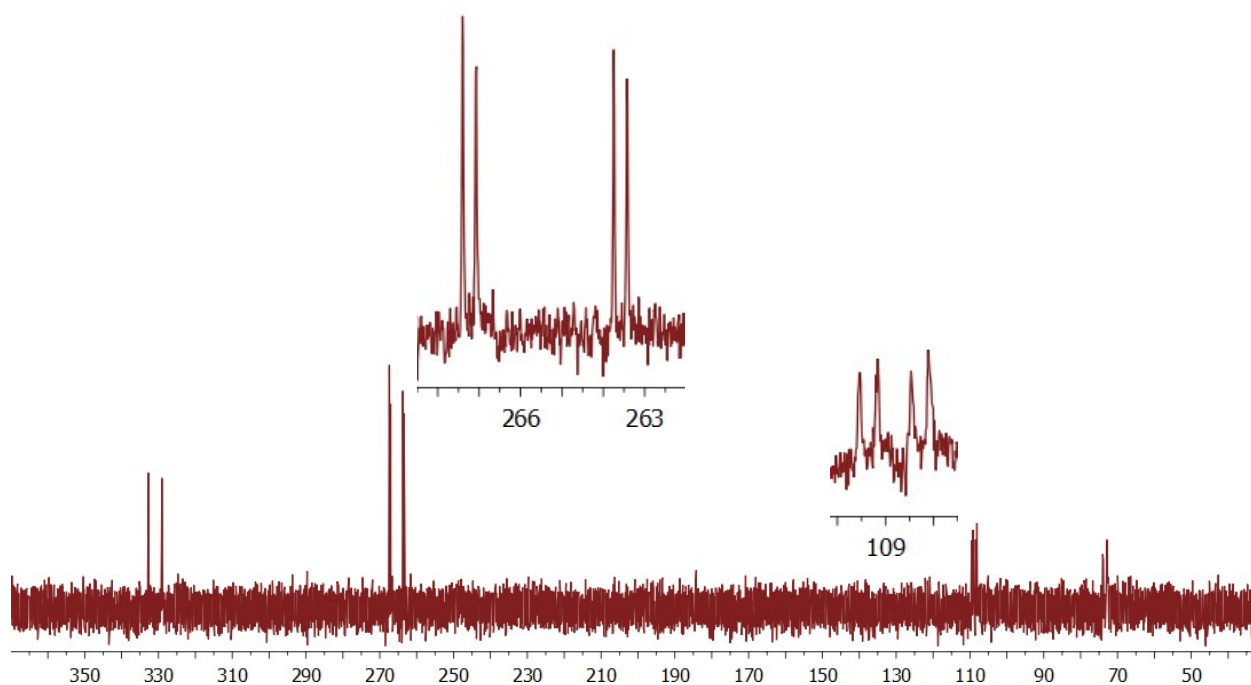


Figure S8. ^{31}P NMR spectrum of the reaction mixture **5** + $(\text{Na}/\text{C}_{10}\text{H}_8)/\text{THF}/20\text{ }^\circ\text{C}/3\text{h}$. δ , ppm: 330.9 (d, $J_{\text{P,P}} = 444$ Hz), 265.4 (dd, $J = 444$, $^2J_{\text{H,P}} = 39$ Hz); 108.8 (dd, $J_{\text{P,P}} = 130$, $^2J_{\text{H,P}} = 45$ Hz), 73.4 (d, $J = 130$ Hz).

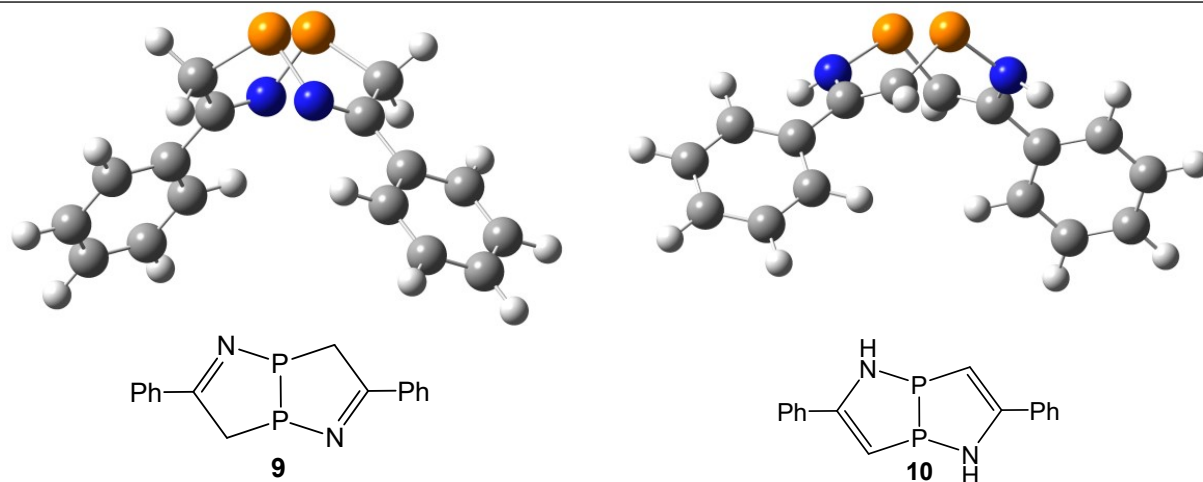
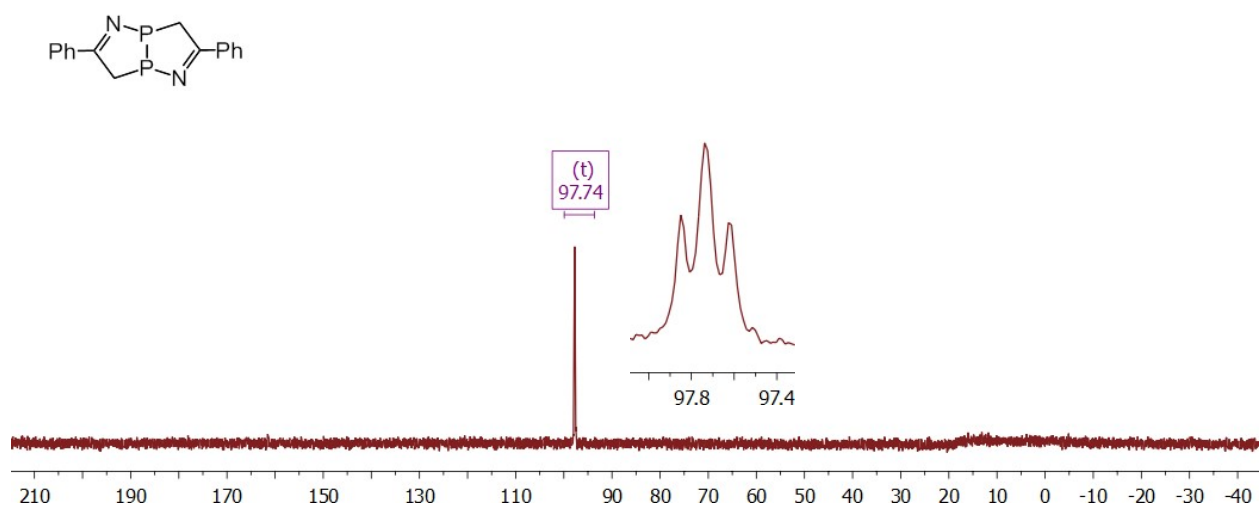
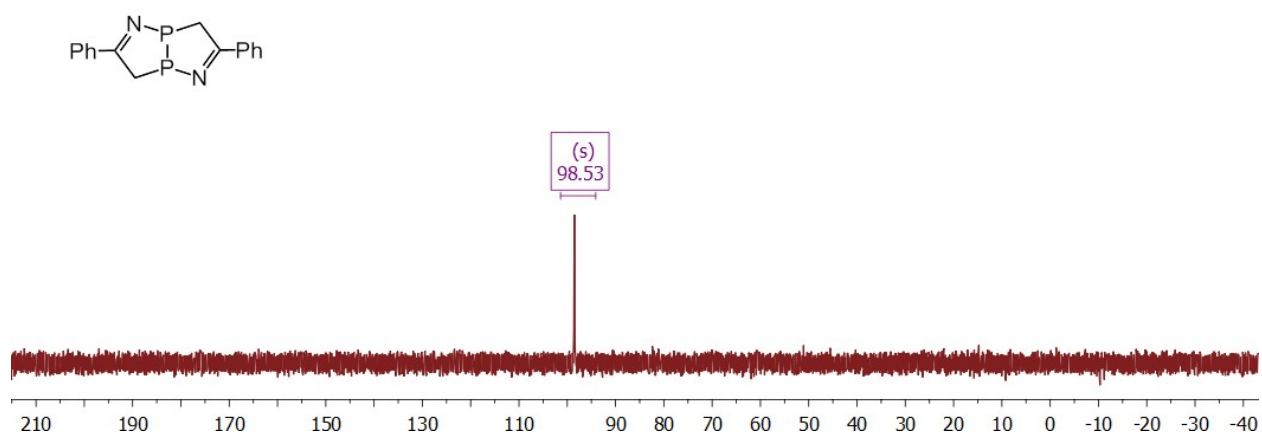


Figure S11. DFT/B3LYP 6-31G(d) optimized geometries of isomer molecules **9** and **10**.

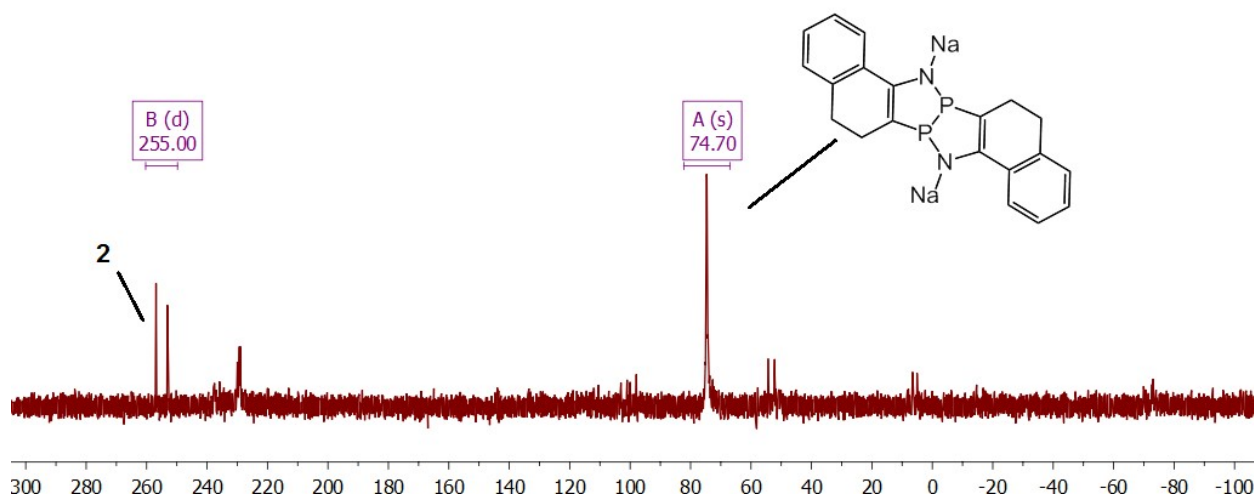


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture **1** + Na/DME/0 °C/15 min.

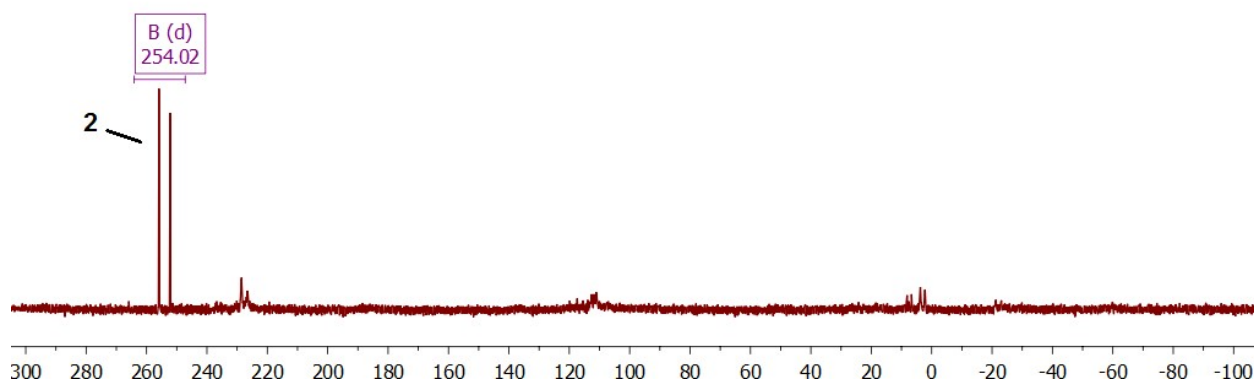


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture **1** + Na/DME /0 °C/90 min.