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Supporting Online Material for

White Phosphorus is Air-Stable Within a Self-Assembled Tetrahedral Capsule

Prasenjit Mal, Boris Breiner, Kari Rissanen, Jonathan R. Nitschke*

*To whom correspondence should be addressed. E-mail: jrn34@cam.ac.uk

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Supporting Information for

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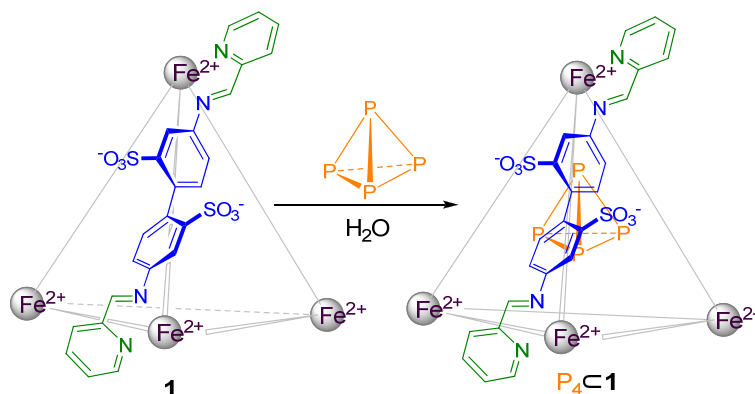
*Prasenjit Mal,^a Boris Breiner,^a Kari Rissanen^b and Jonathan R. Nitschke^{*a}*

^aUniversity of Cambridge, Department of Chemistry
Lensfield Road, Cambridge CB2 1EW, UK
E-mail: jrn34@cam.ac.uk
<http://www-jrn.ch.cam.ac.uk/>

and

^bNanoscience Center, Department of Chemistry
University of Jyväskylä, P.O. Box 35, 40014 JYU, Finland
E-mail: kari.rissanen@jyu.fi

Materials and Methods



Preparation of P₄C1. To a 100 mL Schlenk flask containing degassed water (10 mL) and a stir-bar were added **1** (250 mg, 74.7 μmol) and P₄ (72 mg, 0.58 mmol). The flask was sealed and the atmosphere was purified of dioxygen by three evacuation / argon fill cycles. The reaction was stirred for 72 h at 323 K. The product was then isolated as dark purple crystals by slow diffusion of acetone into the aqueous solution of **1**; isolated yield 237 mg (91%); ¹H NMR (500 MHz, 300 K, D₂O, referenced to 2-methyl-2-propanol at 1.24 ppm as internal standard): δ = 9.75 (s, 12 H, imine), 8.86 (d, *J* = 6.0 Hz, 12 H, 3-pyridine), 8.40 (t, *J* = 7.5 Hz, 12 H, 4-pyridine), 7.89 (t, *J* = 7.5 Hz, 12 H, 5-pyridine), 7.81 (s, br, 12 H, 6,6'-benzidine), 7.33 (d, *J* = 7.5 Hz, 12 H, 6-pyridine), 6.48 (s, 12 H, 3,3'-benzidine), 6.10 (d, *J* = 7.0 Hz, 12 H, 5,5'-benzidine), 3.17 (s, tetramethylammonium), 2.22 (s, acetone) ppm; ¹³C NMR (125 MHz, 300 K, D₂O, referenced to 2-methyl-2-propanol at 30.29 ppm as internal standard): δ = 175.9, 158.0, 156.7, 151.9, 143.4, 140.5, 136.4, 135.1, 133.5, 131.7, 123.1, 121.6, 70.5 (C-OH: 2-methyl-2-propanol), 30.9 (C-Me of acetone), 30.3 (C-Me of 2-methyl-2-propanol) ppm; ³¹P NMR (200.5 MHz, 300 K, D₂O): δ = 510.1 ppm; elemental analysis calcd (%) for Fe₄P₄C₁₄₄H₉₆N₂₄O₃₆S₁₂·10H₂O·SO₄²⁻·5(acetone)·2⁺NMe₄·4Na⁺: P 2.90, C 46.89, H 4.01, N 8.51; found: P 2.77, C 46.81, H 4.14, N 8.67.

X-ray Crystallography. Purple crystals of P₄C1 were obtained by vapor diffusion of 1,4-dioxane into an aqueous solution of P₄C1. The structural analysis was performed using

Bruker Kappa Apex II diffractometer with graphite-monochromatized Mo- $K\alpha$ ($\lambda = 0.71073$ Å) radiation. Collect software (*S1*) was used for the data measurement and DENZO-SMN (*S2*) for the processing. The structure were solved by direct methods with SIR97 (*S3*) and refined by full-matrix least-squares methods in three blocks using the WinGX-software, (*S4*) which utilizes the SHELXL-97 module (*S5*). Multi-scan absorption correction was applied (SADABS2008) (*S6*). All C-H hydrogen positions were calculated using a riding atom model with $U_H = 1.2 \times U_C$. The P_4 tetrahedron inside the cage appeared disordered and was modeled with two orientations with total occupancy of 0.75 (0.45 and 0.30). Due to this disorder bond distance restraints (DFIX, 2.20 Å) between the phosphorous atoms were applied in order to avoid chemically unreasonable bond distances. All atoms except the some of the disordered O-atoms (water) with occupancy 1/3 and H-atoms were refined anisotropically. Thermal parameter restraints (ISOR) were applied to all O-atoms. In addition to $P_4\text{C}1$, tetramethylammonium cations and water molecules were located in the unit cell, which are badly disordered, as reflected in the moderate quality of the diffraction data. None of the tetramethylammonium cations could be located and all water molecules were modeled as isolated oxygen atoms. The remaining residual electron density in close proximity of the cage was treated as disordered water molecules (H-atoms could not be located) until a plateau of ca. $1.5 \text{ e}/\text{Å}^3$ maximum residual electron density was reached. The crystal lattice contains large voids filled with scattered electron density; the SQUEEZE protocol of PLATON (*S7*) was used to model this electron density (down to ca. $1 \text{ e}/\text{Å}^3$). Crystal data for $P_4\text{C}1$: $M = 4055.48.6$, purple prism, $0.25 \times 0.30 \times 0.30 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 21.9507(4) \text{ Å}$, $b = 33.3175(6) \text{ Å}$, $c = 32.8597(6) \text{ Å}$, $\beta = 90.907(1)^\circ$, $V = 24028.7(8) \text{ Å}^3$, $Z = 4$, $D_c = 1.121 \text{ g/cm}^3$, $F000 = 8260$, $\mu = 0.436 \text{ mm}^{-1}$, $T = 123.0(1) \text{ K}$, $2\theta_{\text{max}} = 45.0^\circ$, 31386 reflections used, 16922 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.1295$, 2588 parameters, 666 restraints, $\text{GoF} = 1.235$, $R = 0.141 [I_o > 2\sigma(I_o)]$, $wR = 0.389$ (all reflections), $1.205 < \Delta\rho < -0.729 \text{ e}/\text{Å}^3$. CCDC-727817 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

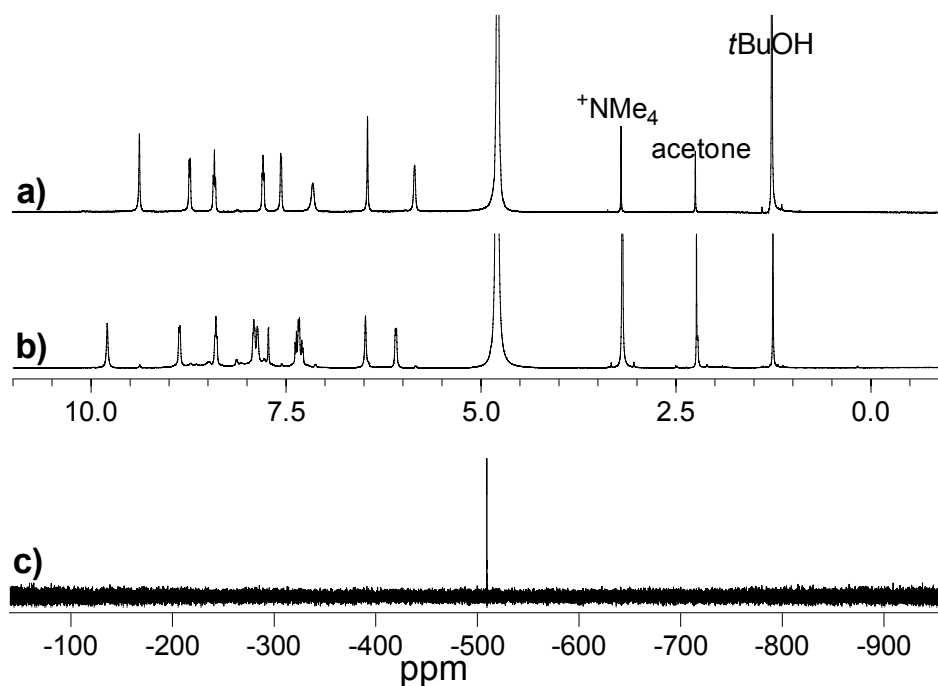


Figure S1. ^1H NMR spectra in D_2O of cage **1** (top), of $\text{P}_4\subset\mathbf{1}$ (middle), and ^{31}P NMR spectrum of $\text{P}_4\subset\mathbf{1}$ (bottom).

Reaction of $\text{P}_4\subset\mathbf{1}$ with cyclohexane to release P_4 . D_2O (0.5 mL), $\text{P}_4\subset\mathbf{1}$ (5.0 mg, 1.5 μmol) and excess cyclohexane (ca. 0.02 mL) were loaded into a Teflon-capped NMR tube, and the solution was degassed with three vacuum / N_2 cycles. The sealed NMR tube was heated in an oil bath to 323 K, and reaction progress was monitored by ^1H NMR (Figure S2). The appearance was noted of ^1H resonances corresponding to $\text{C}_6\text{H}_{12}\subset\mathbf{1}$. The reaction had reached completion after 96 h at 323 K.

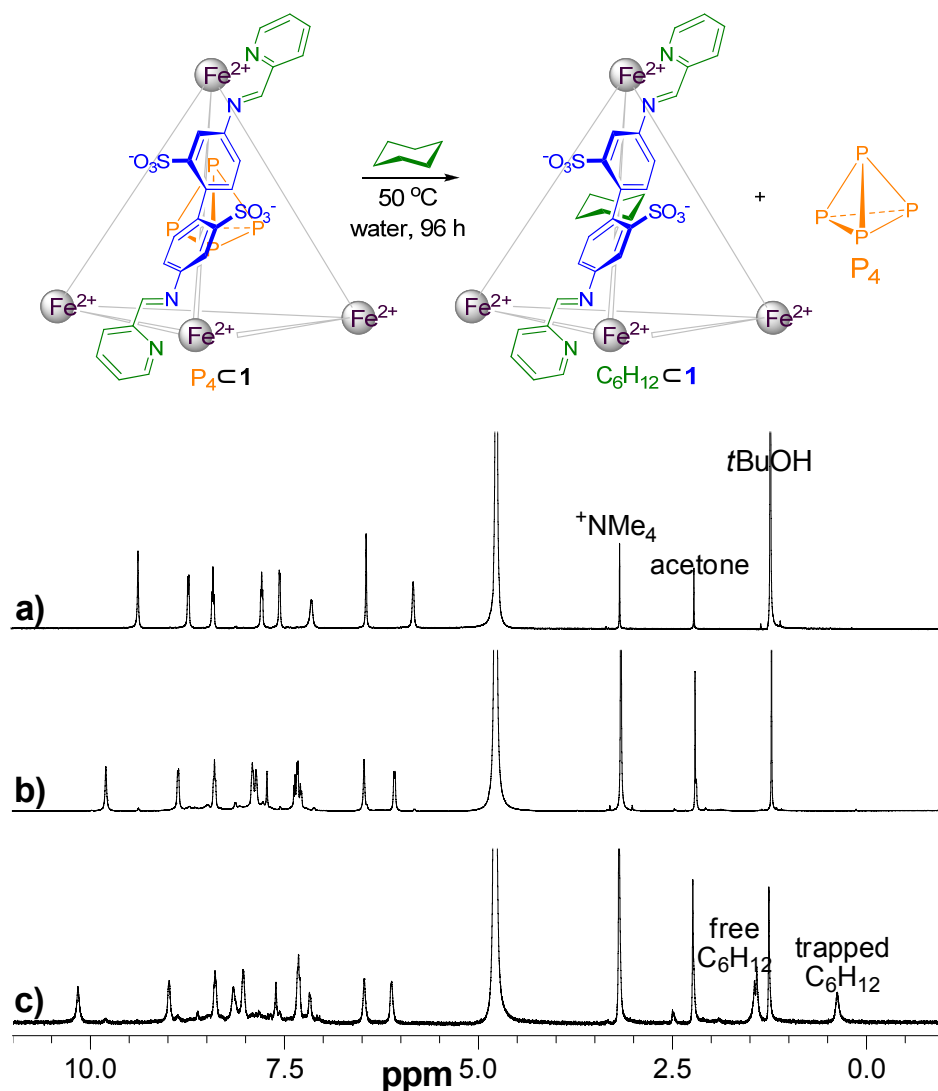
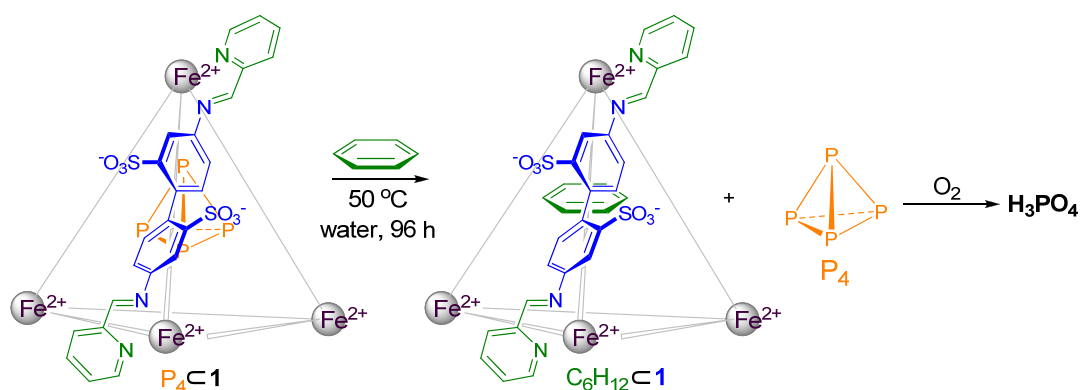


Figure S2. ^1H NMR spectra of a) **1**; b) $\text{P}_4\text{C1}$ c) $\text{P}_4\text{C1}$ following reaction with cyclohexane (96 h at 323 K).

Reaction of $\text{P}_4\text{C1}$ with benzene- d_6 to release P_4 followed by reaction with O_2 . D_2O (0.5 mL), $\text{P}_4\text{C1}$ (5.0 mg, 1.5 μmol) and C_6D_6 (ca. 0.2 mL) were loaded into a Teflon-capped NMR tube, and the solution was degassed with three vacuum / N_2 cycles. The sealed NMR tube was heated in an oil bath to 323 K, and reaction progress was monitored by ^1H NMR (Figure S3). The appearance was noted of ^1H resonances corresponding to $\text{C}_6\text{D}_6\text{C1}$; ^1H

NMR indicated that the reaction had reached completion after 24 h at 323 K. The benzene layer was separated into a second Teflon-capped NMR tube and diluted with 0.4 mL of C_6D_6 . The ^{31}P NMR spectrum of this sample was recorded (Figure 3b, main text), showing the appearance of a new peak at -520 ppm. O_2 was bubbled through the solution for 2-3 min at room temperature, D_2O (ca. 0.5 mL) was added, and the mixture was then heated for a further 24 h at 323 K. The D_2O layer was separated and its ^{31}P NMR spectrum was recorded (Figure 3b, main text), showing the appearance of a new peak at 0 ppm.



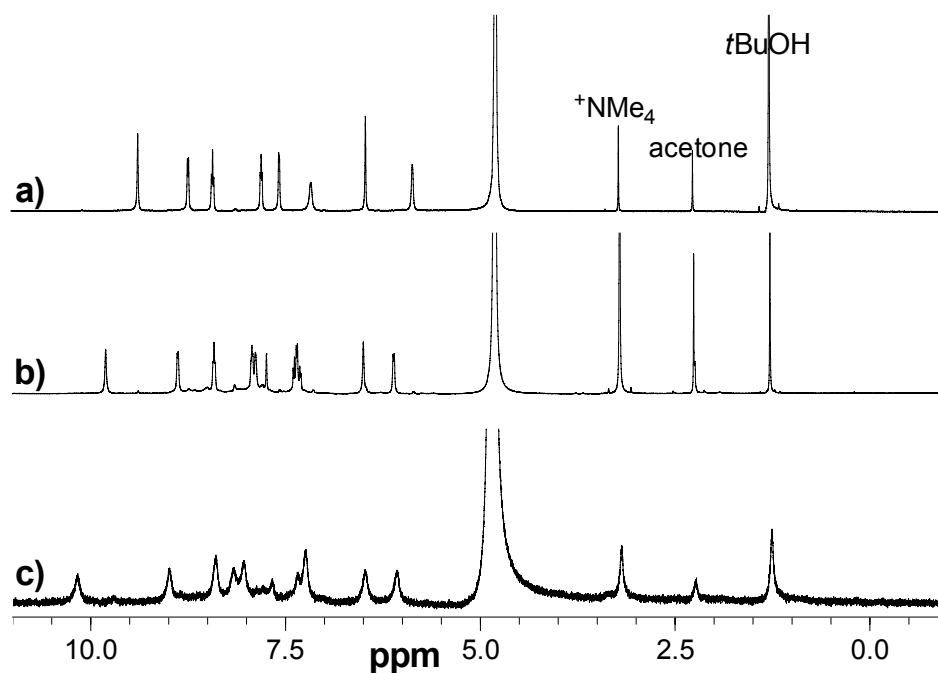


Figure S3. ^1H NMR spectra of a) **1**; b) $\text{P}_4\text{C1}$ c) $\text{P}_4\text{C1}$ following reaction with benzene- d_6 (24 h at 323 K).

Treatment of $\text{P}_4\text{C1}$ with N_2O . $\text{P}_4\text{C1}$ (5.0 mg, 1.5 μmol) and D_2O (0.5 mL) were loaded into a Teflon-capped NMR tube, and N_2O was bubbled through the solution for 2-3 min at room temperature. The tube was then sealed and heated in an oil bath to 323 K for 24 h, after which the ^1H NMR spectrum of $\text{P}_4\text{C1}$ was observed to have remained unchanged.

Treatment of $\text{P}_4\text{C1}$ with Pyridine-N-oxide. D_2O (0.5 mL), $\text{P}_4\text{C1}$ (5.0 mg, 1.5 μmol) and pyridine-N-oxide (1.5 mg, 15.8 μmol) were loaded into a Teflon-capped NMR tube, and the solution was degassed with three vacuum / N_2 cycles. The sealed NMR tube was heated in an oil bath to 323 K. Following 24 h at 323 K, the ^1H NMR spectrum gave no evidence of reaction between $\text{P}_4\text{C1}$ and pyridine-N-oxide.

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