Electronic Supplementary Information

A Fluorophosphate-Based Inverse Keggin Structure

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1. Experimental

General. All reactions between molybdates and $[Cu(MeCN)_4](PF_6)$ were carried out under an Ar or N_2 atmosphere. $(nBu_4N)_2[Mo_2O_7]$ and $(nBu_4N)_4[Mo_8O_{26}]$,[1] $(NH_4)_{42}[Mo_{132}O_{372}(CH_3CO_2)_{30}(H_2O)_{72}]\cdot 300H_2O\cdot 10CH_3CO_2NH_4$ (= $\{Mo_{132}\}$),[2] and $[Cu(MeCN)_4](PF_6)$[3] were synthesized according to published procedures. Note that the acetonitrile-soluble $\{Mo_{132}\}$ derivative **1** was modified not only with respect to cations but also to include mercaptoacetate groups, in order to introduce an additional element which can be determined from C/H/N/S analysis. Where described as dry, anhydrous acetonitrile was bought from Aldrich in SureSeal bottles. Dry KBr was supplied in small sachets by Thermo Fisher. 95% H_2PFO_3 was purchased from Alfa Aesar. All other reagents were obtained commercially as ACS grade and used without further purification. ^{31}P NMR spectra were acquired in acetonitrile on a Bruker DRX-400 spectrometer and externally referenced to 85% $H_3PO_4(aq)$. IR spectra were recorded on a Bruker TENSOR 27 spectrometer. Single crystal X-ray diffraction data were collected on a Bruker CCD-1000 diffractometer with Mo-K_α radiation. C/H/N/S analyses were performed using a Perkin Elmer 2400 CHNS Analyzer.

Synthesis of $(nBu_4N)_{34}(NH_4)_8[Mo_{132}O_{372}(HSCH_2CO_2)_{20}(CH_3CO_2)_{10}(H_2O)_{72}]$ (1). $(NH_4)_{42}[Mo_{132}O_{372}(CH_3CO_2)_{30}(H_2O)_{72}]\cdot 300H_2O\cdot 10CH_3CO_2NH_4$ (2.0 g, 0.070 mmol) and mercaptoacetic acid (2.6 g, 28.22 mmol) were dissolved in water (500 mL) and then extracted with a solution of tetra-*n*-butylammonium bromide (6.4 g, 19.85 mmol) in dichloromethane (500 mL). The aqueous layer was then extracted with 2 × 50 mL portions of dichloromethane and the combined organic layers back-extracted with 4 × 150 mL water, before 2-propanol (30 drops) was added and 300 mL of cyclohexane were layered on top of the dichloromethane solution. After 14 days **1** (1.73 g, 0.0563 mmol, 80%) was recovered by filtration and washed with diethyl ether. IR (KBr pellet, ν / cm^{-1}): 3416 (m), 2962 (m), 2873 (m), 1631 (m), 1566 (m), 1482 (m), 1362 (m), 983 (s), 954 (w), 857 (s), 802 (vs), 734 (vs), 636 (w), 576 (s), 482 (w), 412 (w). Elemental analysis for $C_{604}H_{1490}Mo_{132}N_{42}O_{504}S_{20}$ ($(nBu_4N)_{34}(NH_4)_8[Mo_{132}O_{372}(HSCH_2CO_2)_{20}(CH_3CO_2)_{10}(H_2O)_{72}]$), calculated (found): C 23.62 (23.65), H 4.89 (4.92), N 1.92 (1.87), S 2.09 (2.12)%.

Synthesis of $H_3[Cu(CH_3CN)_4][Mo_{12}O_{46}(PF)_4]\cdot 4CH_3CN\cdot 32H_2O$ (2) and $(nBu_4N)_3[PMo_{12}O_{40}]$ (3). $[Cu(MeCN)_4](PF_6)$ (1.321 g, 3.54 mmol) was added to a solution of **1** (0.8 g, 0.026 mmol) in acetonitrile (50 mL) and refluxed for 72 hours under nitrogen. After reduction in volume to *ca.* 14 mL, the dark blue solution was set to crystallize by ether diffusion producing yellow crystals of **3** (0.010 g, 0.0039 mmol, 1.4%), higher yields (up to 50%) could be achieved by repeatedly re-precipitating crude solid material from acetonitrile/ether mixtures. IR (KBr disc, ν / cm^{-1}): 3454 (w, OH), 2963 (s, CH), 2874 (m, CH), 1470 (m), 1380 (w), 1063 (s), 956 (vs), 880 (s), 807 (vs), 617 (w), 505 (m). Elemental analysis for $C_{48}H_{108}Mo_{12}N_3O_{40}P$ (**3**), calculated (found): C 22.61 (22.54), H 4.27 (4.20), N 1.65 (1.78)%. After several weeks a few dark green crystals of **2** were also observed (0.002 g, 0.8 μmol, 0.24%). IR (KBr pellet, ν / cm^{-1}): 3479 (s, OH), 1622 (m, OH), 1213 (s, PO_3), 1145 (vs, PO_3), 1017 (m, PO_3), 947 (vs, PO_3), 932 (vs, Mo=O), 840 (s, PF) 682 (s, PF), 628 (m), 600 (m), 558 (w).

NMR studies on the reaction of molybdates with H_2PFO_3. Each molybdate (0.2 g: $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo}_2\mathrm{O}_7]$, 0.254 mmol; $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{Mo}_8\mathrm{O}_{26}]$, 0.0929 mmol; **1**, 0.00651 mmol) was combined in a PTFE Erlenmeyer flask with dry acetonitrile (10 mL), H_2PFO_3 (1.03 equivalents relative to the quantity of Mo atoms), $n\mathrm{Bu}_4\mathrm{NF}$ (1.03 equivalents relative to Mo), and where required $[\mathrm{Cu(MeCN)}_4](\mathrm{PF}_6)$ (1.03 equivalents relative to Mo). The solutions were stirred at room temperature overnight before acquisition of ^{31}P NMR spectra, taking on a green color if $[\mathrm{Cu(MeCN)}_4](\mathrm{PF}_6)$ had been added.

2. Single-Crystal X-ray Structure Determination

A suitable single crystal of **2** was mounted on the end of a thin glass fiber under ambient conditions using Fomblin oil. X-ray diffraction intensity data were measured at 193 K on a Bruker CCD-1000 diffractometer [λ(Mo-Kα) = 0.7107 Å, graphite monochomator]. Initial cell constants were obtained from three 30 frame series of ω scans at different starting angles, while final cell constants were calculated from a set of strong reflections from the actual data collection. These datasets were corrected for Lorentz and polarization effects and the absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements[4] using SADABS software.[5] Structure solution and refinement was carried out using the SHELXTL program suite.[5] Compound **2** crystallized in the space group *Cmcm*, and its structure of was solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. The PLATON SQUEEZE routine was used to remove disordered solvent molecules and cations which would not refine successfully,[6] leaving substantial void space. Based on the IR spectra and the number of removed electrons calculated by SQUEEZE (320 per formula unit), 32 water molecules per formula unit have been included to fill this void, along with three protons for charge balance. Crystal data, data collection parameters and refinement statistics are listed in Table S1, bond lengths and angles in Table S2, and an ORTEP representation is provided in Figure S1.

Single crystal X-ray data were also collected for **3**, at 213 K. The unit cell obtained was a good match for the published structure (monoclinic a = 49.96 Å, b = 14.11 Å, c = 26.33 Å, *ß* =114.8°).[7] Attempted structure solution indicated the presence of $[\alpha\text{-PMo}_{12}\text{O}_{40}]$ units, however due to twinning issues the data obtained was not of sufficient quality to allow satisfactory completion.

Table S1. Crystallographic Data for **2**

Empirical formula	$C_8H_{15}CuF_4Mo_{12}N_4P_4O_{46}$ $\cdot 4CH_3CN\cdot 32H_2O$
F_w	3058.67 g mol^{-1}
Crystal system	orthorhombic
a	30.162(5) Å
b	17.875(3) Å
c	20.715(3) Å
α	90°
β	90°
γ	90°
Space group	*Cmcm*
V	11168(3) Å^3
Z	4
ρ_{calcd}	1.819 g cm^{-1}
μ	1.646 mm^{-1}
T	193(2) K
No. reflections	41216
Independent reflections	5187 (R_{int} = 0.0580)
Completeness to θ = 25.03°	99.7%
Data / restraints / parameters	5187 / 92 / 265
GooF on F^2	1.061
Residuals: R_1; wR_2	0.0671; 0.2098

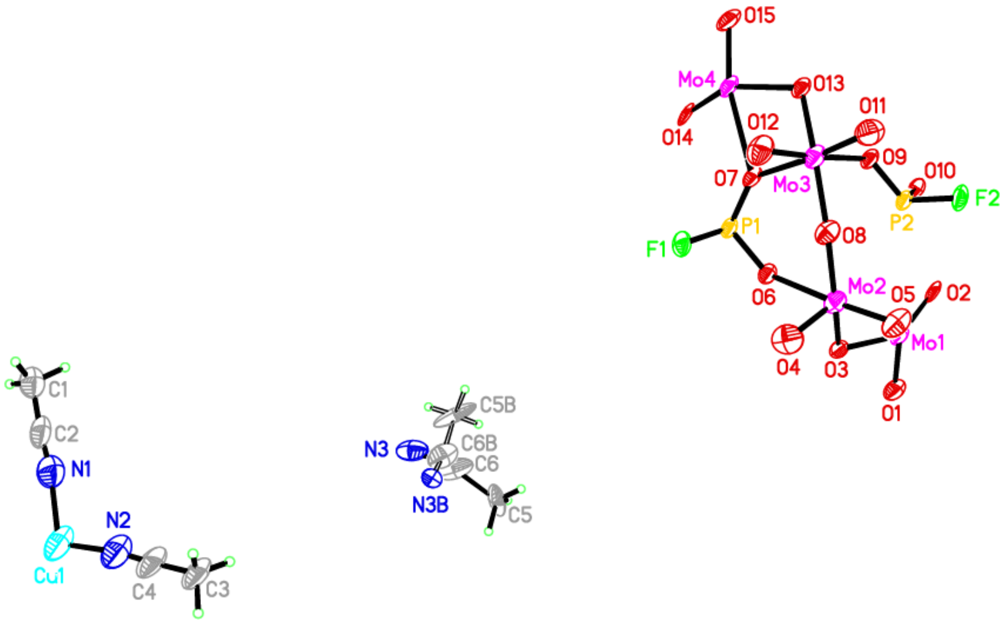

Figure S1. ORTEP representation of the asymmetric unit of compound **2**. ADP ellipsoids are drawn at the 30% probability level, H atoms are shown as circles with arbitrary radius. C atoms are grey; Cu, light blue; F, green; Mo, magenta; N, blue; O, red; P, yellow. C5/C6/N3 and C5B/C6B/N3B are two parts of a disordered acetonitrile molecule.

Table S2. Coordination Bond Lengths and Selected Bond Angles in $H_3[Cu(CH_3CN)_4][Mo_{12}O_{46}(PF)_4]\cdot 4CH_3CN\cdot 32H_2O$ (**2**)

Bond Lengths (Å)		Bond Angles (°)	
F1-P1	1.562(7)	O6-P1-O7	113.0(2)
F2-P2	1.554(6)	O6-P1-O7a	113.0(2)
Mo1-O1	1.693(6)	O7-P1-O7a	114.0(4)
Mo1-O1a	1.693(6)	O6-P1-F1	105.0(4)
Mo1-O2	1.867(2)	O7-P1-F1	105.4(3)
Mo1-O3	1.981(7)	O7a-P1-F1	105.4(3)
Mo1-O10b	2.360(5)	O10-P2-O10b	113.2(4)
Mo1-O10c	2.360(5)	O10-P2-O9	113.6(2)
Mo2-O4	1.693(7)	O10b-P2-O9	113.6(2)
Mo2-O5	1.710(7)	O10-P2-F2	105.3(2)
Mo2-O8	1.867(6)	O10b-P2-F2	105.3(2)
Mo2-O3	2.023(4)	O9-P2-F2	104.7(4)
Mo2-O6	2.347(5)	N1-Cu1-N1a	102.4(10)
Mo2-O10b	2.363(5)	N1-Cu1-N2a	113.0(4)
Mo3-O11	1.683(7)	N1a-Cu1-N2a	113.0(4)
Mo3-O12	1.692(6)	N1-Cu1-N2	113.0(4)

Mo3-O8	1.862(6)	N1a-Cu1-N2	113.0(4)
Mo3-O13	2.002(4)	N2a-Cu1-N2	102.7(10)
Mo3-O7	2.339(5)		
Mo3-O9	2.359(5)		
Mo4-O15b	1.703(6)		
Mo4-O15	1.703(6)		
Mo4-O14	1.862(2)		
Mo4-O13	2.014(4)		
Mo4-O7	2.367(5)		
Mo4-O7b	2.367(5)		
P1-O6	1.511(7)		
P1-O7	1.510(6)		
P1-O7a	1.510(6)		
P2-O10	1.508(5)		
P2-O10b	1.508(5)		
P2-O9	1.506(7)		
Cu1-N1	1.96(2)		
Cu1-N1a	1.96(2)		
Cu1-N2	2.06(2)		
Cu1-N2a	2.06(2)		

3. Comment on the assignment of the formula of 2 based on crystallographic and IR spectroscopic evidence

Compound **2** has been assigned the formula $H_3[Cu(CH_3CN)_4][Mo_{12}O_{46}(PF)_4]\cdot 4CH_3CN\cdot 32H_2O$ (**2**) based on crystallographic and IR spectroscopic evidence: the difficulty of isolating solid **2** has precluded elemental analysis and thermal characterization. Identification of the $[Mo_{12}O_{46}(PF)_4]^{4-}$ anion and $[Cu(CH_3CN)_4]^+$ cation is unambiguous based on the crystal structure and IR bands consistent with PFO_3^- (see main text). The included acetonitrile was also crystallographically located. No other cations or solvent were located and refined successfully but the structure contains substantial void space (36%), with SQUEEZE indicating 320 electrons per formula unit in the void. The IR spectrum (below in section 4) shows evidence for a large amount of water included in the structure – note that commercial, rigorously dry KBr from small sachets was used for the IR spectra, and that intensity of the H_2O stretching region for **2** is dramatically greater than that of **3**. The CH stretches however are extremely weak, precluding inclusion of NBu_4^+ or large quantities of acetonitrile. Absence of the NH bending vibration of NH_4^+, typically strong and observed at around 1400 cm^{-1},[8] eliminates ammonium as a possible constituent and the only logical choice of cation for charge balance (as no Na^+ or other low M_w cations were used in the synthesis) is H^+. As one water molecule has 10 electrons and there are 320 electrons in the void, we get $H_3[Cu(CH_3CN)_4][Mo_{12}O_{46}(PF)_4]\cdot 4CH_3CN\cdot 32H_2O$.

The presence of large amounts of crystal water in this compound is also justifiable based upon the following:

1) Dry MeCN was not used for the synthesis and starting material **1** contains substantial water.
2) The crystallization of **2** was very slow, taking several weeks in which significant amounts of MeCN and Et_2O evaporated, increasing the concentration of water. The quantity of **2** obtained was also very small, so did not require particularly large quantities of water to be present despite its inclusion in the structure.

The apparent irreproducibility of **2** also becomes understandable in the context of its intrinsic vulnerability to hydrolysis of the P–F bond, slow crystallization, and need to include water in the crystal structure.

4. IR spectra

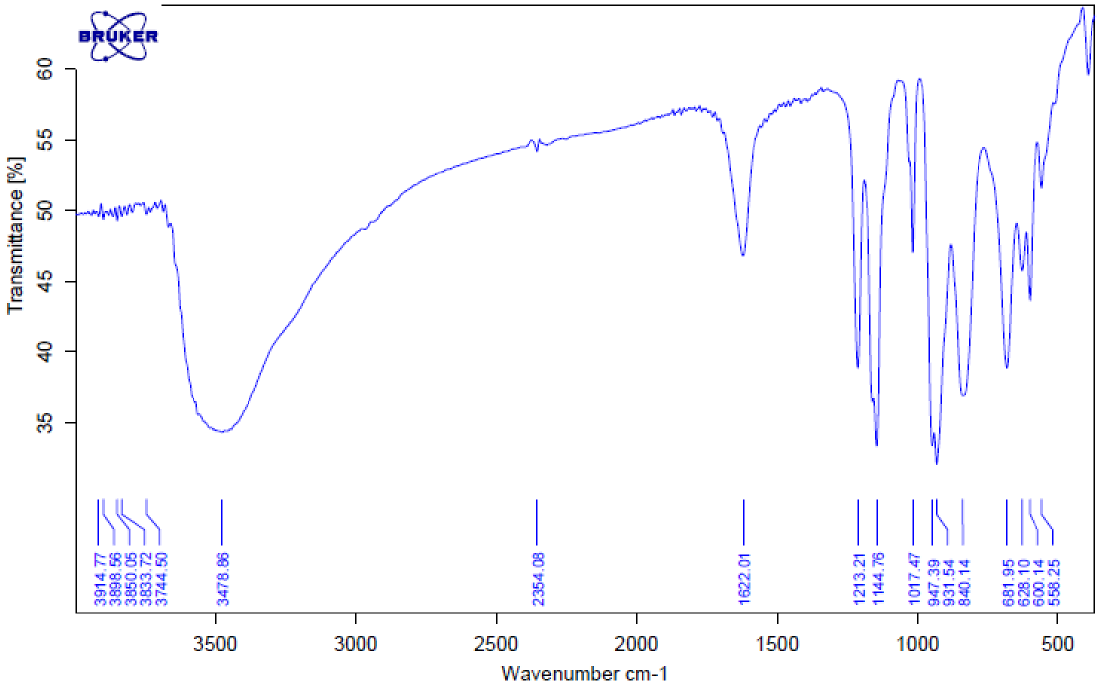

Figure S5. IR spectrum of $H_3[Cu(CH_3CN)_4][Mo_{12}O_{46}(PF)_4]\cdot 4CH_3CN\cdot 32H_2O$ (**2**).

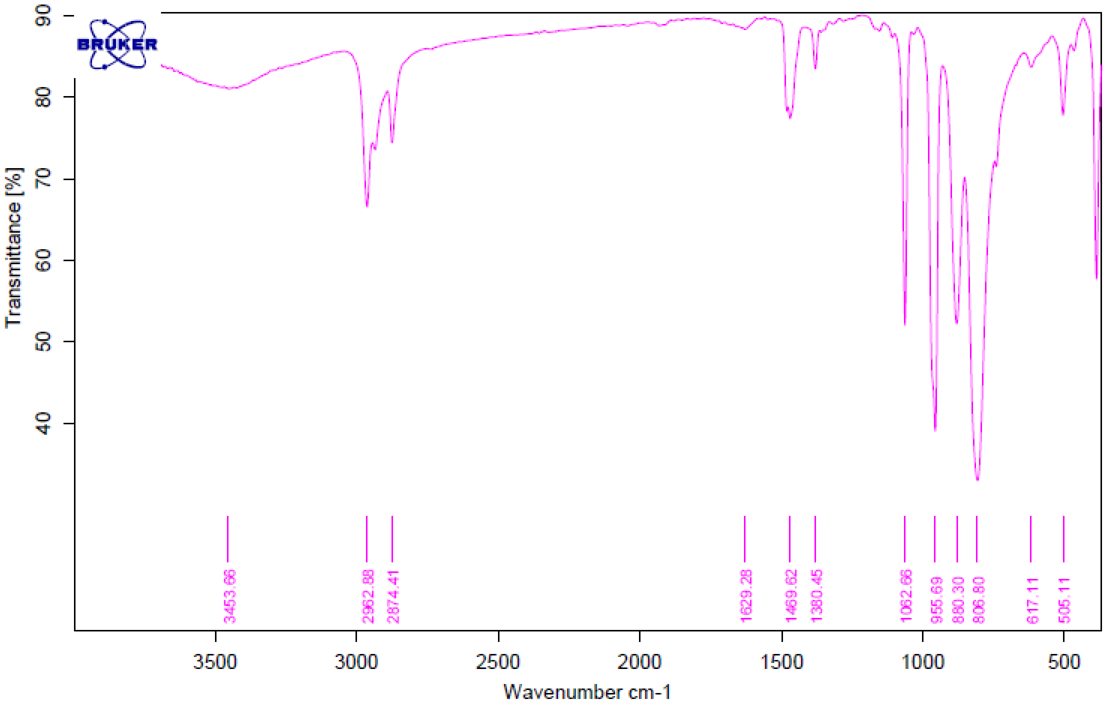

Figure S6. IR spectrum of ($n$$Bu_4N$)[$PMo_{12}O_{40}$] (**3**).

5. Estimation of solution yields of PFO_3-based products (for reactions containing $[Cu(MeCN)_4](PF_6)$ reference)

The following section estimates yields of fluorophosphomolybdate products by referencing to the known quantity of PF_6^{-} present in reactions where $[Cu(MeCN)_4](PF_6)$ was added. To avoid errors from baseline noise, peaks in each multiplet are integrated individually and summed. In all of these spectra, the quantity of PFO_3^{2-} observed by NMR is much lower than the initial quantity added, which was similar to that of PF_6^{-}. Yet even when acquiring data out to +100 ppm (well outside the range expected for phosphate or fluorophosphate) we observed no further signals. We surmise that most of the PFO_3^{2-} remains uncomplexed (giving broad signals of the type shown in Fig. 3, main text), possibly speciating to PO_4^{3-} and $PF_2O_2^{-}$ which will also give broad signals in these conditions: these signals are lost in the considerable baseline noise.

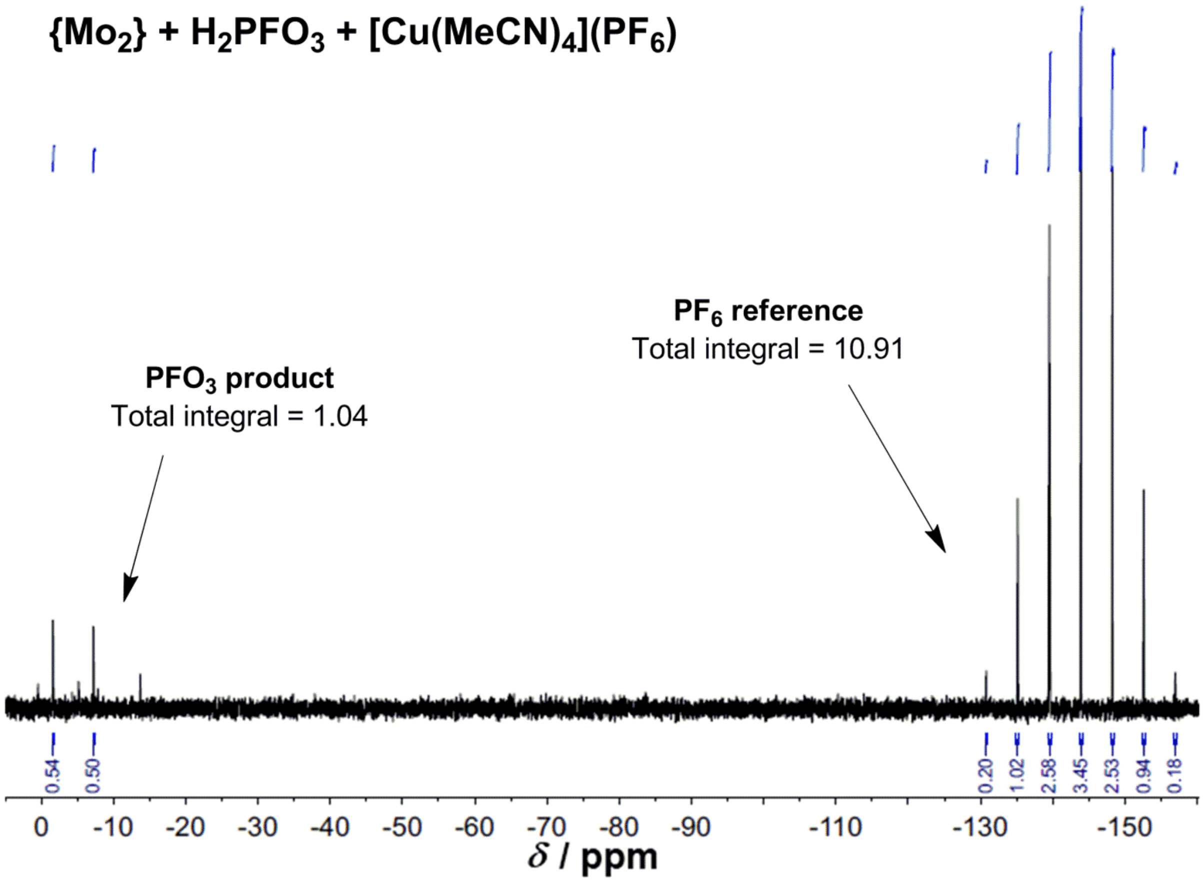

Figure S2. Integrated ^{31}P NMR spectrum (in CH_3CN/CD_3CN) of a mixture of $(n Bu_4N)_2[Mo_2O_7]$, H_2PFO_3 and $[Cu(MeCN)_4](PF_6)$.

For the reaction of $(n Bu_4N)_2[Mo_2O_7]$ with H_2PFO_3 and $[Cu(MeCN)_4](PF_6)$: a PF_6:PFO_3 ratio of 21:2 is observed (Fig. S2). The mixture contains 0.254 mmol $[Mo_2O_7]^{2-}$ (0.508 mmol Mo), and 0.523 mmol PF_6^{-}. Hence, there are 0.0498 mmol of PFO_3 units. As the proposed $\{Mo_7P\}$ aggregate, this would consume 0.349 mmol of Mo, or 69% of the Mo in the system.

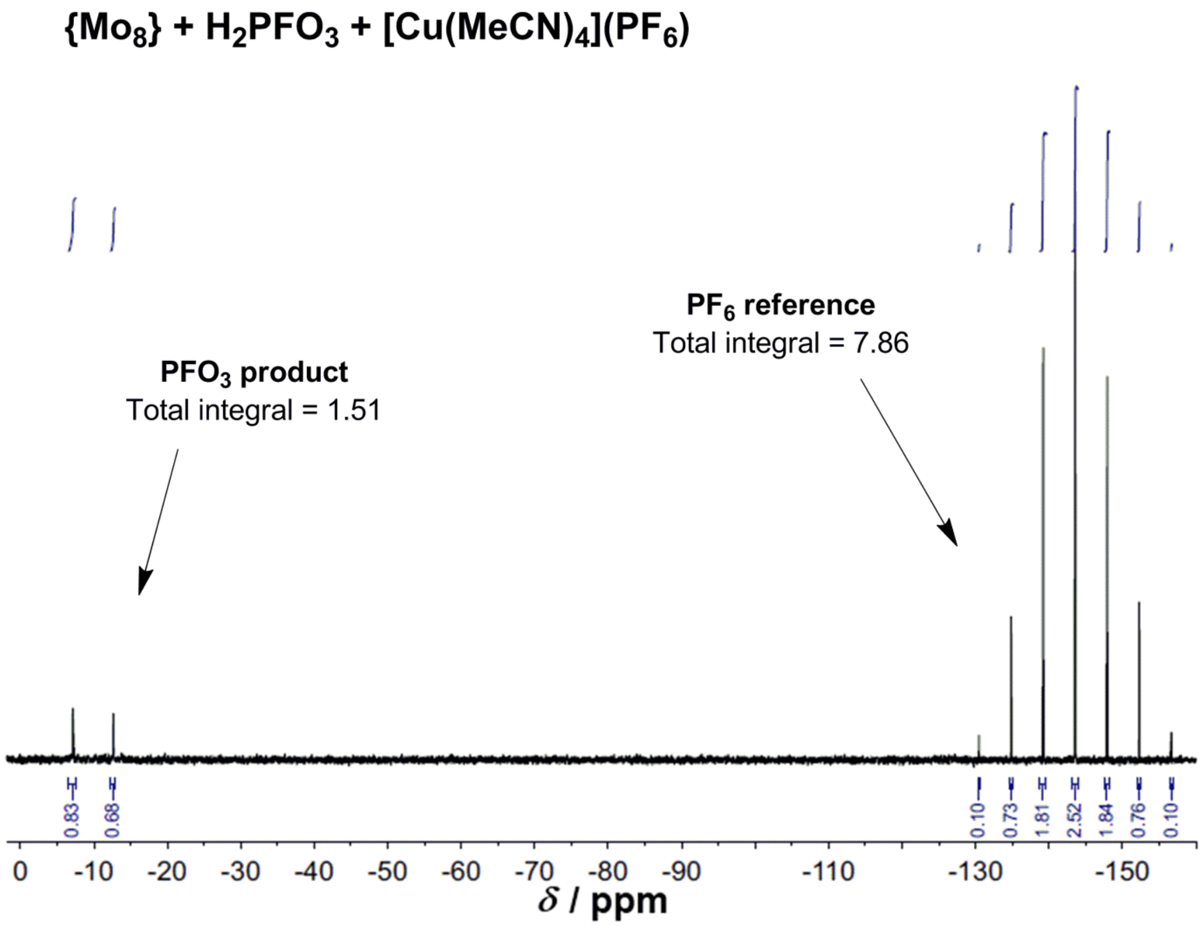

Figure S3. Integrated ^{31}P NMR spectrum (in CH_3CN/CD_3CN) of a mixture of $(n\text{Bu}_4\text{N})_4[\text{Mo}_8\text{O}_{26}]$, H_2PFO_3 and $[\text{Cu(MeCN)}_4](\text{PF}_6)$.

For the reaction of $(n\text{Bu}_4\text{N})_4[\text{Mo}_8\text{O}_{26}]$ with H_2PFO_3 and $[\text{Cu(MeCN)}_4](\text{PF}_6)$: a PF_6:PFO_3 ratio of 26:5 is observed (Fig. S3). The mixture contains 0.0929 mmol $[\text{Mo}_8\text{O}_{26}]^{4-}$ (0.743 mmol Mo), and 0.765 mmol PF_6^-. Hence, there are 0.147 mmol of PFO_3 units. As the proposed $\{\text{Mo}_{12}\text{P}_4\}$ aggregate, this would consume 0.442 mmol of Mo, or 60% of the Mo in the system. This means that aggregates with higher Mo:P ratios, e.g. $\{\text{Mo}_6\text{P}\}$ and $\{\text{Mo}_7\text{P}\}$, are very unlikely to be responsible for the observed signal. $\{\text{Mo}_5\text{P}_2\}$ can be excluded based on chemical shift arguments (see main text).

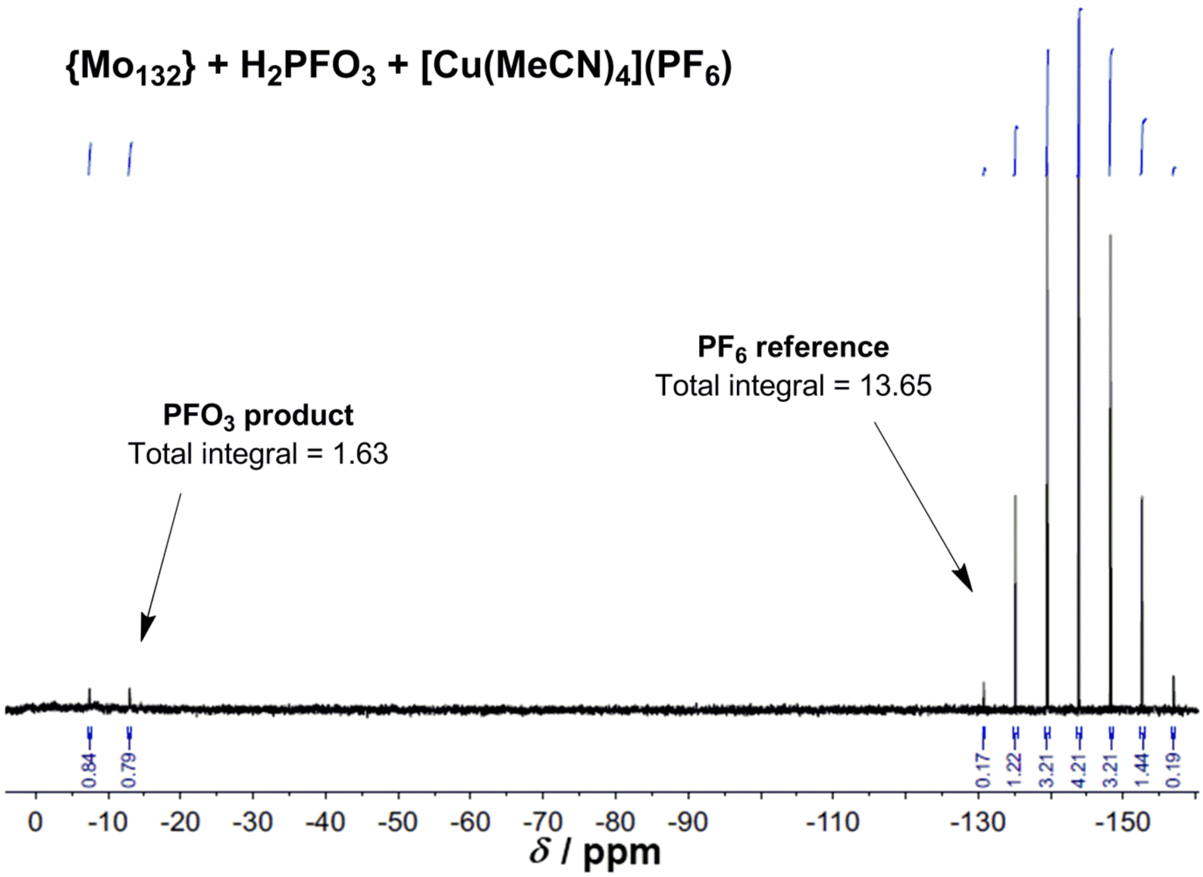

Figure S4. Integrated ^{31}P NMR spectrum (in CH_3CN/CD_3CN) of a mixture of **1**, H_2PFO_3 and $[Cu(MeCN)_4](PF_6)$.

For the reaction of 1 with H_2PFO_3 and $[Cu(MeCN)_4](PF_6)$: a PF_6:PFO_3 ratio of 8.37:5 is observed (Fig. S4). The mixture contains 0.00651 mmol **1** (0.859 mmol Mo), and 0.885 mmol PF_6^-. Hence, there are 0.106 mmol of PFO_3 units. As the proposed $\{Mo_{12}P_4\}$ aggregate, this would consume 0.317 mmol of Mo, or 37% of the Mo in the system. The yield of inverse Keggin produced by reaction with $\{Mo_{132}\}$ is therefore rather lower than that from $\{Mo_8\}$. Indeed, the brown color caused by the $\{Mo^V_2\}$ groups in $\{Mo_{132}\}$ does not disappear completely during reaction, indicating that the Keplerate is not completely consumed.

6. References

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