Synthesis of a Diniobium Tetraphosphorus Complex by a 2(3–1) Process

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January 11, 2012

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S.1 Synthetic details

S.1.1 General information

All manipulations were performed in a Vacuum Atmospheres model MO-40M glovebox under an inert atmosphere of purified N_2. All solvents were obtained anhydrous and oxygen-free by bubble degassing (N_2) and purification through columns of alumina and Q5. 1,3-Cyclohexadiene was purchased from Aldrich, dried over $NaBH_4$,[1] and then vacuum transferred into a fresh flask, brought into the box where it was stored at −35 °C over molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Labs. Benzene-d_6 was degassed and stored over molecular sieves for at least 2 days prior to use. Celite 435 (EM Science) was dried by heating above 200 °C under dynamic vacuum for at least 24 h prior to use. All glassware was oven-dried at temperatures greater than 150 °C prior to use. NMR spectra were obtained on Varian Inova 300 and 500 instruments equipped with Oxford Instruments superconducting magnets or on Bruker Avance 400 instruments equipped with Magnex Scientific superconducting magnets. ^{1}H and ^{13}C NMR spectra were referenced to residual benzene-d_6 (^{1}H = 7.16 ppm, ^{13}C = 128.06 ppm, respectively). ^{31}P NMR spectra were referenced externally to 85% H_3PO_4 (0 ppm). Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN. For Raman studies, an Invictus solid-state laser at 785 nm, manufactured by Kaiser Optics, was routed through fiber-optic cables to a Hololab series 5000 Raman Microscope. The Raman scattering was observed *via* 180 ° reflectance through the objective of the Raman microscope. Each spectrum was corrected for dark current and cosmic ray interference using the Hololab software. IR spectra were collected on a Bruker Tensor 37 FT-IR spectrometer.

S.1.2 Synthesis of $P_4Nb_2(ODipp)_6$ ($P_4\mathbf{1}_2$)

A 250 mL round bottom flask equipped with a Teflon-coated stir-bar was charged with IMo(N[^{t}Bu]Ar)$_3$ (0.788 g, 1.05 mmol) and Et_2O (50 mL). Next, [Na(THF)$_3$][**1**-P_3] (1.00 g, 1.05 mmol) was added as a solid to the stirring solution of IMo(N[^{t}Bu]Ar)$_3$. The reaction mixture was stirred vigorously for 5 h, after which the brown reaction

mixture was filtered through a pad of Celite to remove the white solids formed during the reaction time. Volatile materials were removed under vacuum from the filtrate, providing a solid dark brown residue which was then dissolved in the minimum amount of THF (4 mL), and the solution so obtained was cooled for 20 h at −35 °C. The resulting yellow crystals of PMo(N[^{t}Bu]Ar)$_3$ were collected by suction filtration using a pre-chilled sintered frit, washed with 0.5 mL thawing THF and brought to constant mass (547 mg, 0.832 mmol, 79%) under reduced pressure. All volatile materials were removed under vacuum from the red-brown filtrate, and the residue triturated with *n*-hexane (2 × 1 mL) to remove traces of THF. This material was redissolved in 1 mL diethyl ether and 3 mL *n*-pentane and the solution was placed in the glovebox freezer at −35 °C for 12 h. The dark red blocks of P$_4$**1**$_2$ that formed were collected by suction filtration, washed with the minimum amount of cold *n*-pentane, and brought to constant mass (419 mg, 0.305 mmol, 58%) under vacuum. The volatile materials were removed from the filtrate under reduced pressure, and the dark-red residue was redissolved in 4 mL *n*-pentane and placed in the the freezer at −35 °C for 12 h. A second crop of dark red crystals was collected by suction filtration (94 mg, 0.068 mmol, 13%), bringing the total yield to 513 mg, 0.373 mmol, 71%. Similar yields were obtained when the synthesis was carried out on a larger scale (5.25 mmol [Na(THF)$_3$][**1**-P$_3$]). Elem. Anal. Calcd(found): for $C_{72}H_{102}Nb_2O_6P_4$: C 62.97(62.77), H 7.48(7.69), P 9.02(8.91), where in parenthesis are the found values.

^{1}H NMR (benzene-d_6 300 MHz, 20 °C) δ: 1.15 (d, 72 H, $^1J_{HH}$ = 6.7 Hz), 3.75 (sep, 12H, $^1J_{HH}$ = 6.7 Hz), 6.88–6.98 (m, 18H). ^{13}C{^{1}H} NMR (benzene-d_6, 20 °C, 125.8 MHz) δ: 24.46 (Me), 28.42 (C*H*Me$_2$), 123.93 (Ar), 124.41 (Ar), 138.52 (Ar), 160.80 (Ar) ppm. ^{31}P{^{1}H} NMR spectrum (benzene-d_6, 20 °C, 121.5 MHz) δ: 123.9 (s) ppm. FT-IR (KBr pellet): 453, 592, 702, 749, 792, 864, 898, 934, 1043, 1097, 1112, 1196, 1253, 1326, 1360, 1381, 1431, 1460, 1587, 2866, 2923, 2951, 3057, 3413 cm^{-1}. (see Figure S.2). Raman (785 nm excitation): 421, 487, 547, 603, 710, 878, 911,1045, 1108, 1193, 1253, 1329, 1431, 1585, 1689, 1738, 1783 cm^{-1} (see Figure S.1).

The Raman breathing mode of the *cyclo*-P$_4$ ligand for the truncated model P$_4$Nb$_2$(OH)$_6$ was calculated to arise at 433 cm^{-1}. The P$_4$Nb$_2$(OH)$_6$ model was built and optimized

using DFT methods,[2] maintaining frozen coordinates for the P_4Nb_2 core. The Raman spectrum was calculated using the numerical frequency routine of ORCA. Attempts to collect Raman data using a 633 nm laser were not successful because the sample was burned even at low laser power values (0.1% of total laser power).

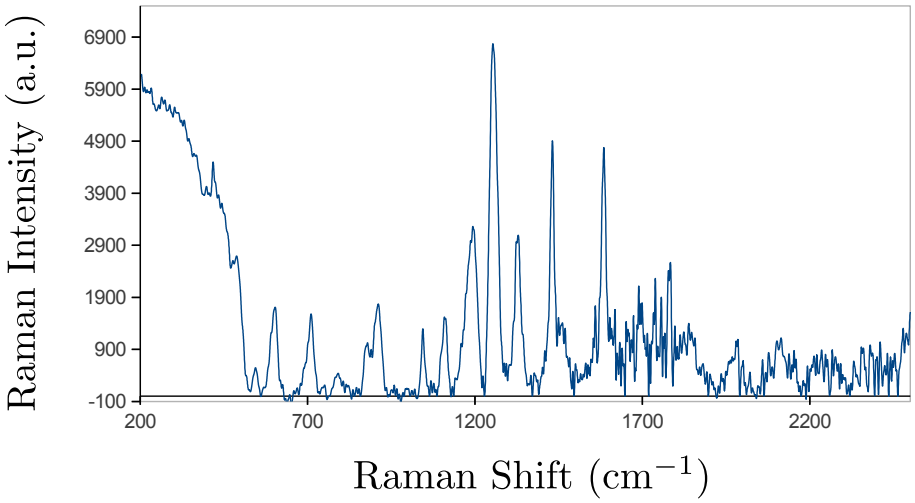


Figure S.1: Raman spectrum of solid $P_4\mathbf{1}_2$, acquired using an Invictus solid-state laser at 785 nm.

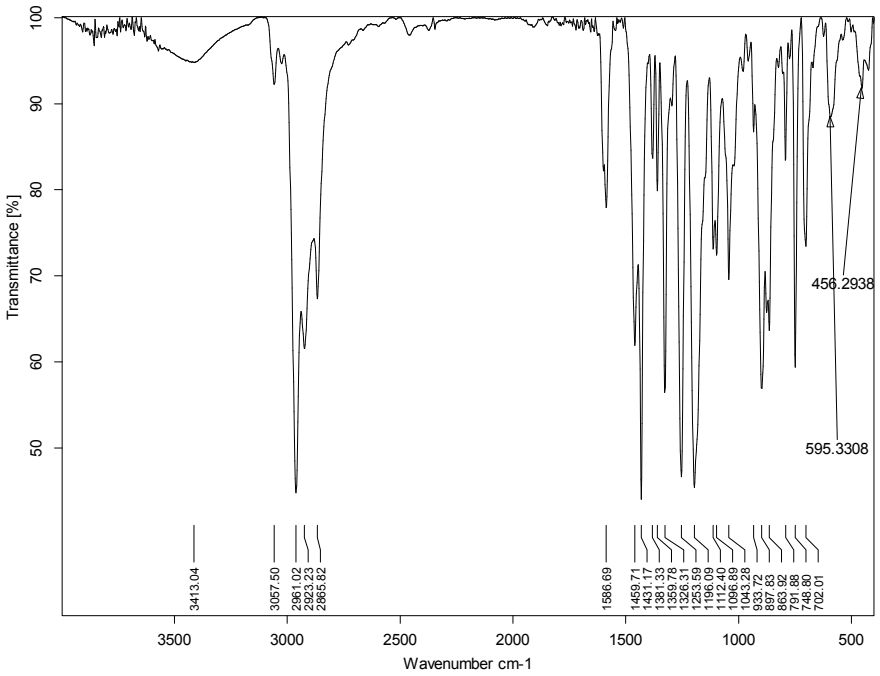


Figure S.2: IR spectrum of $P_4\mathbf{1}_2$ in a KBr pellet.

S.1.3 *In-situ* generation of $C_6H_8P_2Nb(ODipp)_3$ (**1**-$P_2C_6H_8$)

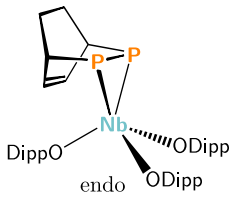


Figure S.3: Proposed structure of the adduct $C_6H_8P_2Nb(ODipp)_3$ (**1**-$P_2C_6H_8$).

Four independent experiments were performed in the following way: Solid $IMo(N[^tBu]Ar)_3$ (20 mg, 0.026 mmol), solid $[Na(THF)_3][\mathbf{1}\text{-}P_3]$ (25 mg, 0.026 mmol) and 1,3-cyclohexadiene (1 mL) were placed in a 25 mL scintillation vial and the mixture was stirred vigorously for either 50 min (experiment 1 and 2), 75 min (experiment 3) or 90 min (experiment 4). After the reaction time elapsed, the mixture was observed to have became brown and cloudy. Next, PPh_3 was added to the reaction mixture as a 0.278 M stock solution prepared by dissolving 100 mg PPh_3 in 1200 mg benzene

(78 mg, 0.024 mmol for experiment 1; 91 mg, 0.028 mmol for experiments 2, 3 and 4). The mixture was quickly transferred into an NMR tube and frozen, and the tube was flame-sealed and placed in an NMR probe pre-cooled to 0 °C for NMR analysis. $^{31}P\{^{1}H\}$ NMR (1,3-C_6H_8, 0 °C, 202.4 MHz) δ: −69 (s) ppm. The measured yields for generation of **1**-$P_2C_6H_8$ ranged from 45% to 77% (see below).

To accurately measure the peak intensities, inverse-gated proton decoupled ^{31}P NMR spectra were acquired.[3] A delay time (d1) of 10 seconds was applied between acquisitions to allow complete relaxation of the ^{31}P nuclei. The measured spectra for all four experiments are shown below, in Figures S.4, S.5, S.6 and S.7. The reaction time, the percent of [Na(THF)$_3$][**1**-P_3] consumed (completion percent), and the observed yield of formation of **1**-$P_2C_6H_8$ for the four experiments are summarized in Table 1. The ^{13}C NMR spectrum was also measured for the reaction mixture produced in experiment # 2 (see Figure S.8).

Exp.	Time (min)	PPh_3 (mg)	Completion (%)	Yield (%)
1	50	6	77	58
2	50	7	69	77
3	75	7	75	69
4	90	7	88	45

Table 1: Summary of reaction parameters and observed yields for experiments 1–4.

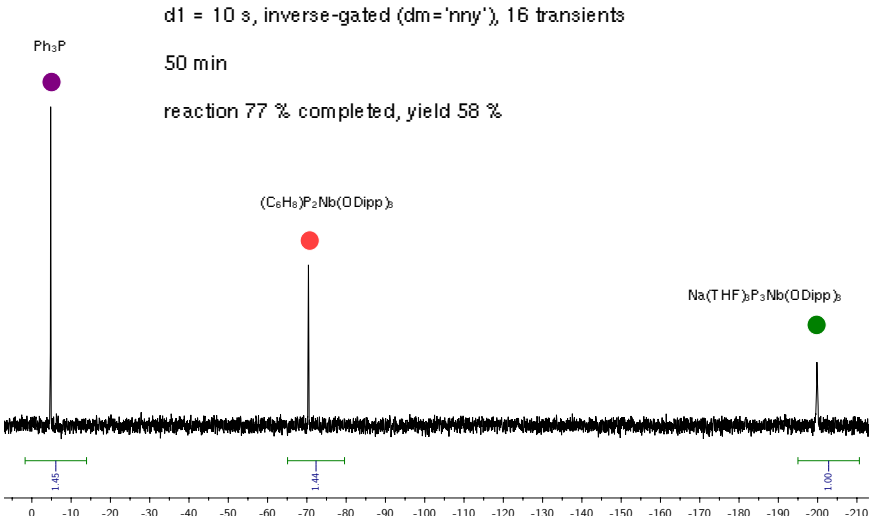


Figure S.4: Experiment 1 (t = 50 min): Inverse-gated $^{31}P\{^{1}H\}$ NMR spectrum (1,3-C_6H_8, 0 °C, 202.4 MHz) of **1**-$P_2C_6H_8$ formed *in-situ*, with PPh_3 as standard, delay time of 10 seconds, 16 transients.

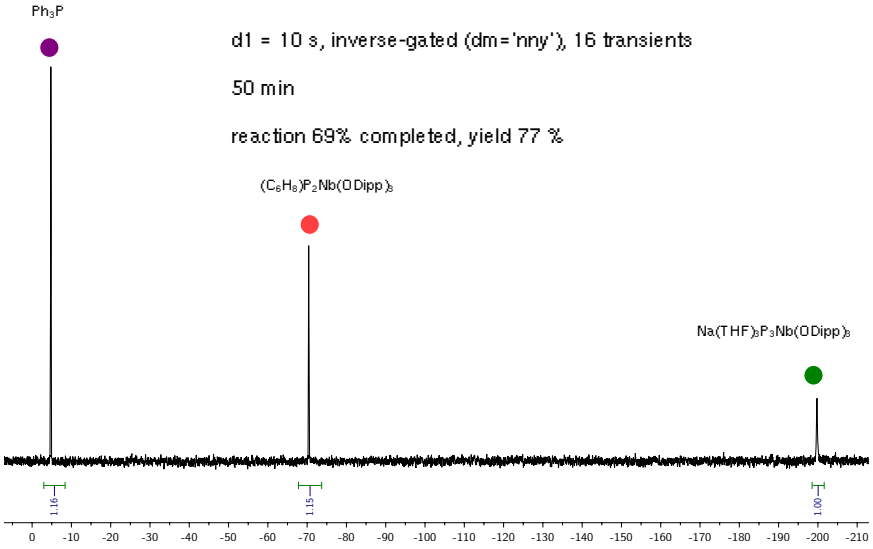


Figure S.5: Experiment 2 (t = 50 min): Inverse-gated $^{31}P\{^{1}H\}$ NMR spectrum (1,3-C_6H_8, 0 °C, 202.4 MHz) of **1**-$P_2C_6H_8$ formed *in-situ*, with PPh_3 as standard, delay time of 10 seconds, 16 transients.

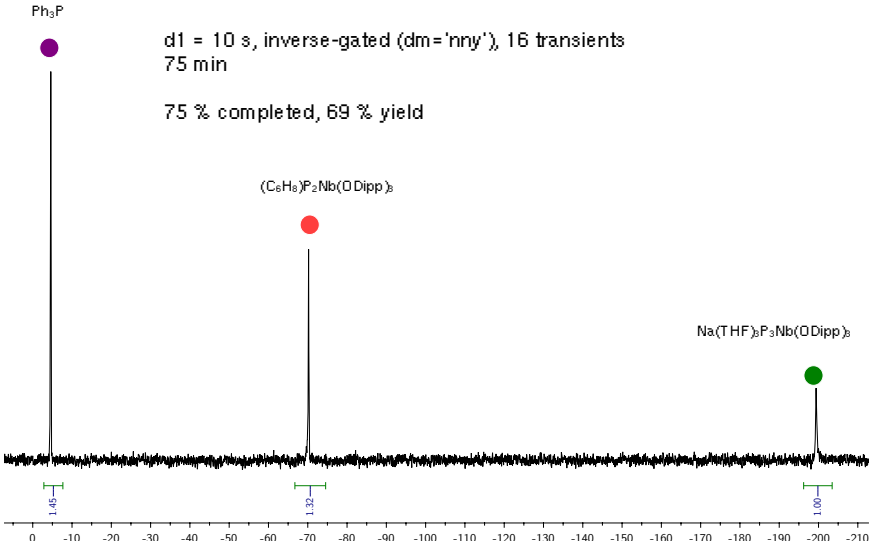


Figure S.6: Experiment 3 (t = 75 min): Inverse-gated $^{31}P\{^{1}H\}$ NMR spectrum (1,3-C_6H_8, 0 °C, 202.4 MHz) of **1**-$P_2C_6H_8$ formed *in-situ*, with PPh_3 as standard, delay time of 10 seconds, 16 transients.

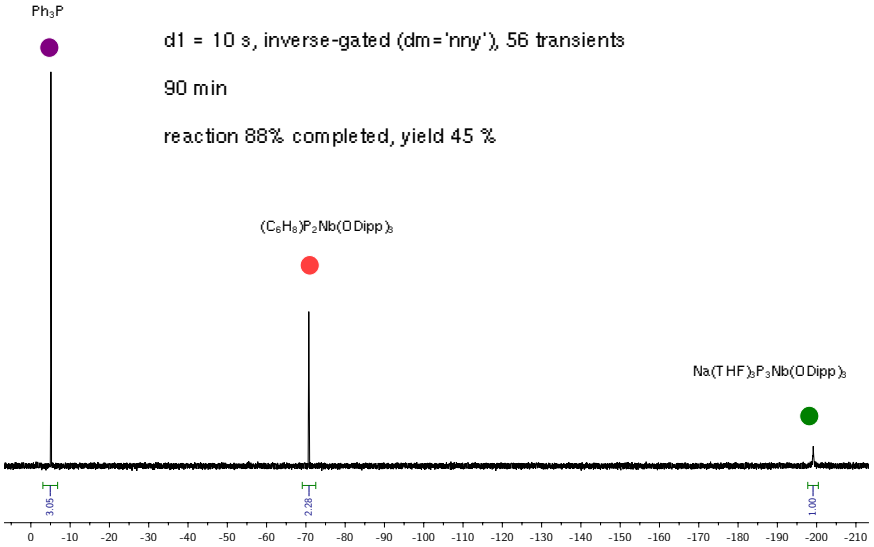


Figure S.7: Experiment 4 (t = 90 min): Inverse-gated $^{31}P\{^{1}H\}$ NMR spectrum (1,3-C_6H_8, 0 °C, 202.4 MHz) of **1**-$P_2C_6H_8$ formed *in-situ*, with PPh_3 as standard, delay time of 10 seconds, 56 transients.

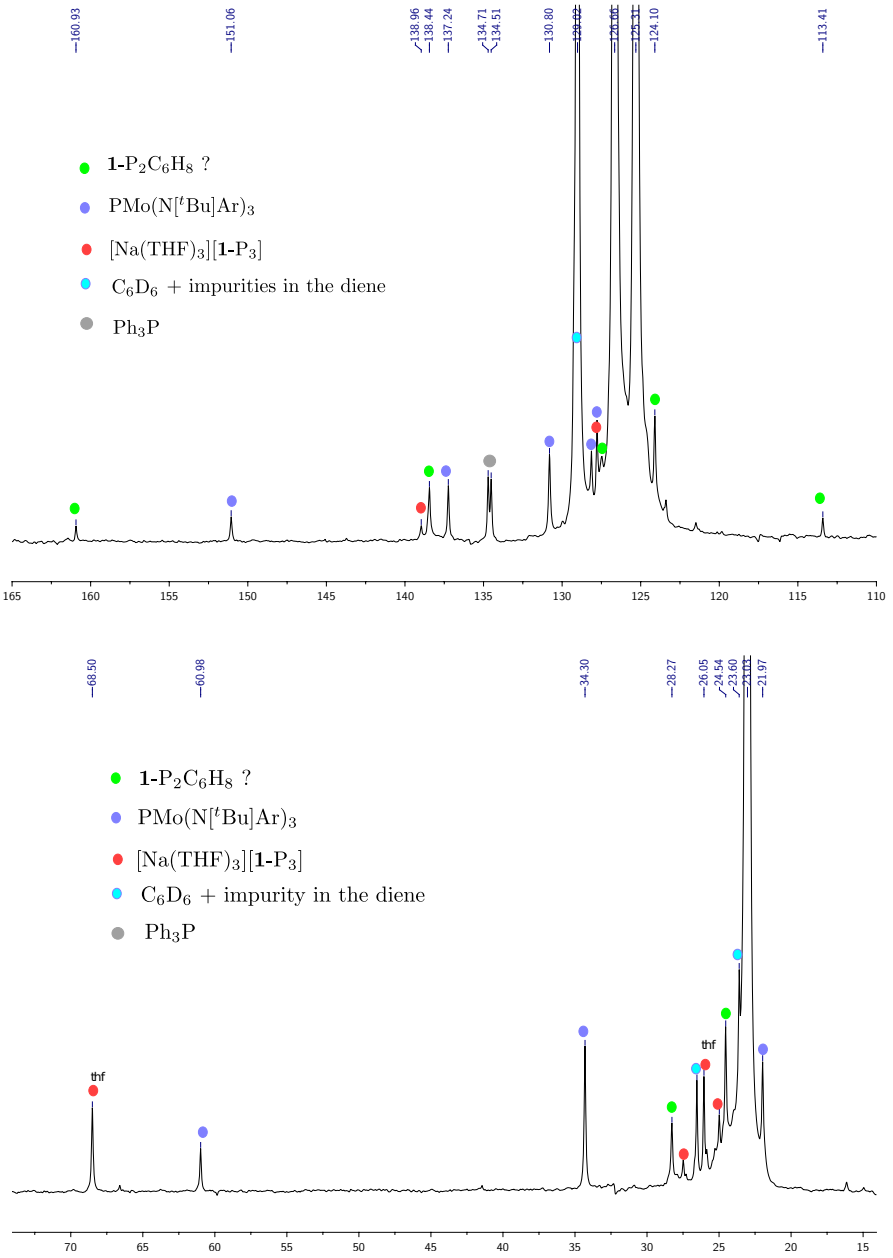


Figure S.8: ^{13}C NMR spectrum (1,3-C_6H_8, 0 °C, 100.6 MHz) of **1**-$P_2C_6H_8$ formed *in-situ*, with PPh_3 as standard: zoom in the aryl region (top), zoom in the alkyl region (bottom).

S.1.4 Formation of $P_4\mathbf{1}_2$ *via* **1**-$P_2C_6H_8$

Solid IMo(N[^{t}Bu]Ar)$_3$ (20 mg, 0.026 mmol, 1 equiv), solid [Na(THF)$_3$][**1**-P$_3$] (25 mg, 0.026 mmol, 1 equiv) and 1,3-cyclohexadiene (700 μL, 7.349 mmol, 282 equiv) were placed in a 25 mL scintillation vial and the mixture was stirred vigorously for 40 min. After the reaction time elapsed, the mixture had become brown and cloudy. Next, PPh_3 (12 mg, 0.045 mmol) was added to the reaction mixture, as an internal standard from a stock solution in benzene prepared by dissolving 100 mg PPh_3 in 1.2 g benzene. The reaction mixture was quickly brought to constant mass under reduced pressure. The brown solids were triturated twice with *n*-hexane, dried and dissolved in benzene-d_6 for NMR analysis. The spectroscopic yield for the formation of $P_4\mathbf{1}_2$ was 30%; no starting materials were detected. A delay time of 15 seconds was applied in the acquisition of the ^{31}P NMR spectrum (see Figure S.9). A delay time of 4 seconds was applied in the acquisition of the ^{1}H NMR spectrum (see Figure S.10).

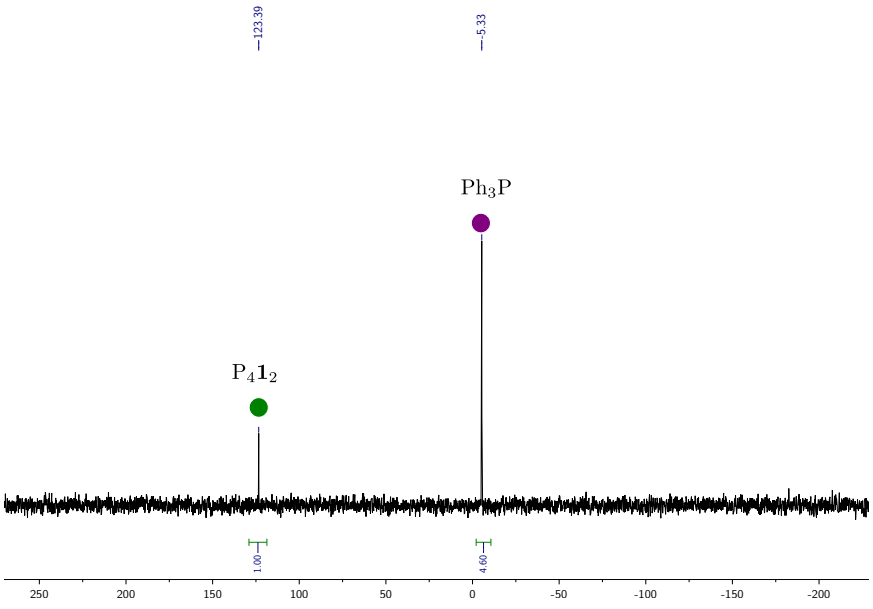


Figure S.9: ^{31}P{^{1}H} NMR spectrum (benzene-d_6, 20 °C, 121.5 MHz) of $P_4\mathbf{1}_2$ formed in the presence of 1,3-cyclohexadiene, with PPh_3 as standard, delay time of 15 seconds, 4 transients.

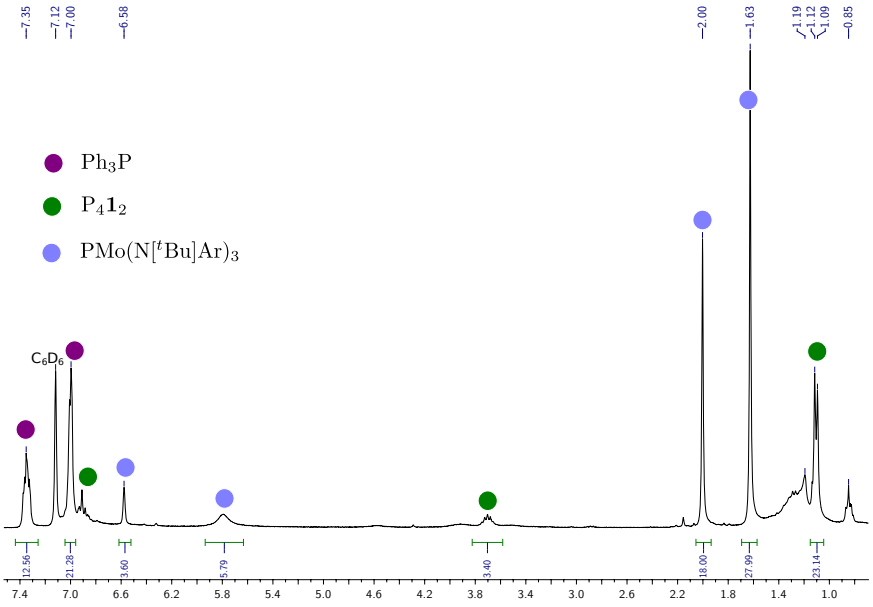


Figure S.10: ^{1}H NMR spectrum (benzene-d_6, 20 °C, 300 MHz) of $P_4\mathbf{1}_2$ formed in the presence of 1,3-cyclohexadiene, with PPh_3 as standard, delay time of 4 seconds, 16 transients.

S.1.5 Half-life determination of 1-$P_2C_6H_8$ at 10 °C

Solid [Na(THF)$_3$][**1**-P$_3$] (25 mg, 0.026 mmol) and solid IMo(N[^{t}Bu]Ar)$_3$ (20 mg, 0.026 mmol) were placed in an NMR tube equipped with a 14/20 female glass adapter. To this NMR tube 1,3-cyclohexadiene (0.5 mL, 5.24 mmol)and 0.2 mL toluene were added. A sealed capillary containing PCl_3 in benzene-d_6 was introduced into the tube as an external standard. The tube containing the mixture was frozen, degassed and flame sealed. Next, the mixture was thawed, the tube was shaken well and placed in an NMR probe pre-cooled to 10 °C. The NMR signal intensities were monitored relative to the PCl_3 standard, and the data were plotted (see Figures S.11). The temperature was calibrated using a methanol standard before and after the run.

The signal intensity of the consumed **1**-$P_2C_6H_8$ plotted in figure S.11 (right) was calculated using the formula:

$$I = 1 - (I_{\mathbf{1}\text{-}P_2C_6H_8} + 2/3\ I_{[Na(THF)_3][\mathbf{1}\text{-}P_3]}),$$

where $I_{\mathbf{1}\text{-}P_2C_6H_8}$ and $I_{[Na(THF)_3][\mathbf{1}\text{-}P_3]}$ are observed NMR signal intensities of $\mathbf{1}$-$P_2C_6H_8$ and $[Na(THF)_3][\mathbf{1}\text{-}P_3]$, respectively. The normalized signal intensity of the consumed $\mathbf{1}$-$P_2C_6H_8$ was fitted to the following linear regression: f(x) = 0.0007737374x + 0.1607906617, with R^2 = 0.986. The $t_{1/2}$ at 10 °C of $\mathbf{1}$-$P_2C_6H_8$ was measured to be around 10 h.

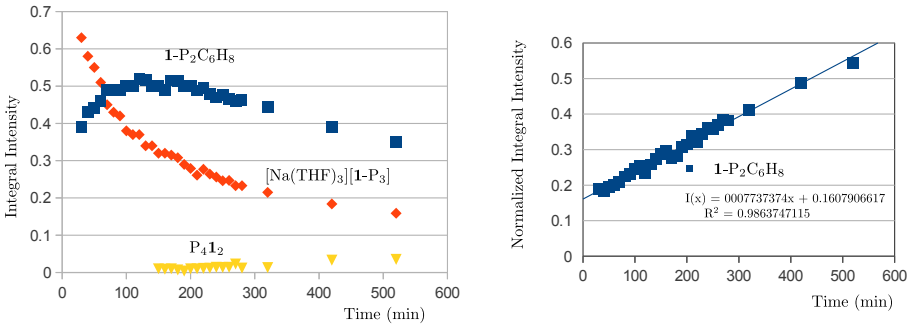


Figure S.11: (Left) Plot of the observed NMR signal intensities of $\mathbf{1}$-$P_2C_6H_8$, $[Na(THF)_3][\mathbf{1}\text{-}P_3]$ and $P_4\mathbf{1}_2$ in the $^{31}P\{^1H\}$ NMR spectrum in a mixture of 1,3-C_6H_8 and toluene, at 10 °C, at 202.2 MHz over 10 h, with PCl_3 as a standard. (Right) Plot of the signal intensity of the consumed $\mathbf{1}$-$P_2C_6H_8$, calculated as described in S.1.5.

S.1.6 Treatment of $P_4\mathbf{1}_2$ with Na/Hg

A solution of $P_4\mathbf{1}_2$ (70 mg, 0.051 mmol) in THF (5 mL) was added with stirring to a 25 mL scintillation vial equipped with a teflon-coated stir bar and containing freshly prepared 1% Na/Hg (120 mg, 0.051 mmol). The Na/Hg amalgam had been prepared by adding 50 mg Na to 50 g Hg. After 5 h, the dark red reaction mixture was decanted away from the amalgam and filtered through a glass-paper filter inside a pipette. Next, the volatile materials were removed under reduced pressure. A portion of the crude material was dissolved in C_6D_6 and analyzed by NMR spectroscopy (see figures S.12, S.13). The aliquot was returned to the flask, and the volatile materials removed again, under reduced pressure. The resulting red solids were set to crystallize from a concentrated THF/Et_2O mixture, at −35 °C. The $[Na(THF)_3][\mathbf{1}\text{-}P_3]$ salt was separated as orange crystals by filtration (39 mg, 0.041 mmol) corresponding to 80% yield (based on the phosphorus).

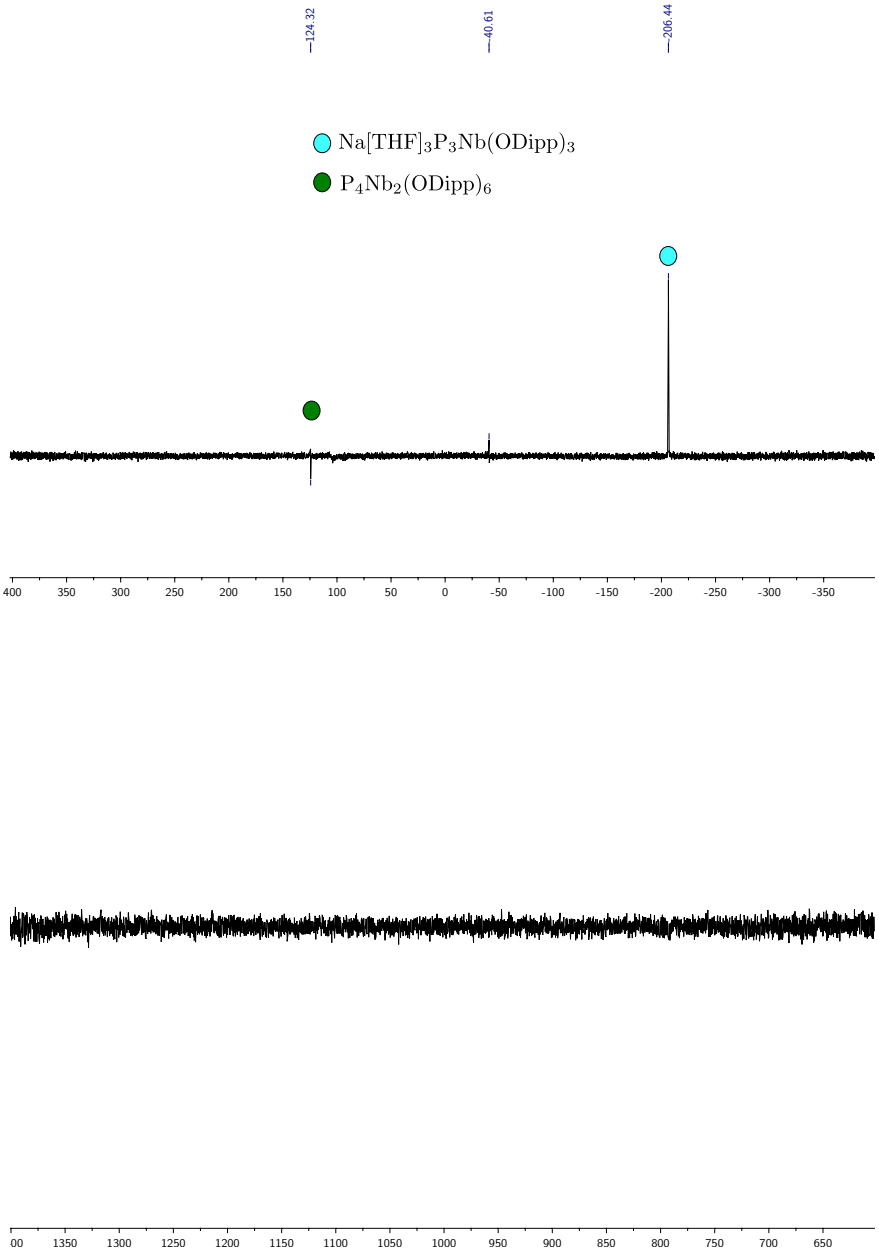


Figure S.12: The crude $^{31}P\{^{1}H\}$ NMR spectrum (benzene-d_6, 20 °C, 121.5 MHz) obtained from the treatment of $P_4\mathbf{1}_2$ with Na/Hg: – 400 ppm to 400 ppm (top), 600 ppm to 1400 ppm (bottom).

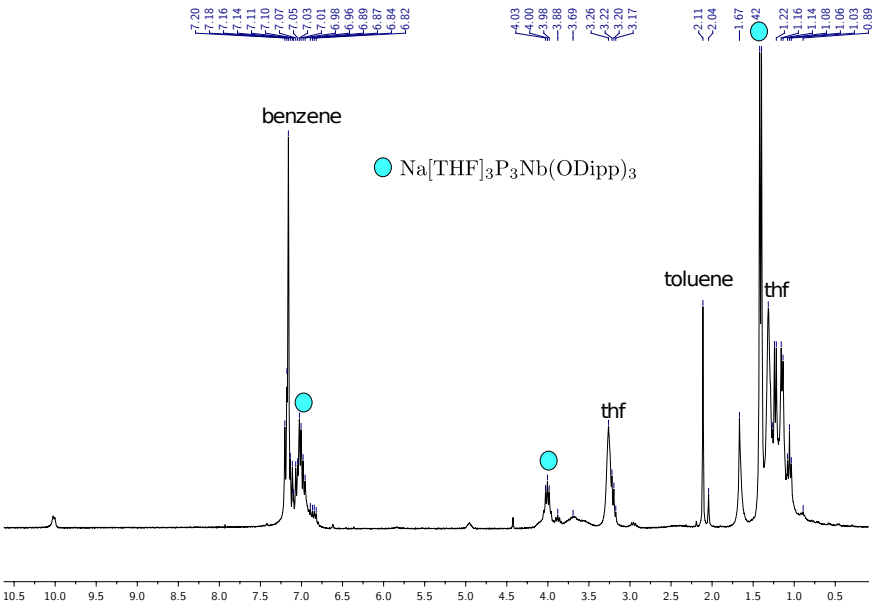


Figure S.13: The crude ^{1}H NMR spectrum (benzene-d_6, 20 °C, 300 MHz) obtained from the treatment of $P_4\mathbf{1}_2$ with Na/Hg.

S.1.7 Generation of $P_2(C_6H_8)_2$ from 1-$P_2C_6H_8$

Method 1: A scintillation vial equipped with a teflon-coated stir bar was charged with solid IMo(N[^{t}Bu]Ar)$_3$ (40 mg, 0.052 mmol), solid [Na(THF)$_3$][**1**-P$_3$] (50 mg, 0.052 mmol), 1,3-cyclohexadiene (1.4 mL, 147 mmol, 282 equiv) and pyridine-*N*-oxide (5 mg, 0.056 mmol) from a stock solution prepared by dissolving 25 mg pyridine-*N*-oxide in 500 mg toluene. The reaction mixture was stirred vigorously for 5 h and then filtered through a Celite pad. The volatile materials were removed under reduced pressure, and the residue was dissolved in benzene-d_6 for NMR analysis. (see Figure S.14)

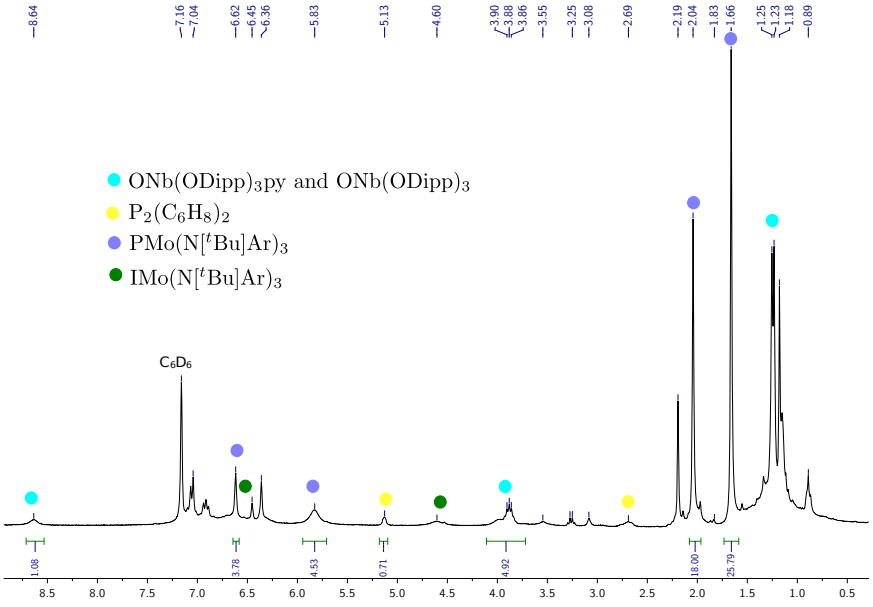


Figure S.14: ^{1}H NMR spectrum (benzene-d_6, 20 °C, 300 MHz) spectrum of the crude reaction mixture obtained from the generation of $P_2(C_6H_8)_2$ from **1**-$P_2C_6H_8$ using Method 1.

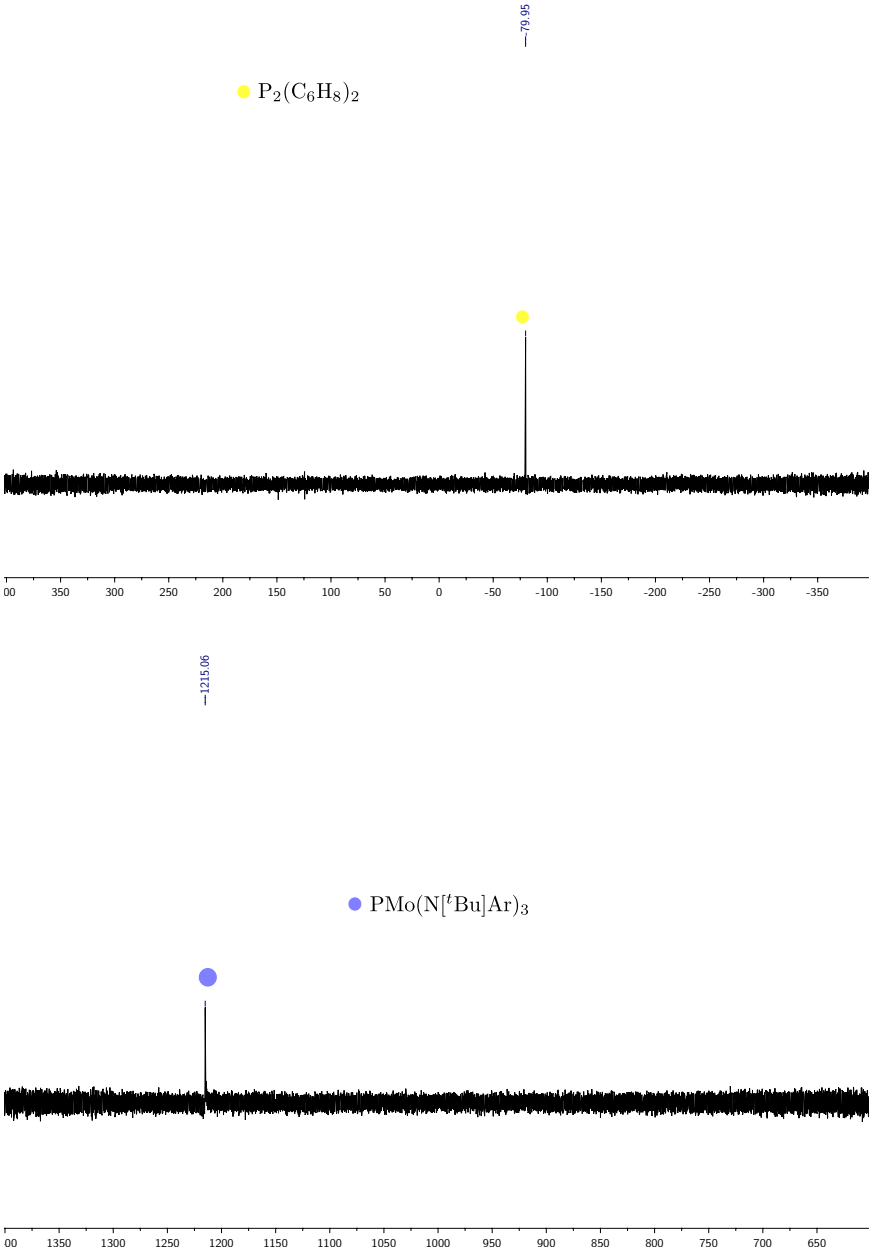


Figure S.15: $^{31}P\{^{1}H\}$ NMR spectrum (benzene-d_6, 20 °C, 121.5 MHz) spectra of the crude reaction mixture obtained from the generation of $P_2(C_6H_8)_2$ from **1**-$P_2C_6H_8$ using Method 1: – 400 ppm to 400 ppm (top), 600 ppm to 1400 ppm (bottom).

Method 2. Solid IMo(N[^{t}Bu]Ar)$_3$ (40 mg, 0.052 mmol), solid [Na(THF)$_3$][**1**-P$_3$] (50 mg, 0.052 mmol) and 1,3-cyclohexadiene (1.4 mL, 147 mmol, 282 equiv) were

added to a scintillation vial equipped with a teflon-coated stir bar. The reaction mixture was stirred vigorously for 1.5 h, after which pyridine-*N*-oxide (5 mg, 0.056 mmol) was added as a stock solution in toluene (prepared by dissolving 25 mg pyridine-*N*-oxide in 500 mg toluene). The reaction mixture was stirred for an additional 5 h, and then filtered through a Celite pad. All volatile materials were removed from the filtrate under reduced pressure, and the residue so obtained was dissolved in benzene-d_6 for NMR analysis (see Figure S.16).

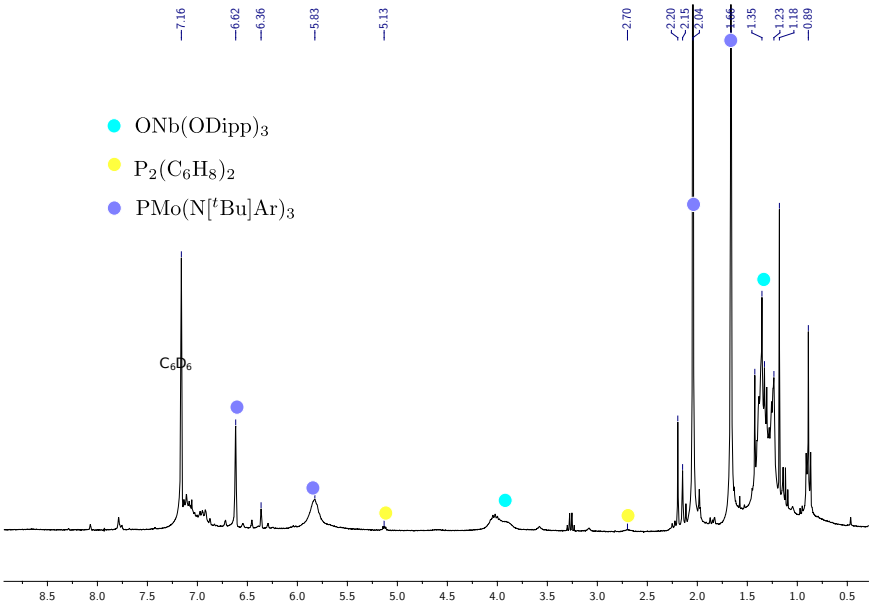


Figure S.16: ^{1}H NMR spectrum (benzene-d_6, 20 °C, 300 MHz)

S.2 X-ray crystallography of $P_4\mathbf{1}_2$

Diffraction-quality red block of $P_4\mathbf{1}_2$ were grown from benzene at room temperature. A crystal was mounted in hydrocarbon oil on a nylon loop or a glass fiber. Low-temperature (100 K) data were collected on a Bruker D8 three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated

Table 2: Crystallographic Data for $P_4\mathbf{1}_2$

Reciprocal Net code / CCDC number	X8_10012 / 854065
Empirical formula, FW (g/mol)	$C_{72}H_{102}Nb_2O_6P_4$, 1373.37
Color / Morphology	Red / Plate
Crystal size (mm^3)	$0.05 \times 0.10 \times 0.10$
Temperature (K)	100(2)
Wavelength (Å)	1.54178
Crystal system, Space group	Monoclinic, $P2_1/c$
Unit cell dimensions (Å, °)	a = 18.9443(9), α = 90
	b = 21.5650(11), β = 99.909(3)
	c = 17.9908(9), γ = 90
Volume ($Å^3$)	7240.2(6)
Z	4
Density (calc., g/cm^3)	1.260
Absorption coefficient (mm^{-1})	3.784
$F(000)$	2896.0
Theta range for data collection (°)	3.23 to 66.59
Index ranges	$-22 \leq h \leq 22$, $-24 \leq k \leq 25$
	$-21 \leq l \leq 21$
Reflections collected	69443
Independent reflections, R_{int}	12663 (0.0394)
Completeness to θ_{max} (%)	99.0
Max. and min. transmission	0.8334 and 0.7035
Data / restraints / parameters	12663 / 65 / 856
Goodness-of-fit[a]	1.059
Final R indices[b] [$I > 2\sigma(I)$]	R_1 = 0.0368, wR_2 = 0.0910
R indices[b] (all data)	R_1 = 0.0444, wR_2 = 0.0968
Largest diff. peak and hole ($e \cdot Å^{-3}$)	1.702 and −0.386

[a] GooF = $\left[\frac{\Sigma[w(F_o^2-F_c^2)^2]}{(n-p)}\right]^{\frac{1}{2}}$ [b] $R_1 = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$; $wR_2 = \left[\frac{\Sigma[w(F_o^2-F_c^2)^2}{\Sigma[w(F_o^2)^2]}\right]^{\frac{1}{2}}$; $w = \frac{1}{\sigma^2(F_o^2)+(aP)^2+bP}$; $P = \frac{2F_c^2+\max(F_o^2,0)}{3}$

Cu Kα radiation (λ = 1.54178 Å). A semi-empirical absorption correction was applied to the diffraction data using SADABS.[4] All structures were solved by direct or Patterson methods using SHELXS[5,6] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[6,7] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). Descriptions of the refinement follow below. Further details are provided in Table 1, and in the form of a *.cif* file available from the CCDC.[8]

The compound $P_4\mathbf{1}_2$ crystallized in the monoclinic space group $P2_1/c$ with one molecule per asymmetric unit and no solvent molecule. The *cyclo*-P_4 ring was found to be disordered over three positions. This was refined within SHELXL with the help of rigid bond restraints as well as similarity restraints on the anisotropic displacement parameters for neighboring atoms and on 1,2- and 1,3-distances throughout the disordered *cyclo*-P_4 ring.[9] The three domains were refined to 75%, 20% and 5%. The ratio of the three components was refined freely with SHELXL, and the sum of the three occupancies was constrained to unity.[9]

S.3 Computational details

S.3.1 Computational methods

All DFT calculations were carried out using ORCA 2.8 quantum chemistry program package from the development team at the university of Bonn.[2] In all cases the LDA functional employed was that of Perdew (PW-LDA)[10] while the GGA part was handled using the functionals of Becke and Perdew (BP86).[11] In addition, all calculations were carried out using the Zero-Order Regular Approximation (ZORA),[12] in conjunction with the SARC-TZV(2pf) basis set for niobium, the SARC-TZV basis set hydrogen, and SARC-TZV(p) set for all other atoms.[13] Spin-restricted Kohn–Sham determinants have been chosen to describe the closed-shell wavefunctions, employing the RI approximation and the tight SCF convergence criteria provided by ORCA. The calculations

for the *exo* and the *endo* Diels-Alder isomers of **1**-$P_2C_6H_8$ were reoptimized using the COSMO solvation model as implemented in ORCA, set for the dielectric constant of toluene.[14]

All structures were derived from the X-ray coordinates of the major component (75 % occupancy) of the $P_4\mathbf{1}_2$ molecule using MOLDEN[15] for model building. The $P_4\mathbf{1}_2$ model with frozen coordinates for the P_4Nb_2 unit, and the $P_4Nb_2(OH)_6$ model were calculated keeping the coordinates of the P_4Nb_2 unit frozen, and allowing the ancillary ligands to optimize.

Single point calculations were run to determine the final energies. The coordinates of all optimized structures are provided in sections S.3.2 through S.3.8. Frequency calculations were only performed on the truncated molecule $P_4Nb_2(OH)_6$ and the *endo*-**1**-$P_2C_6H_8$ isomer.

The ^{31}P NMR chemical shifts, calculated as described below, were -100 ppm for *endo*-**1**-$P_2C_6H_8$, and $+60$ ppm for *exo*-**1**-$P_2C_6H_8$ (experimental value for **1**-$P_2C_6H_8$ is -69 ppm). The absolute, isotropic shielding for the ^{31}P nuclei of the *exo* and the *endo* Diels-Alder isomers of **1**-$P_2C_6H_8$ was calculated using the EPR/NMR module of ORCA.[2] To compare to experiment, P_4 was chosen as the molecule of reference for the ^{31}P nuclei. P_4 was optimized using the same basis set, functional choice and localization procedure as the molecules of interest. The chemical shifts were obtained by substraction of the reference value from the computed value.

Below is an example of input file used in the frequency calculation performed on the *endo*-**1**-$P_2C_6H_8$ calculated structure.

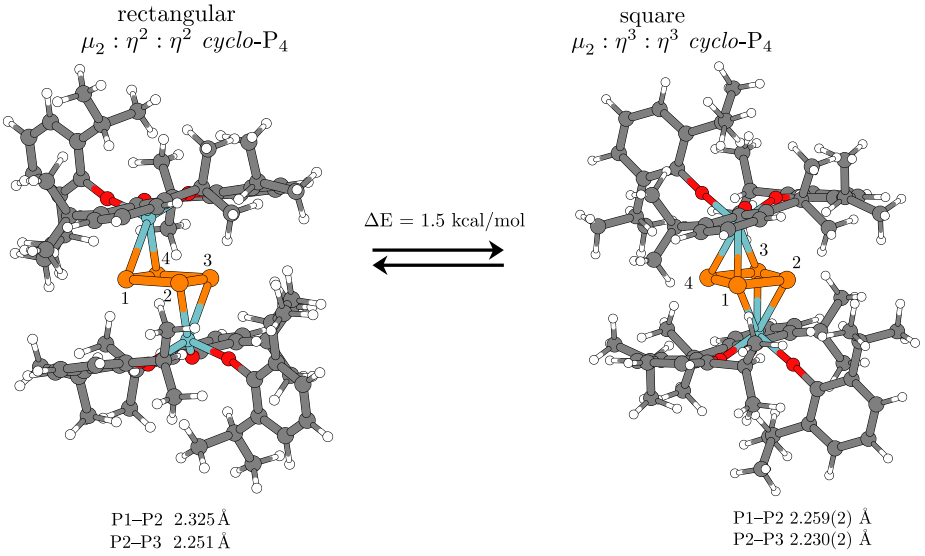
```
! GoodOPT RKS ZORA Numfreq
! PrintBasis
% PAL NPROCS 32 END
% scf
GUESS MORead
MOInp = "$ ORCA_RESULTDIR/AV_trP2Nb_Good.gbw" end
% output
print[p_mos] 1
```

end # output

** xyzfile 0 1 $ ORCA_RESULTDIR/AV_isoP2Nb_Good.xyz*

% eprnmr Nuclei = all P { aiso, shift, adip, aorb }

end



* ORCA: DFT, BP86, H(TZV); C, O, P(TZV(d)); Nb(TZV(2pf))

Figure S.17: On the left is displayed the calculated structure of $P_4\mathbf{1}_2$ optimized freely from X-ray coordinates, with an $\mu_2,\eta^{2:2}$ *cyclo*-P_4 ligand. On the right is displayed the calculated structure of $P_4\mathbf{1}_2$ optimized from the X-ray coordinates, with frozen coordinates for the P_4Nb_2 unit, with an $\mu_2,\eta^{3:3}$ *cyclo*-P_4 ligand. Single point calculations reveal a 1.5 kcal/mol energy difference between the two isomers.

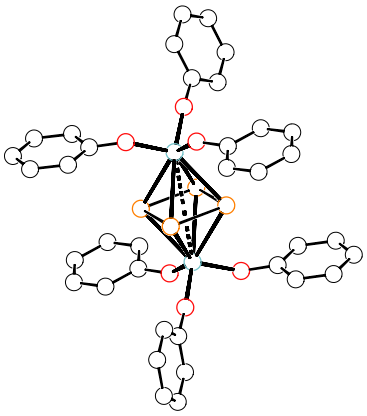


Figure S.18: Calculated structure of $P_4Nb_2(OPh)_6$.

References

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S.3.2 Cartesian coordinates for optimized $P_4\mathbf{1}_2$

186 atoms

Nb	0.021529	0.052691	2.393495	O	1.477975	-0.008320	3.572981
P	1.067743	1.172379	0.387234	P	1.035071	-1.152620	0.404121
O	-0.914262	1.686107	2.889346	C	-1.245669	2.997785	2.652603
C	-2.607615	3.331674	2.448752	C	-0.238853	3.999860	2.680718
C	-0.627264	5.322562	2.427223	C	-2.931220	4.671667	2.203272
C	-1.954281	5.664447	2.176846	H	0.132863	6.106625	2.438257
H	-2.227228	6.702813	1.976426	H	-3.976206	4.943328	2.035602
C	-3.717675	2.296162	2.549438	H	-3.243933	1.313143	2.682072
C	-4.572853	2.236124	1.273661	H	-3.945953	2.040913	0.392481
H	-5.323796	1.434665	1.349171	H	-5.114662	3.178980	1.103067
C	1.204574	3.710682	3.074700	H	1.351355	2.621728	3.052042
C	2.232446	4.328410	2.114188	H	2.198765	5.428356	2.128861
H	2.070302	3.998675	1.078850	H	3.250581	4.032153	2.409418
C	-4.591531	2.563717	3.789575	H	-5.081410	3.547328	3.727250
H	-3.992623	2.546102	4.711498	H	-5.382834	1.803721	3.882135
C	1.461354	4.180373	4.520157	H	0.741283	3.735360	5.220938
H	2.475493	3.901380	4.845028	H	1.368698	5.274649	4.599218
O	-1.062779	-1.483030	2.891087	C	-1.527069	-2.759557	2.693282
C	-0.637641	-3.857663	2.799289	C	-1.166559	-5.144258	2.617860
C	-2.516647	-5.349543	2.351088	C	-3.378383	-4.254034	2.276580
C	-2.912721	-2.946959	2.452090	H	-0.498582	-6.005133	2.693722
H	-2.901652	-6.361513	2.207431	H	-4.437914	-4.422665	2.078801
C	-3.862750	-1.759870	2.464729	H	-3.332905	-0.914546	1.995368
C	-5.155007	-1.987540	1.671298	H	-5.732228	-1.052544	1.618428
H	-4.949397	-2.317643	0.643120	H	-5.806005	-2.736673	2.147816
C	-4.185351	-1.365801	3.920103	H	-3.273021	-1.118869	4.479355
H	-4.852170	-0.491083	3.951486	H	-4.689415	-2.194888	4.440350
C	0.829562	-3.694538	3.172247	H	1.077485	-2.626323	3.095180

C	1.773789	-4.448525	2.222812	H	1.621657	-4.148829	1.176555
H	1.632700	-5.538296	2.285930	H	2.821874	-4.240896	2.486366
C	1.065720	-4.122916	4.633553	H	0.414350	-3.571870	5.326015
H	0.860712	-5.196771	4.765597	H	2.109857	-3.938362	4.928670
C	2.341481	-0.137478	4.634270	C	3.658853	-0.578304	4.370307
C	4.523081	-0.704200	5.465220	C	4.101415	-0.410251	6.761625
C	2.795877	0.024706	6.986199	C	1.881464	0.175850	5.935032
H	5.546003	-1.045041	5.299944	H	4.793364	-0.517925	7.599635
H	2.478242	0.257756	8.003559	C	4.116796	-0.853283	2.945510
H	3.258388	-1.284176	2.403196	C	4.493060	0.462462	2.235998
H	3.657850	1.176364	2.232713	H	4.775474	0.269974	1.190328
H	5.347683	0.942825	2.737348	C	5.270262	-1.860782	2.852109
H	5.049671	-2.789874	3.397398	H	6.210774	-1.448337	3.248787
H	5.451987	-2.121350	1.799838	C	0.446890	0.622399	6.185689
H	0.114295	1.190475	5.302074	C	-0.486652	-0.595053	6.335905
H	-1.527046	-0.266591	6.481602	H	-0.459764	-1.243971	5.450768
H	-0.195930	-1.199104	7.209169	C	0.298354	1.553593	7.398203
H	-0.721126	1.965029	7.428149	H	1.003097	2.396292	7.358840
H	0.456929	1.020758	8.348184	Nb	-0.020949	-0.043522	-2.393060
O	-1.474474	0.023379	-3.576081	P	-1.077016	-1.144584	-0.380582
P	-1.035226	1.180012	-0.416304	O	0.897512	-1.689532	-2.883585
C	1.215662	-3.002769	-2.636463	C	2.573920	-3.348452	-2.427346
C	0.199202	-3.994991	-2.659156	C	0.573983	-5.319651	-2.395435
C	2.883916	-4.689792	-2.171867	C	1.897136	-5.672803	-2.140547
H	-0.193824	-6.096225	-2.401984	H	2.159559	-6.712434	-1.932755
H	3.925904	-4.970588	-2.000766	C	3.694520	-2.324847	-2.534037
H	3.230552	-1.337677	-2.670667	C	4.552201	-2.267319	-1.259859
H	3.928524	-2.061476	-0.378814	H	5.310820	-1.473575	-1.340479
H	5.085127	-3.214456	-1.085269	C	-1.240323	-3.693415	-3.057867
H	-1.376719	-2.603056	-3.037514	C	-2.276811	-4.299554	-2.099383

H	-2.254885	-5.399810	-2.113281	H	-2.113359	-3.970985	-1.063891
H	-3.290996	-3.992725	-2.397425	C	4.563826	-2.607123	-3.774046
H	5.043464	-3.595520	-3.707532	H	3.963755	-2.587753	-4.695184
H	5.362853	-1.855897	-3.871381	C	-1.497005	-4.162849	-4.503383
H	-0.771205	-3.724862	-5.202646	H	-2.507759	-3.875542	-4.831529
H	-1.413462	-5.258007	-4.580781	O	1.078033	1.480234	-2.892195
C	1.553971	2.753946	-2.704892	C	0.675243	3.859533	-2.822524
C	1.215947	5.142582	-2.650860	C	2.567387	5.337304	-2.382734
C	3.418356	4.234259	-2.296816	C	2.940746	2.930180	-2.462183
H	0.556459	6.009130	-2.736072	H	2.961693	6.346702	-2.246474
H	4.478964	4.394551	-2.097802	C	3.879228	1.733915	-2.463570
H	3.342251	0.898397	-1.984794	C	5.175217	1.957405	-1.674984
H	5.743321	1.017386	-1.613200	H	4.975536	2.300599	-0.649921
H	5.832304	2.694936	-2.161155	C	4.196348	1.322302	-3.915363
H	3.281516	1.076307	-4.470858	H	4.856656	0.442408	-3.938535
H	4.705900	2.142192	-4.444744	C	-0.793001	3.707450	-3.196302
H	-1.049844	2.641504	-3.117056	C	-1.731662	4.471386	-2.249242
H	-1.584216	4.171095	-1.202443	H	-1.579905	5.559676	-2.313166
H	-2.781268	4.273365	-2.514126	C	-1.024809	4.134469	-4.658730
H	-0.376830	3.577356	-5.349500	H	-0.812165	5.206550	-4.793043
H	-2.070009	3.956738	-4.954288	C	-2.337540	0.151271	-4.637825
C	-3.652988	0.598842	-4.375624	C	-4.516773	0.723986	-5.470958
C	-4.096442	0.422655	-6.766125	C	-2.792815	-0.018987	-6.988936
C	-1.878980	-0.169646	-5.937195	H	-5.538156	1.070063	-5.307028
H	-4.787935	0.529896	-7.604568	H	-2.476355	-0.257952	-8.005294
C	-4.109634	0.881539	-2.951902	H	-3.248884	1.308837	-2.410545
C	-4.494308	-0.429881	-2.238800	H	-3.663422	-1.148858	-2.233581
H	-4.775812	-0.233035	-1.193670	H	-5.351692	-0.906468	-2.739029
C	-5.256771	1.896555	-2.862102	H	-5.029934	2.822623	-3.409965
H	-6.199670	1.488942	-3.258107	H	-5.437365	2.161334	-1.810670

C	-0.446363	-0.623626	-6.185642	H	-0.117280	-1.191542	-5.300626
C	0.493020	0.589148	-6.337207	H	1.532144	0.255751	-6.480654
H	0.467723	1.240217	-5.453626	H	0.206242	1.192541	-7.212249
C	-0.301014	-1.557744	-7.396257	H	0.716767	-1.973487	-7.424696
H	-1.009198	-2.397510	-7.355672	H	-0.456804	-1.026172	-8.347406

S.3.3 Cartesian coordinates for optimized $P_4 1_2$ with frozen coordinates for the P_4Nb_2 unit

186 atoms

Nb	14.386347	20.973407	2.746337	Nb	12.240087	22.007126	6.447593
P	14.414010	22.563675	4.903616	P	12.577762	22.489492	3.590208
P	12.202936	20.401784	4.278369	P	14.027755	20.473811	5.592132
O	14.467628	19.016889	2.589633	O	16.318200	21.267630	2.810659
O	14.119736	21.337803	0.884457	O	12.169485	23.962838	6.602558
O	10.309227	21.713603	6.390413	O	12.517781	21.644506	8.307366
C	12.546684	17.571734	2.237823	C	13.791534	17.861885	2.858640
C	13.750068	15.723871	3.995473	H	14.208574	14.996100	4.667154
C	15.806800	17.196777	4.277903	H	15.890556	18.284018	4.433249
C	16.864100	16.791933	3.231217	H	16.796802	15.715776	3.008479
H	17.880519	16.997958	3.599879	H	16.723329	17.345024	2.292728
C	14.414518	16.925984	3.729918	C	12.515185	15.432951	3.415243
H	12.012562	14.488933	3.636902	C	16.087763	16.514122	5.622300
H	15.312018	16.748130	6.365726	H	17.053718	16.855661	6.022222
H	16.149881	15.419042	5.528012	C	11.932194	16.348974	2.543412
H	10.975688	16.106170	2.075897	C	11.919406	18.487396	1.196959
H	12.398030	19.474988	1.286279	C	10.408926	18.687016	1.391994
H	9.846404	17.758153	1.213676	H	10.029957	19.433462	0.678096
H	10.173447	19.032811	2.408475	C	12.222247	17.964562	-0.220075
H	13.302093	17.842381	-0.377380	H	11.840695	18.660221	-0.982690
H	11.746879	16.984782	-0.382785	C	17.286787	22.150318	3.198609

C 16.068229 24.099199 2.026362 H 15.264636 23.341813 1.987770
C 18.547444 20.154397 4.209607 H 17.678926 19.648093 3.765765
C 19.410722 22.531296 4.295799 H 20.276045 22.150731 4.843886
C 17.200292 23.529732 2.866419 C 18.238824 24.372728 3.282470
H 18.188588 25.435289 3.034789 C 19.333351 23.890233 3.998031
H 20.126834 24.570742 4.314243 C 16.532612 24.337870 0.577478
H 17.329124 25.097690 0.551224 H 15.700659 24.694281 -0.047707
H 16.929138 23.420644 0.121461 C 15.449142 25.372337 2.620919
H 15.143294 25.231386 3.667303 H 14.562013 25.668537 2.041561
H 16.152418 26.217948 2.591032 C 18.530657 19.888296 5.724604
H 19.375687 20.380162 6.230446 H 18.604045 18.809356 5.930814
H 17.603512 20.260492 6.183680 C 19.812462 19.565999 3.559010
H 19.816517 19.731763 2.472230 H 19.871679 18.481467 3.738542
H 20.727866 20.018503 3.970176 C 18.407245 21.637591 3.901933
C 14.151743 21.613412 -0.452120 C 13.349616 22.670529 -
0.953535 C 13.415183 22.944858 -2.324534 H 12.812731 23.756686
-2.735407 C 15.849607 19.706412 -0.753809 H 15.380101 19.344488
0.173516 C 14.983003 20.834663 -1.298363 C 12.421825 23.444507
-0.030142 H 12.905986 23.487360 0.959095 C 14.236363 22.205115
-3.175551 H 14.273129 22.438721 -4.241814 C 17.257008 20.219655
-0.391846 H 17.767131 20.620222 -1.281900 H 17.871925 19.400972
0.012501 H 17.214537 21.010761 0.367339 C 15.955978 18.509153
-1.713176 H 14.969369 18.169804 -2.059749 H 16.446857 17.665932
-1.205087 H 16.561927 18.744877 -2.601395 C 12.158179 24.888207
-0.478467 H 13.092335 25.437063 -0.667063 H 11.600977 25.425050
0.303136 H 11.548839 24.933109 -1.394155 C 11.093616 22.687191
0.156723 H 10.558906 22.596007 -0.801448 H 10.439256 23.217336
0.864670 H 11.261546 21.673373 0.545828 C 15.006162 21.163370
-2.660415 H 15.640509 20.584882 -3.334546 C 12.845605 25.117649
6.332021 C 10.820222 25.786971 4.930065 H 10.739583 24.701778

4.758954	C	12.880797	27.258082	5.199724	H	12.418903	27.987451
4.532224	C	14.094995	25.404654	6.944319	C	12.216916	26.056286
5.467683	C	14.729274	24.485684	7.977971	H	14.249186	23.498722
7.889724	C	9.772965	26.171423	5.994624	H	9.838624	27.244399
6.232631	H	9.926248	25.604766	6.922890	H	8.753304	25.967088
5.634112	C	10.520368	26.488600	3.599773	H	9.550648	26.149451
3.207010	H	11.287272	26.269250	2.842819	H	10.455159	27.581843
3.711708	C	14.708601	26.627514	6.636950	H	15.668648	26.868350
7.098070	C	14.120243	27.546285	5.771666	H	14.622720	28.489891
5.547938	C	16.237981	24.284817	7.770949	H	16.465508	23.940746
6.752048	H	16.621298	23.536408	8.480426	H	16.803188	25.212403
7.947003	C	14.437950	25.005408	9.398634	H	14.915263	25.984531
9.559500	H	14.825041	24.307836	10.156638	H	13.359471	25.127958
9.565000	C	8.119417	23.078585	3.471140	H	9.051528	22.700276
3.027133	H	8.051709	24.155913	3.254749	H	7.279692	22.583878
2.959134	C	6.810611	23.421466	5.617186	H	5.898428	22.969986
5.197872	H	6.757764	24.504589	5.428226	H	6.792082	23.264371
6.705125	C	7.284939	19.092125	5.224385	H	6.488726	18.411881
4.914555	C	11.172187	17.608005	6.587476	H	12.062078	17.311821
7.162473	H	11.472145	17.745098	5.538929	H	10.467421	16.763937
6.624374	C	10.103352	18.651801	8.634012	H	9.306204	17.892987
8.668110	H	9.710640	19.571256	9.088860	H	10.938707	18.296777
9.255554	C	8.381403	18.610376	5.937574	H	8.430604	17.548729
6.189269	C	10.559152	18.884401	7.181393	H	11.364467	19.640306
7.212645	C	8.081991	22.824527	4.988100	H	8.946401	23.331991
5.438776	C	7.209334	20.449723	4.920505	H	6.343214	20.829541
4.373304	C	9.337570	20.831136	6.008716	C	8.216165	21.343083
5.306483	C	9.423300	19.452884	6.345735	C	12.494988	21.381818
9.646831	C	13.298061	20.326966	10.151076	C	13.244153	20.066108
11.525275	H	13.847713	19.256453	11.938639	C	11.671414	22.169481

10.492222	C	10.695249	24.496721	10.893849	H	10.094899	24.266871
11.787382	H	10.199060	25.334081	10.381336	H	11.682735	24.842171
11.231849	C	12.432566	20.816367	12.376290	H	12.405196	20.593885
13.445216	C	15.546111	20.287270	9.024792	H	15.382045	21.298976
8.628705	H	16.191933	19.747132	8.316597	H	16.088213	20.382574
9.978383	C	10.799493	23.291818	9.943994	H	11.262620	23.647493
9.011091	C	11.659874	21.854156	11.857553	H	11.032447	22.440281
12.531555	C	14.471733	18.098254	9.684540	H	15.086480	18.056213
10.596688	H	15.020624	17.551840	8.903706	H	13.535243	17.556934
9.883144	C	14.214340	19.540197	9.226865	H	13.722739	19.492913
8.241451	C	9.391130	22.771632	9.595106	H	9.430721	21.973674
8.843056	H	8.771764	23.585062	9.186927	H	8.887612	22.378300
10.492051							

S.3.4 Cartesian coordinates for optimized $P_4Nb_2(OPh)_6$ (Ph = C_6H_5)

78 atoms

Nb	14.662129	20.890492	3.035263	Nb	12.143761	22.223104	
6.185547	P	14.440935	22.797448	4.900777	P	12.689553	22.419050
3.460051	P	12.366818	20.314472	4.320436	P	14.118697	20.695347
5.760646	O	14.867308	18.950270	2.965710	O	16.576617	21.076987
3.349454	O	14.582183	21.287829	1.177834	O	11.968314	24.162443
6.296924	O	10.232542	22.073809	5.826072	O	12.168020	21.776484
8.032734	C	13.245954	17.443264	2.031363	C	14.166239	17.793254
3.035620	C	13.727739	15.691700	4.161343	H	13.921176	15.008057
4.991146	C	14.409571	16.907907	4.100920	C	12.811006	15.341364
3.163989	H	12.282234	14.387651	3.214099	C	12.574869	16.222019
2.102521	H	11.863654	15.954154	1.317901	C	17.527216	21.935076
3.793861	C	19.374628	22.390328	5.295019	H	20.019383	22.076595
6.119057	C	17.724437	23.183901	3.178472	C	18.743443	24.024984

3.628145	H	18.892190	24.993314	3.145113	C	19.572378	23.634394
4.685213	H	20.367445	24.296789	5.032702	C	18.361813	21.538028
4.853478	C	14.362088	21.718598	-0.089413	C	13.092372	22.175581
-0.476051	C	12.889478	22.606163	-1.788162	H	11.901226	22.961351
-2.088199	C	15.420368	21.692792	-1.011944	C	13.938068	22.585460
-2.714002	H	13.771951	22.922655	-3.738751	C	15.200169	22.127780
-2.319366	H	16.022891	22.106213	-3.037329	C	12.672490	25.317469
6.217603	C	13.129164	27.402789	5.069800	H	12.946018	28.076477
4.229613	C	13.585760	25.675491	7.224905	C	12.442592	26.189639
5.138768	C	14.261770	26.893643	7.145059	H	14.968023	27.167764
7.931931	C	14.037970	27.762196	6.071072	H	14.570303	28.713533
6.014118	C	7.252393	19.547151	4.400391	H	6.461120	18.893151
4.029091	C	8.023627	19.162841	5.502693	H	7.832900	18.208019
5.997667	C	7.502453	20.774578	3.776603	H	6.902024	21.083889
2.918039	C	9.287211	21.225699	5.353330	C	8.510244	21.616763
4.248445	C	12.366045	21.317094	9.294839	C	13.412861	20.424457
9.572200	C	13.595309	19.968523	10.878449	H	14.410483	19.274330
11.094119	C	11.507674	21.748252	10.318314	C	12.745466	20.392704
11.905974	H	12.894717	20.031465	12.925162	C	11.704251	21.281941
11.619157	H	11.036627	21.617316	12.415733	H	8.711320	22.581730
3.780172	H	9.639072	19.704038	6.846303	C	9.036989	19.993360
5.982956	H	13.073839	18.132984	1.202984	H	15.136557	17.191285
4.863758	H	14.066645	20.101921	8.760543	H	10.701192	22.442394
10.077583	H	12.283408	22.188074	0.255880	H	16.396950	21.328552
-0.689655	H	17.076608	23.479053	2.350890	H	13.749927	24.993786
8.061517	H	11.721654	25.899697	4.372586	H	18.200070	20.560981
5.311695							

S.3.5 Cartesian coordinates for optimized $P_4Nb_2(OH)_6$

O	14.661818	18.979172	2.848252	Nb	14.407410	20.925976	2.782261
O	14.105122	21.049960	0.894481	P	14.298737	22.748967	4.744011
P	14.101284	20.725831	5.670679	P	12.287008	20.343604	4.396540
P	12.473269	22.363642	3.470613	Nb	12.186474	22.183713	6.368323
O	12.499638	22.062221	8.253669	O	16.305631	21.394460	2.788550
O	11.942770	24.130460	6.300562	O	10.289197	21.716826	6.369036
H	9.942490	20.878307	6.021376	H	13.086519	21.464551	8.746179
H	12.672428	24.746490	6.120145	H	13.508687	21.659172	0.426768
H	13.945365	18.362304	3.071226	H	16.933101	21.059968	3.451772

S.3.6 Cartesian coordinates for optimized 1-P_2

93 Coordinates from ORCA-job job

H	-3.544301	3.989771	5.617497	C	-3.000471	4.552733	4.855884
H	-2.485140	2.801291	3.719273	H	-3.376057	6.457056	5.785104
H	-2.524484	2.185910	1.470748	C	-2.405570	3.888910	3.786069
H	-4.162216	4.743840	-1.444189	C	-2.902382	5.942235	4.947415
H	-2.925556	3.617876	0.499940	H	-3.353475	8.649229	5.822373
H	-3.934321	5.213626	-3.132311	C	-2.096312	2.990373	0.853862
H	-0.794457	8.201220	5.882486	C	-3.397710	4.952673	-2.207045
H	-1.624459	2.519612	-0.021728	H	-2.838689	4.023296	-2.388174
H	-4.128525	7.206591	-0.813724	C	-1.698891	4.579761	2.790549
C	-2.211928	6.687948	3.986196	C	-3.264301	8.893399	4.752815
H	-4.208750	8.618275	4.261389	C	-0.757652	8.555667	4.840831
H	-0.284185	2.126622	2.801803	H	-3.753542	7.709343	-2.481631
C	-1.062252	3.813444	1.641246	C	-1.608369	5.985882	2.912284
C	-3.309958	7.379456	-1.529483	H	0.119467	8.091901	4.365805

C	-2.061671	8.197769	4.100616	H	-3.149814	9.985217	4.681993
H	-0.600978	9.645120	4.855862	C	-2.485807	6.091661	-1.735463
H	-2.077004	5.808039	-0.751002	C	0.087402	2.916122	2.130638
H	-0.633024	4.552546	0.945987	H	-2.155927	5.418116	-4.397129
H	-2.685544	8.195241	-1.142644	H	0.586549	2.429347	1.278858
O	-0.950724	6.724461	1.964151	H	-1.977836	8.587172	3.073305
H	0.845646	3.491452	2.682120	C	-1.307138	5.977462	-4.000984
C	-1.300687	6.357549	-2.654940	H	-1.720871	10.259431	1.663820
H	-0.267928	5.981850	-5.896913	C	-0.244580	6.293658	-4.850437
H	-2.626414	10.794063	0.229603	H	3.345943	10.019836	5.066257
C	-0.171672	7.070068	-2.169474	O	-0.187157	7.466300	-0.861693
Nb	0.521897	7.403833	0.954192	H	-2.058632	11.985623	1.426559
C	-1.796895	11.051897	0.905364	H	4.585335	8.821313	4.629666
C	4.085985	9.744366	4.300992	O	1.173990	9.156567	1.230235
P	2.186220	6.099205	2.286867	P	2.329745	5.850710	0.249153
C	0.837979	7.018541	-4.359753	H	4.854246	10.532033	4.269748
H	2.783854	8.631718	3.020708	C	0.904603	7.426027	-3.018938
H	-0.273603	10.260547	-0.385203	C	-0.481551	11.216950	0.119949
C	3.432621	9.522194	2.930836	C	1.466356	10.445632	1.592105
H	1.657079	7.279004	-5.034160	C	2.555184	10.674317	2.467447
C	0.679429	11.496465	1.065351	H	-1.396266	11.955728	-1.707632
H	0.970232	10.169225	-2.830722	H	2.007200	8.356672	-1.449106
H	5.092797	8.322003	2.164606	H	-0.983120	13.245745	-0.570021
C	-0.641797	12.281444	-0.976410	C	2.066215	8.289828	-2.546137
C	4.496038	9.196564	1.863631	C	2.814256	11.999606	2.840136
C	1.937053	9.721218	-3.099906	C	0.993664	12.800074	1.471521
H	3.542704	6.669538	-2.499398	H	2.011954	9.726749	-4.198342
H	4.035992	8.970930	0.891466	H	3.639093	12.209526	3.522822
H	5.180048	10.048078	1.725057	H	0.404160	13.633952	1.086254
H	0.300655	12.455718	-1.514575	C	2.043366	13.055288	2.353589

C	3.438776	7.690834	-2.892535	H	3.605184	7.651844	-3.979848
H	2.736828	10.365542	-2.703631	H	2.266605	14.080545	2.656328
H	4.243039	8.306139	-2.461334				

S.3.7 Cartesian coordinates for optimized *endo*-1-$P_2C_6H_8$

107 atoms

C	-0.213243	-0.385315	0.499399	C	0.031523	-0.340917	1.969427
C	1.526027	-0.180615	2.316854	C	2.437929	-1.119856	1.483498
C	1.644485	-1.979107	0.477076	C	0.597329	-1.205123	-0.245607
P	-0.668854	-2.035132	2.586931	P	0.616092	-3.355118	1.360384
Nb	-1.616983	-2.663394	0.278555	O	-3.020473	-1.296991	0.211123
C	-3.572371	-0.108700	0.605451	C	-3.646561	0.949038	-0.341750
C	-4.190673	2.171834	0.071279	C	-4.680347	2.348190	1.366766
C	-4.655113	1.279340	2.261331	C	-4.118198	0.031562	1.909037
C	-3.243103	0.714779	-1.789878	C	-2.782586	1.979007	-2.527016
C	-4.232659	-1.136974	2.879540	C	-3.768383	-0.790188	4.302593
O	-2.605148	-4.152181	0.891748	C	-3.466183	-5.167579	1.223323
C	-4.723241	-5.226989	0.568418	C	-5.578995	-6.279810	0.915764
C	-5.216814	-7.229655	1.873762	C	-3.977838	-7.137933	2.506662
C	-3.071505	-6.112512	2.199008	C	-5.107389	-4.201828	-0.491015
C	-4.505633	-4.577824	-1.860321	C	-1.742833	-6.003182	2.932285
C	-1.937746	-5.325232	4.302440	O	-1.150325	-3.226114	-1.543553
C	-0.235597	-3.651497	-2.469338	C	0.333363	-4.950789	-2.354099
C	1.263625	-5.350837	-3.323676	C	1.621509	-4.522629	-4.387440
C	1.021864	-3.270029	-4.507072	C	0.084019	-2.811712	-3.570554
C	-0.096300	-5.942423	-1.280411	C	1.093749	-6.605659	-0.569135
C	-0.622011	-1.483921	-3.811285	C	0.347954	-0.330504	-4.119595
C	-1.033875	-7.008464	-1.881793	C	-1.660509	-1.635883	-4.940511
C	-1.029485	-7.355223	3.091872	C	-6.622438	-3.986789	-0.619948
C	-4.404847	0.035936	-2.544736	C	-5.678464	-1.672141	2.894731

H	-5.078119	1.410456	3.259833	H	-5.097270	3.310924	1.670629
H	-4.245014	3.000762	-0.636383	H	-2.402093	0.003383	-1.789847
H	-1.975488	2.496931	-1.988167	H	-2.407806	1.714300	-3.526578
H	-3.606768	2.693070	-2.674045	H	-3.584154	-1.944867	2.513907
H	-4.414993	-0.034955	4.774821	H	-2.737512	-0.407499	4.307862
H	-3.796187	-1.688429	4.937784	H	-5.286487	0.694966	-2.567511
H	-4.695296	-0.907015	-2.060839	H	-4.119353	-0.187740	-3.583476
H	-6.011161	-1.956171	1.886210	H	-5.755096	-2.559572	3.541829
H	-6.376624	-0.911329	3.277574	H	1.709573	-6.345233	-3.250277
H	2.351730	-4.858374	-5.126916	H	1.277445	-2.634493	-5.357909
H	-1.173337	-1.229017	-2.894480	H	-0.201996	0.618775	-4.201569
H	1.109365	-0.212438	-3.334285	H	0.874430	-0.485053	-5.073077
H	-2.398923	-2.414566	-4.701673	H	-2.199515	-0.690525	-5.105356
H	-1.170317	-1.912312	-5.886658	H	-0.664320	-5.391534	-0.518800
H	1.765745	-5.855286	-0.128253	H	1.683669	-7.235373	-1.252462
H	0.734241	-7.253578	0.244112	H	-1.905616	-6.549810	-2.369580
H	-0.506787	-7.614871	-2.635058	H	-1.401346	-7.687114	-1.097032
H	-3.705075	-7.880062	3.259606	H	-5.904540	-8.038788	2.129025
H	-6.553757	-6.357002	0.431508	H	-1.083227	-5.356007	2.333619
H	-2.388602	-4.328643	4.193725	H	-0.971232	-5.204414	4.815048
H	-2.594147	-5.929949	4.947791	H	-0.919690	-7.871838	2.127269
H	-1.568186	-8.028204	3.775925	H	-0.024193	-7.200248	3.511039
H	-4.668254	-3.237308	-0.189328	H	-4.749338	-3.810380	-2.610826
H	-3.412263	-4.665337	-1.812934	H	-4.913085	-5.538883	-2.210298
H	-6.820490	-3.137836	-1.290852	H	-7.091133	-3.768238	0.350658
H	-7.128255	-4.864013	-1.051629	H	2.319317	-2.499958	-0.214087
H	-0.570990	0.433845	2.460614	H	1.662793	-0.349623	3.395588
H	1.803046	0.869160	2.125640	H	3.024686	-1.784568	2.135175
H	3.164580	-0.518914	0.912768	H	0.534533	-1.256987	-1.331392
H	-0.950510	0.277730	0.045046				

S.3.8 Cartesian coordinates for optimized *exo*-1-$P_2C_6H_8$

107

C	0.171507	-0.129598	0.006806	C	0.120860	-0.058021	1.417892
C	1.275626	-0.066094	2.233508	C	2.514635	-0.132118	1.583184
C	2.603115	-0.188262	0.192075	C	1.442215	-0.189262	-0.581102
O	-1.104090	0.010821	2.038748	Nb	-2.874138	0.367986	2.539190
O	-3.375208	2.178473	2.038249	C	-3.495906	3.533976	2.209101
C	-2.367982	4.298706	2.607964	C	-2.533180	5.683407	2.750254
C	-3.752946	6.309107	2.505022	C	-4.841561	5.542689	2.093836
C	-4.741760	4.155107	1.932731	C	-0.987773	3.693508	2.823857
C	-0.023621	4.113777	1.698258	C	-5.926632	3.364468	1.398669
C	-6.018724	3.521623	-0.131678	C	1.154703	-0.056283	3.750455
C	2.356779	0.578035	4.462376	C	-1.100672	-0.110824	-0.830673
C	-0.972587	-0.877217	-2.155103	P	-3.164379	-1.138088	4.582824
P	-2.435545	0.896377	5.000789	O	-3.980870	-0.834623	1.463445
C	-4.771424	-1.958398	1.445311	C	-6.142218	-1.818418	1.106814
C	-6.950265	-2.961805	1.130878	C	-6.425192	-4.214829	1.445255
C	-5.061093	-4.342193	1.696824	C	-4.199827	-3.235280	1.687020
C	-6.684957	-0.486477	0.611064	C	-6.430553	-0.364427	-0.905505
C	-2.695493	-3.449312	1.802656	C	-2.129794	-3.889992	0.437294
C	-8.166665	-0.253172	0.933630	C	-2.292228	-4.440200	2.903904
C	-7.259205	3.739295	2.066636	C	-0.403218	4.035613	4.203339
C	0.902365	-1.481787	4.281117	C	-1.566589	1.335336	-1.092467
H	-4.645861	-5.332561	1.893854	H	-7.073665	-5.093357	1.468784
H	-8.011175	-2.872063	0.890656	H	-6.106646	0.312233	1.099178
H	-8.378245	-0.382923	2.004972	H	-8.457824	0.769452	0.650959
H	-8.823930	-0.936103	0.374200	H	-2.233797	-2.484124	2.054542
H	-2.645838	-5.461081	2.693379	H	-2.686477	-4.131599	3.882094
H	-1.195769	-4.488931	2.982773	H	-6.962562	-1.158140	-1.452230
H	-5.359803	-0.454763	-1.134950	H	-6.781082	0.606560	-1.286798

H	-2.386188	-3.172367	-0.354854	H	-1.033195	-3.976315	0.481225
H	-2.537030	-4.869750	0.143013	H	-1.675138	6.287298	3.054383
H	-3.853141	7.389643	2.627462	H	-5.793605	6.034677	1.884131
H	-5.734758	2.302219	1.609828	H	-8.056976	3.060053	1.731209
H	-7.196560	3.675149	3.162084	H	-7.576219	4.760708	1.807516
H	-5.097714	3.179830	-0.624530	H	-6.861005	2.939434	-0.536459
H	-6.175880	4.576005	-0.406160	H	-1.087855	2.599264	2.782449
H	-1.068381	3.704444	5.012903	H	-0.235114	5.117199	4.318986
H	0.566661	3.534848	4.341093	H	-0.422395	3.854460	0.707552
H	0.150999	5.200807	1.712799	H	0.949345	3.613353	1.814593
H	3.428738	-0.135361	2.178937	H	3.580910	-0.236619	-0.291800
H	1.524101	-0.244154	-1.667679	H	0.267198	0.544508	4.008699
H	0.001550	-1.925903	3.835526	H	0.760030	-1.466645	5.371882
H	1.756005	-2.139198	4.053370	H	2.592205	1.575426	4.062506
H	3.262433	-0.042732	4.380679	H	2.136391	0.687110	5.534122
H	-1.889021	-0.613378	-0.246606	H	-2.513727	1.340582	-1.653035
H	-1.727287	1.890366	-0.158273	H	-0.817332	1.882975	-1.684456
H	-1.957446	-0.953426	-2.638885	H	-0.590276	-1.896570	-2.002482
H	-0.305447	-0.365569	-2.865414	C	-5.055094	-0.781526	5.066656
C	-4.073434	1.624021	5.866360	C	-4.483601	0.668653	6.927459
C	-5.226657	1.781106	4.862534	C	-5.013901	-0.510295	6.527681
C	-5.646220	0.413177	4.280219	H	-3.760300	2.596137	6.268570
H	-5.582419	-1.711032	4.817525	H	-4.306448	0.900031	7.980480
H	-5.290105	-1.292604	7.238435	H	-4.958176	2.490793	4.071407
H	-6.075205	2.226776	5.408153	H	-6.745473	0.332595	4.280262
H	-5.372795	0.324717	3.211928				