Electronic Supplementary Material (ESI) for Dalton Transactions.

The preservation of sarin and *O,O'*-diisopropyl fluorophosphate inside coordination cage hosts

Jack C. Dorrat,[a] Rosemary J. Young,[a] Christopher G. P. Taylor,[d] Max B. Tipping,[d] Andrew J. Blok,[b] David R. Turner,[a] Alasdair I. McKay,[a] Simon Ovenden,[b] Michael D. Ward,*[d] Genevieve H. Dennison,*[b,c] Kellie L. Tuck*[a]

[a]School of Chemistry, Monash University, Melbourne, VIC, 3800, Australia, E-mail: Kellie.Tuck@monash.edu

[b]CBRN Defence Branch, Sensors and Effectors Division, Defence Science and Technology Group, Fishermans Bend, VIC, 3207, Australia.

[c]Weapon Seekers and Tactical Sensors Branch, Sensors and Effectors Division, Defence Science and Technology Group, Edinburgh, SA, 5111, Australia. E-mail: Genevieve.Dennison@defence.gov.au

[d]Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK. E-mail: M.D.Ward@warwick.ac.uk

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Cage preparation

For preparation of the $\mathbf{H}^{\mathbf{PEG}}$•OH cage, the $[Cd_8(\mathbf{L}^{\mathbf{PEG}})_{12}](NO_3)_{16}$ complex was dissolved in water and then filtered using a syringe filter (0.22 μm).[1] For preparation of the $\mathbf{H}^{\mathbf{W}}$•OH cage, the complex $[Co_8(\mathbf{L}^{\mathbf{W}})_{12}](BF_4)_{16}$ was heated at 80 °C in water for 15 hours.[2] To obtain the $\mathbf{H}^{\mathbf{W}}$•Cl_{16} and **H**•Cl_{16} cages, the complexes $[Co_8(\mathbf{L}^{\mathbf{W}})_{12}](BF_4)_{16}$ and $[Co_8(\mathbf{L})_{12}](BF_4)_{16}$ were separately converted to their chloride form using the ion exchange resin Dowex® chloride according to the previously published procedure.[3] Residual resin was removed by filtration with use of a syringe filter (0.22 μm).

The concentration of the respective cages were determined using the absorbance at 292 nm (ε = 3.088 x 10^5 M^{-1} cm^{-1}) in MQ water. Buffered solutions of the cages were prepared using the appropriate quantities of solid boric acid and anhydrous borax. For example, to obtain 2 mL of a 50 mM buffer with a pH value of 8.7, boric acid (50 mM, 6.1 mg) and borax (12.5 mM, 5.0 mg) were added. The resulting suspension was sonicated for 3 minutes and then left to settle for 30 minutes. For the ^{19}F and ^{31}P NMR spectral experiments the final solution was 10% D_2O/90%H_2O (50 mM boric buffer, pH 8.7).

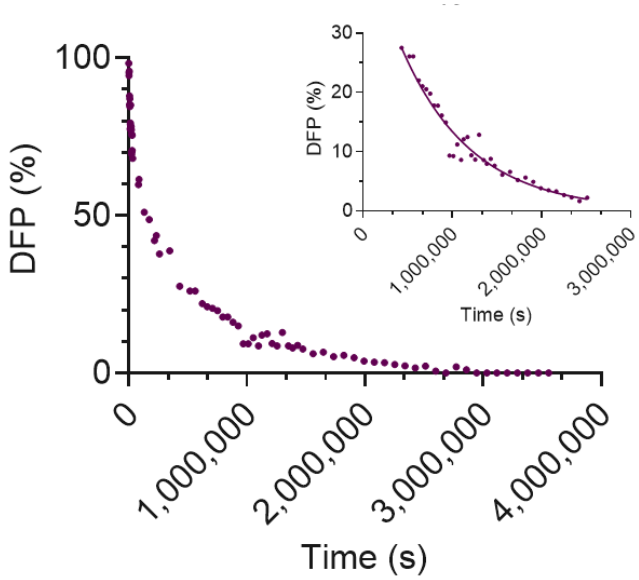

Fig. S1 - Representative hydrolysis curve of DFP (7.5 mM) with $\mathbf{H}^{\mathbf{PEG}}\bullet$OH (0.5 mM) over time. Insert: the hydrolysis data fitted to a first order decay model to determine the hydrolysis rate constant and half-life.

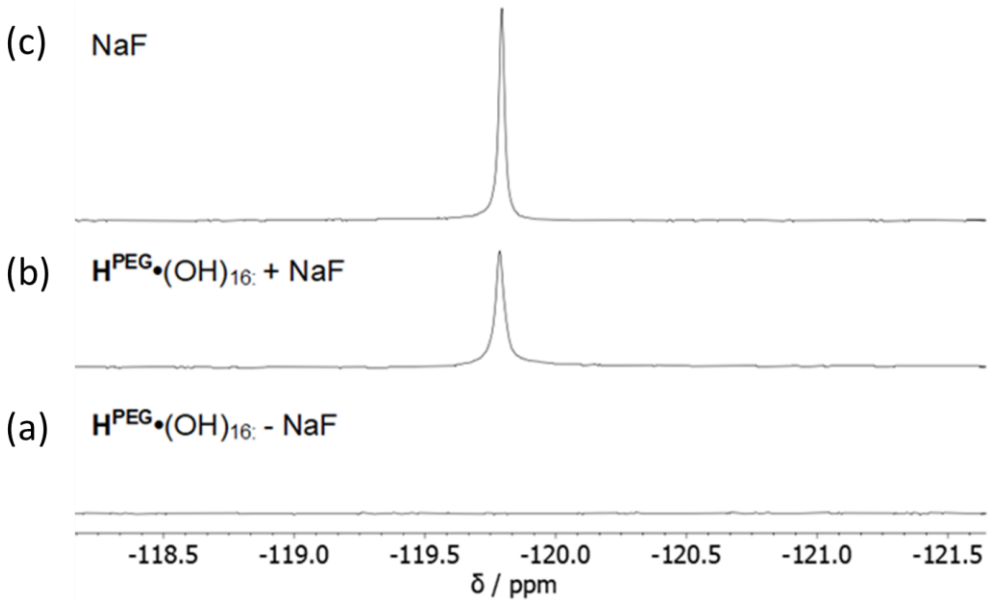

Fig. S2 - ^{19}F NMR spectra: (a) $\mathbf{H}^{\mathbf{PEG}}\bullet$OH (0.2 mM), (b) $\mathbf{H}^{\mathbf{PEG}}\bullet$OH (0.2 mM) + NaF (7.5 mM) and (c) NaF (7.5 mM); H_2O/D_2O (90:10 v/v) with boric buffer (pH 8.6, 50 mM).

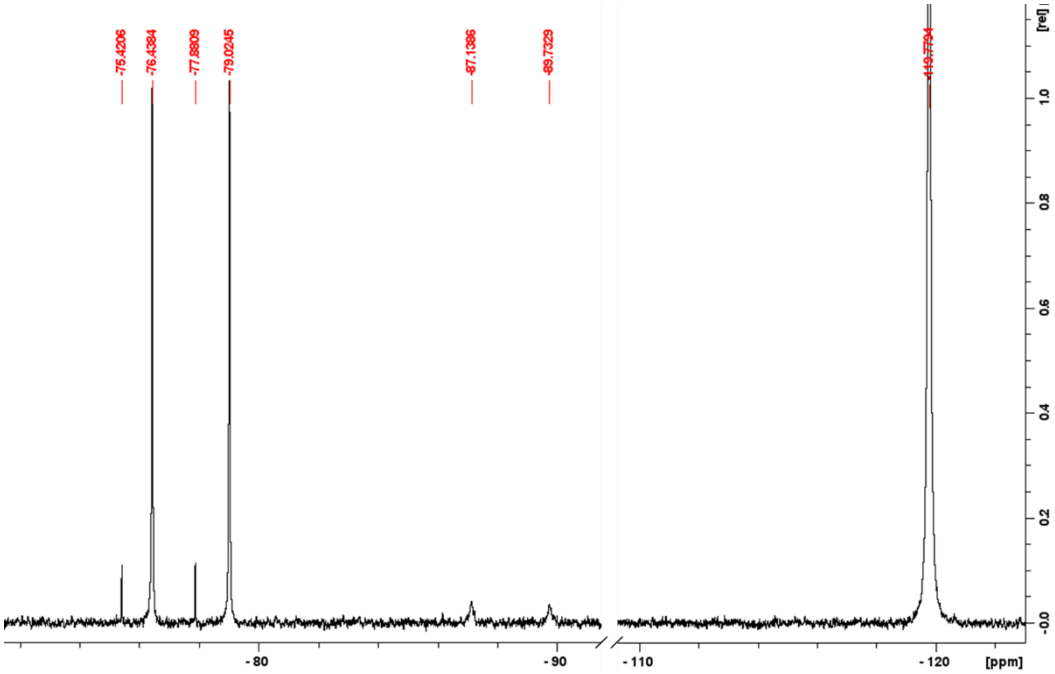

Fig. S3 - ^{19}F NMR spectrum of DFP (7.5 mM) and $\mathbf{H^{W}}$•OH (0.5 mM), H_2O/D_2O (90:10 v/v) with boric buffer (pH 8.6, 50 mM).

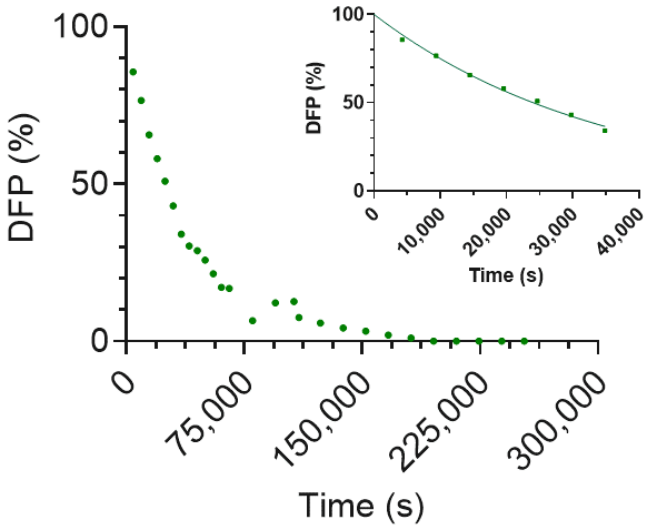

Fig. S4 - Representative hydrolysis curve of DFP (7.5 mM) with $\mathbf{H^{W}}$•OH (0.5 mM) present over time. Insert: the hydrolysis data (0-9 hours) fitted to a first order decay model to determine the hydrolysis rate constant and half-life.

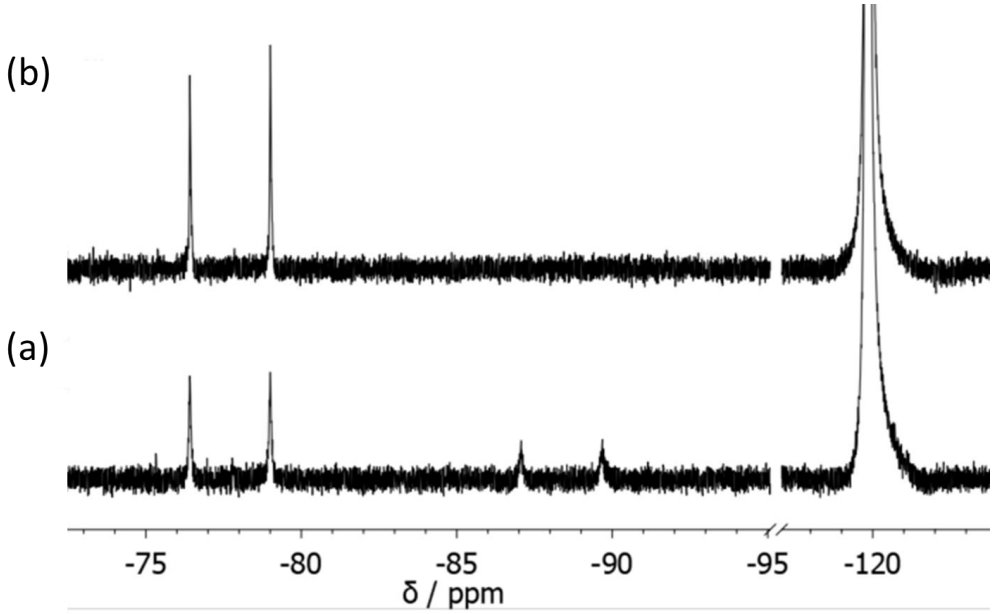

Fig. S5 - ^{19}F NMR spectra: (a) DFP (3.0 mM) and **H^{W}•**OH (0.6 mM); (b) DFP (3.0 mM) and **H^{W}•**OH (0.6 mM) + cycloundecanone (22 mM); H_2O/D_2O (90:10 v/v) with boric buffer (pH 8.6, 50 mM).

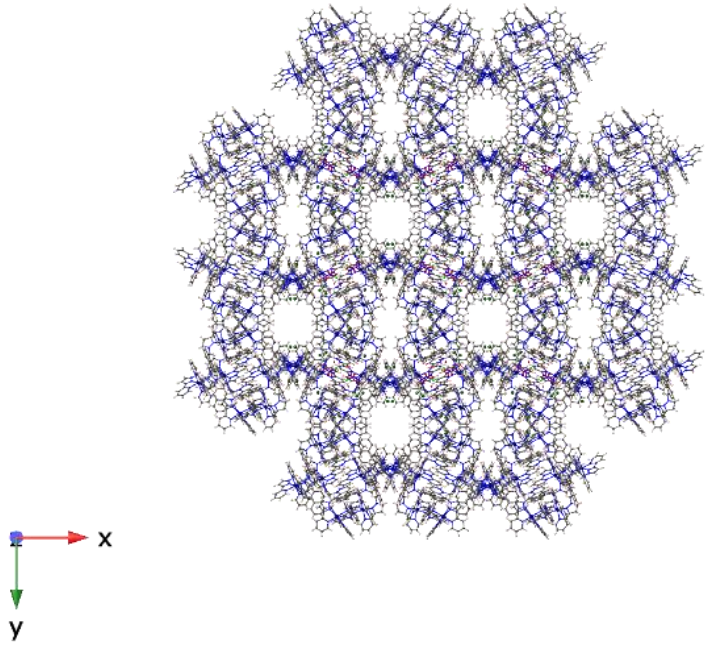

Fig. S6 - Extended packing of **H**•Cl_{16}•DFP viewed down the z-axis showing solvent accessible channels through which the organophosphate guests can access the cages.

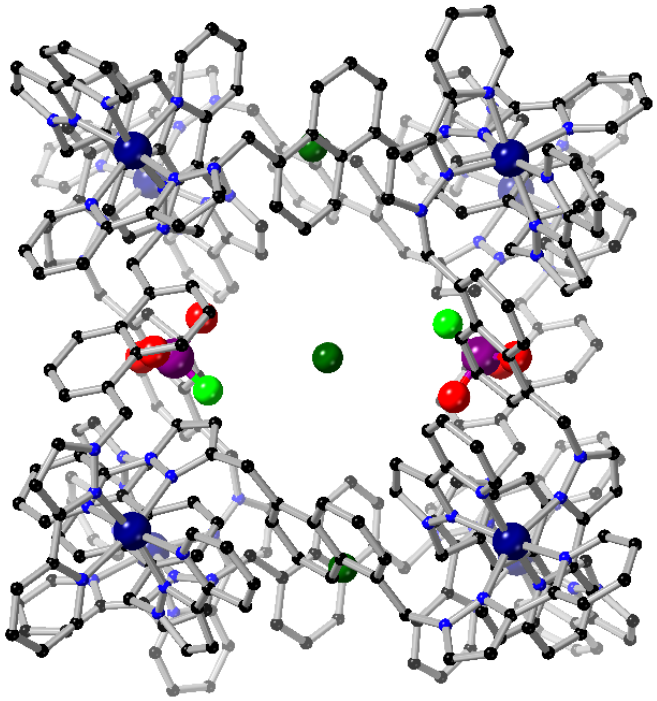

Fig. S7 - Crystal structure of **H**•Cl_{16}•DFP showing DFP resolved in its lower occupancy position (16% occupancy) 2.7 Å further inside the window of the cage than the major position (58% occupancy). H atoms are omitted for clarity, Co – dark blue, C – black, N – blue, O – red, P – purple, F – light green, Cl – dark green.

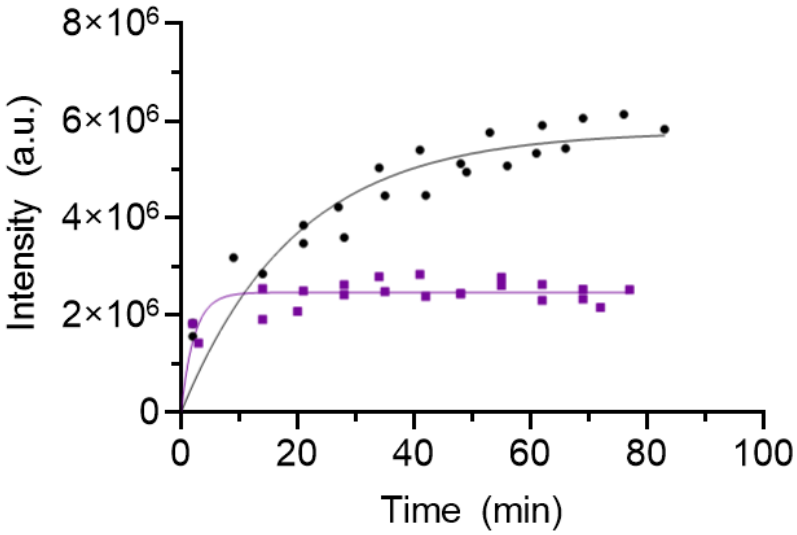

Fig. S8 - The reaction progress profiles of the hydrolysis of GB; formation of *O*-isopropyl methylphosphonic acid (IMPA) over time as determined by NMR integration; without cage (black) and with $\mathbf{H}^{PEG}$•OH (0.50 mM, purple), measurements in D_2O/H_2O/MeCN (10:85:5 v/v/v) with 50 mM boric buffer, pH 8.7 determined *via* ^{31}P NMR spectroscopic analysis.

References

1. G. D. Jackson, M. B. Tipping, C. G. P. Taylor, J. R. Piper, C. Pritchard, C. Mozaceanu and M. D. Ward, A family of externally-functionalised coordination cages. *Chemistry*, 2021, **3**, 1203-1214.

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3. W. Cullen, A. J. Metherell, A. B. Wragg, C. G. P. Taylor, N. H. Williams and M. D. Ward, Catalysis in a cationic coordination cage using a cavity-bound guest and surface-bound anions: Inhibition, activation, and autocatalysis. *J. Am. Chem. Soc.*, 2018, **140**, 2821-2828.