On the origin of the Murchison phosphonates. Implications for pre-biotic chemistry

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SUPPLEMENTARY MATERIAL

SM1. Materials and Methods

**SM2. Computational Analyses on the Hydrolysis of HCP**

SM1. Materials and Methods

SM1.1 General

Solvents were pre-dried, THF, toluene and pentane were pre-dried over sodium wire and dichloromethane was pre-dried over calcium chloride before being distilled under a dinitrogen atmosphere and degassed before use. THF was distilled over sodium-benzophenone, toluene over sodium metal, pentane over lithium aluminium hydride and dichloromethane over calcium hydride. Drying columns containing molecular sieves (A4) and phosphorus pentoxide were used to dry all di-nitrogen gas which itself was vent-gas from a liquid di-nitrogen Dewar. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker DPX300 spectrometer (operating frequency 300.1 MHz for ^{1}H and 75.48 MHz for ^{13}C) or Bruker DRX500 spectrometer (operating frequency 500.13 MHz for ^{1}H) or Bruker ARX250 spectrometer (operating frequency 101.26 MHz for ^{31}P) unless noted otherwise. All spectra were recorded at 300 K unless stated otherwise, chemical shifts (δ) are given in parts per million (ppm) downfield of tetramethylsilane (TMS) at zero ppm for ^{1}H resonances using CHCl$_3$ δ 7.24 ppm as an internal standard. ^{13}C{^{1}H} spectra were referenced to the centre triplet peak of deuterated chloroform (δ 77.16 ppm). Coupling constants J are given in Hertz (Hz). Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q) and some combination of these, broad (br) or multiplet (m). Infrared spectra were recorded using a MIDAC FT-IR spectrometer (4000-600 cm^{-1}) as KBr discs or nujol mulls, recorded in wavenumbers (cm^{-1}) and referenced to the polystyrene vibration at 1601 cm^{-1}. Only principal absorptions are reported.
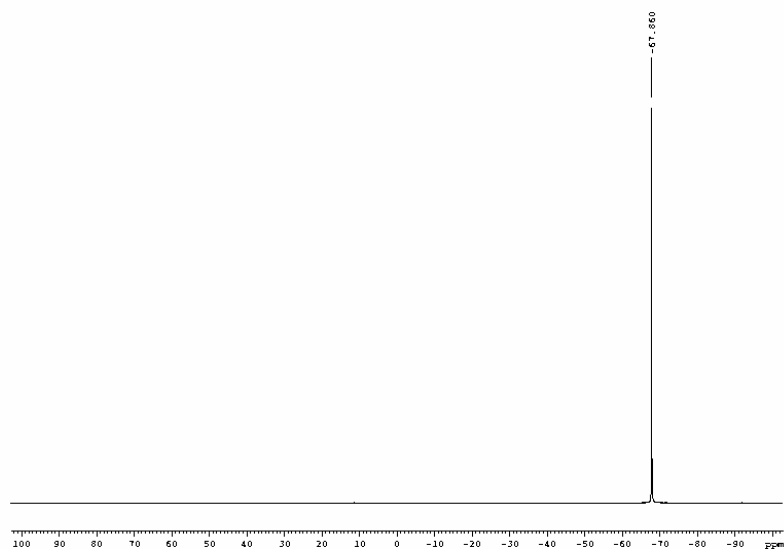

SM1.2 Preparation of (2,2-Dimethylpropylidyne)phosphine

From G. Becker, H. Schmidt, G. Uhl and W. Uhl., Inorg. Synth., 27, 243 (1990).

SM1.2 – Image 1 ^{1}H-NMR spectrum of (2,2-dimethylpropylidyne)phosphine (250 MHz; 300K; CDCl$_3$) – the signal at 0.135 ppm is residual (Me$_3$Si)$_2$O from the synthesis.
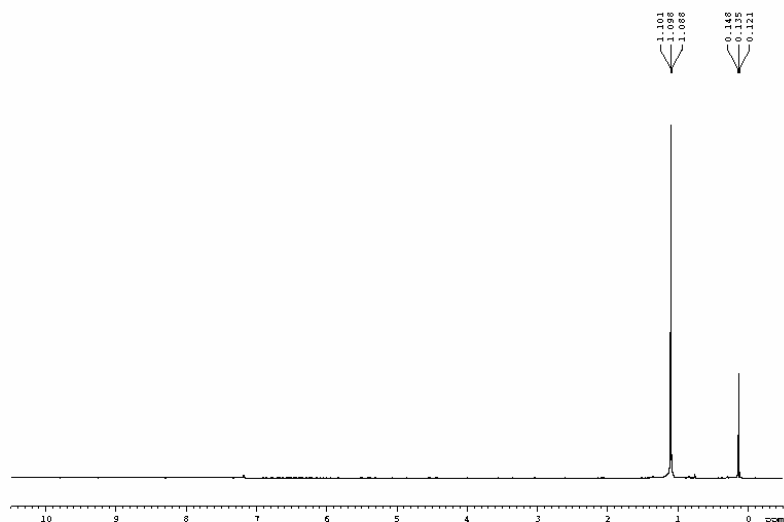
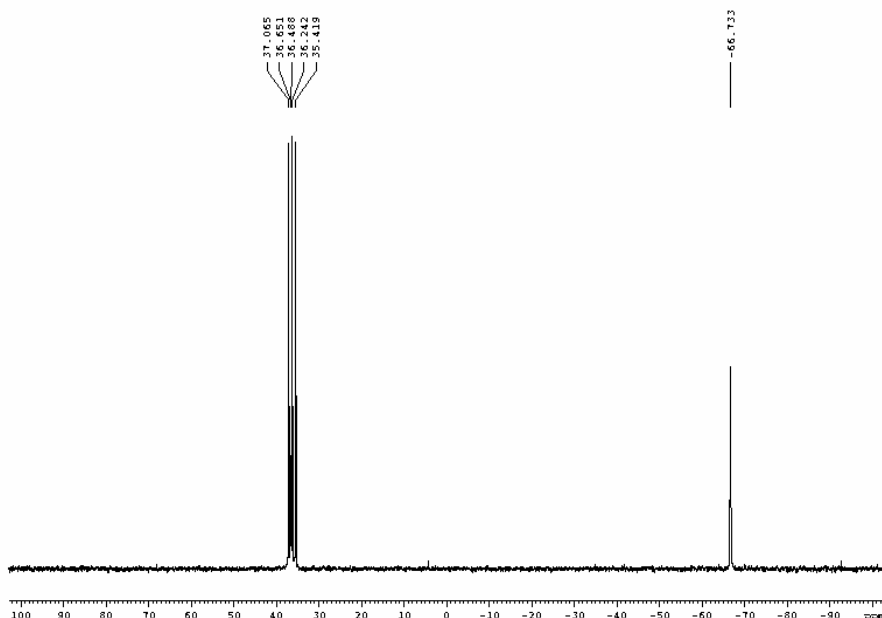**SM1.2 – Image 2 ^{31}P{^{1}H}-NMR spectrum of (2,2-dimethylpropylidyne)phosphine (101.3 MHz; 300K; CDCl$_3$)**

SM1.3 Anaerobic Reaction of (2,2-Dimethylpropylidyne)phosphine with D₂O

An NMR sample was composed of P≡CCMe$_3$ (100 mg); D$_2$O (0.3 cm^3); oxygen-free

atmosphere of di-nitrogen; 101.3 kPa; 300K in a Teflon-sealed, borosilicate NMR tube. The

NMR tube had been previously cleaned thorughly with dilute (2M) aqueous HCl followed by

rinsing with deionized water until the washings were no longer acidic (universal indicator

paper). This was then followed by acetone rinsing and drying at ambient temperature under

vacuum. The two-phase D$_2$O: P≡CCMe$_3$ system was neither stirred, shaken nor agitated in

any way. Consequently, we envisage reaction to take place at the interface between the

materials aided by liquid-liquid diffusion.

SM1.3 – Image 1 ^{31}P{^{1}H}-NMR spectrum of reaction products formed in reaction
between (2,2-dimethylpropylidyne)phosphine and D$_2$O (101.3 MHz; 300K; D$_2$O; 6 days)

SM1.3 – Image 2 ^{31}P-NMR spectrum of reaction products formed in reaction between (2,2-dimethylpropylidyne)phosphine and D$_2$O (101.3 MHz; 300K; D$_2$O; 6 days)
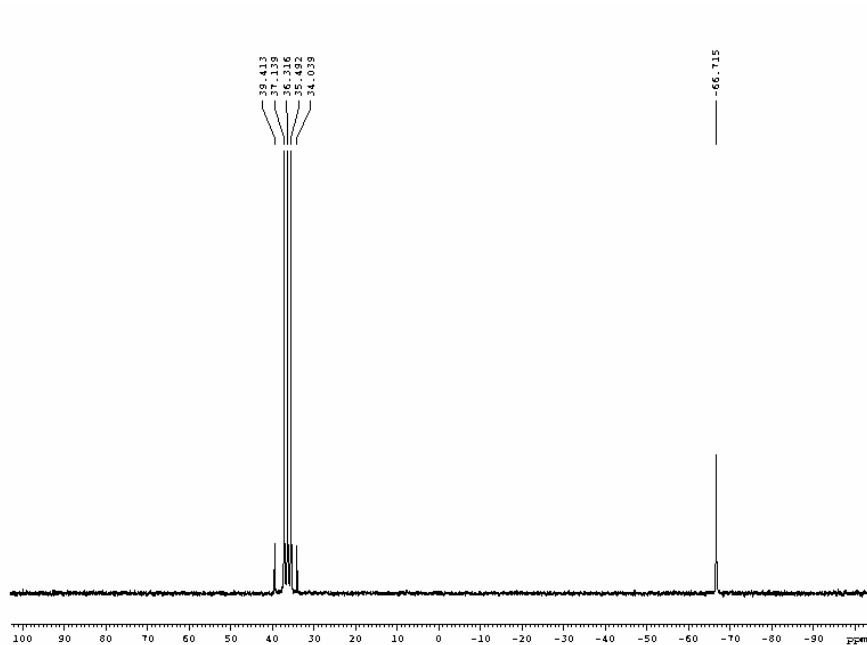
SM1.3 – Image 3 ^{31}P{^{1}H}-NMR spectrum of reaction products formed in reaction between (2,2-dimethylpropylidyne)phosphine and D$_2$O (101.3 MHz; 300K; D$_2$O; 11 days)
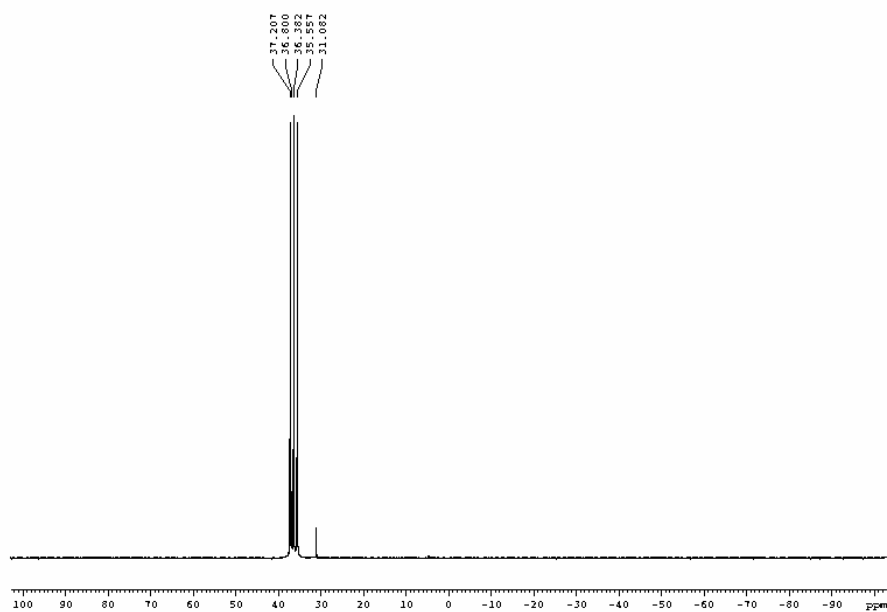
SM1.3 – Image 4 ^{31}P-NMR spectrum of reaction products formed in reaction between (2,2-dimethylpropylidyne)phosphine and D$_2$O (101.3 MHz; 300K; D$_2$O; 11 days)

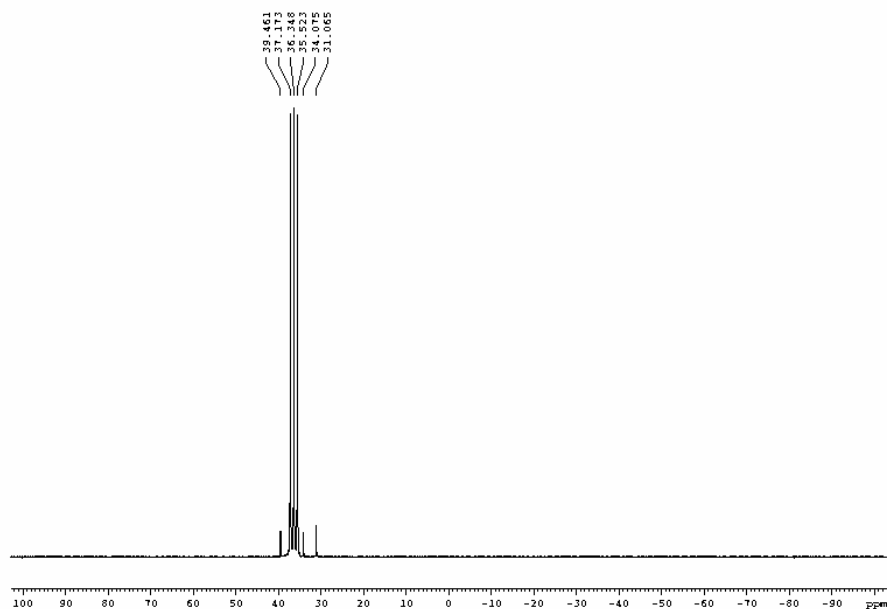**SM1.4 Electrospray Mass Spectrometric Analysis of the Products from Reaction of (2,2-Dimethylpropylidyne)phosphine with D_2O**

Samples were analysed by injection of 0.1 ml of an *ca*. mM aqueous solution into a Bruker

microTOF instrument operating under electrospray conditions with a 1:1 v/v

acetonitrile:water mobile phase at 0.6 mlmin^{-1}. The instrument was calibrated externally

using sodium formate.

SM1.4 – Image 1. [^{t}BuCD$_2$P(O)H(O)]$^-$ (Theor: 138.08)
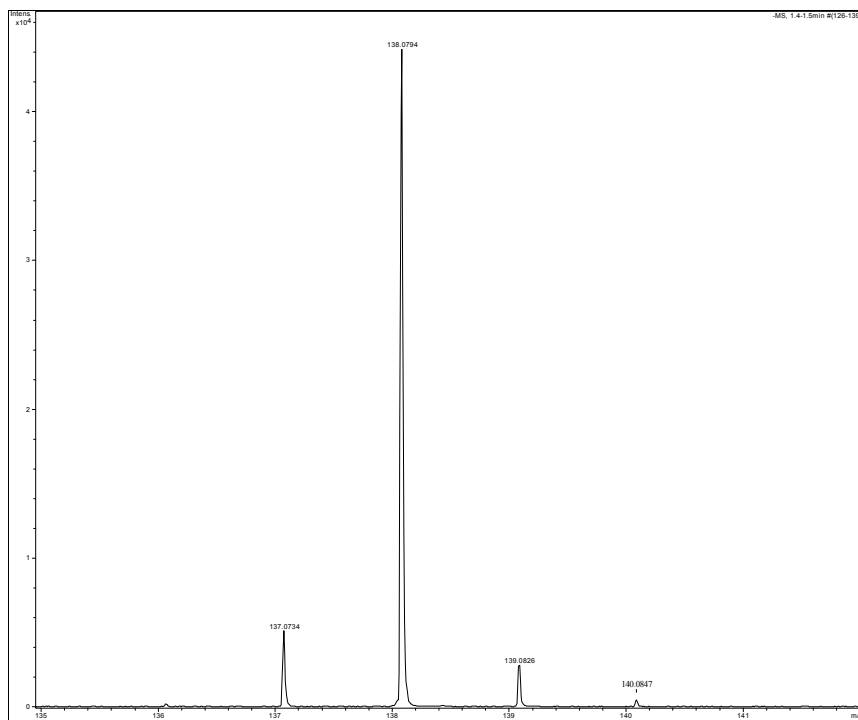
SM1.4 – Image 2. [^{t}BuCD$_2$P(O)(OH)(O)]$^-$ (Theor: 153.06)
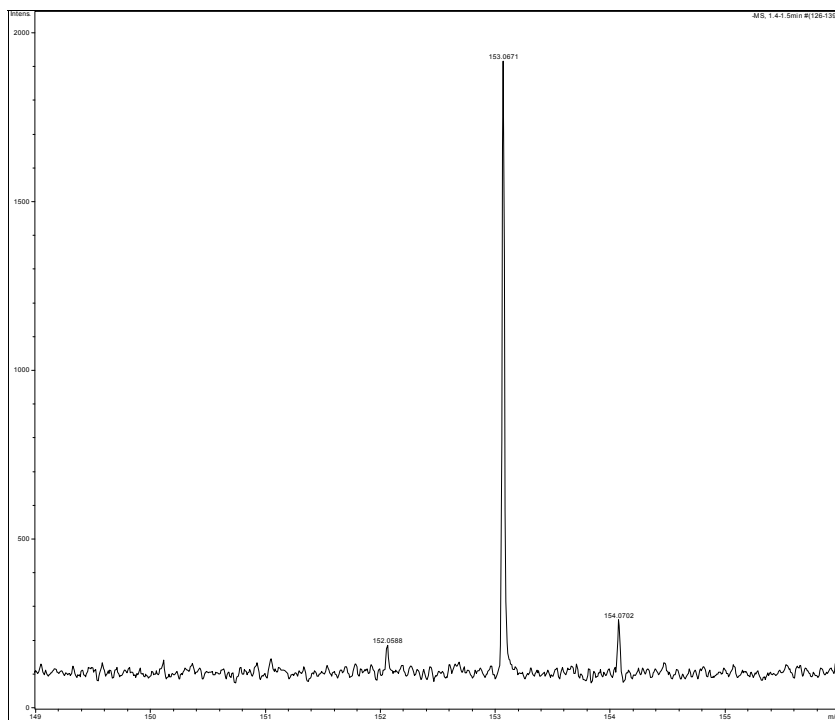
SM1.5 ^{13}C{^{1}H}-NMR Analysis of the Products from Reaction of (2,2-Dimethylpropylidyne)phosphine with D$_2$O – Simulation of [CD$_2$P(O)D] carbon

SM1.5 – Image 1 ^{13}C{^{1}H}-NMR spectrum of ^{t}BuCD$_2$P(O)D(OD) formed in reaction between (2,2-dimethylpropylidyne)phosphine and D$_2$O (125.7 MHz; 300K; D$_2$O)
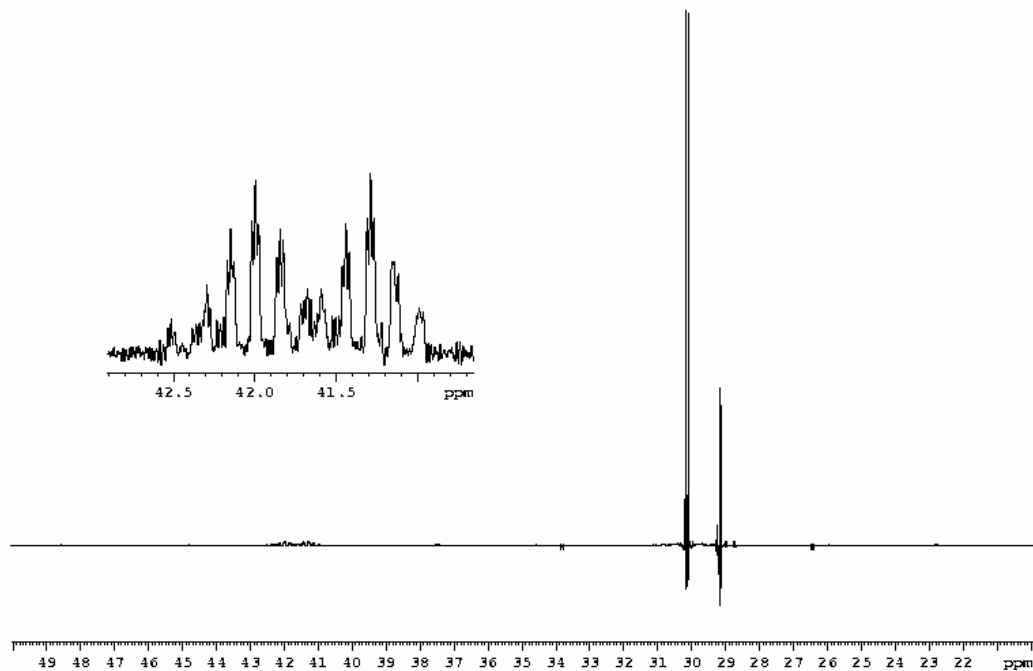
***SM1.5 – Image 2** Partial $^{13}C\{^1H\}$-NMR spectrum of $^tBuCD_2P(O)D(OD)$ emphasising $^1J_{PC}$, $^1J_{CD}$ and $^2J_{CD}$ coupling of the $[CD_2P(O)D]$ carbon. Experimental (top; 125.7 MHz; 300K) and simulated (bottom) using gNMR version 4.1.2 (Adept Scientific, UK).*
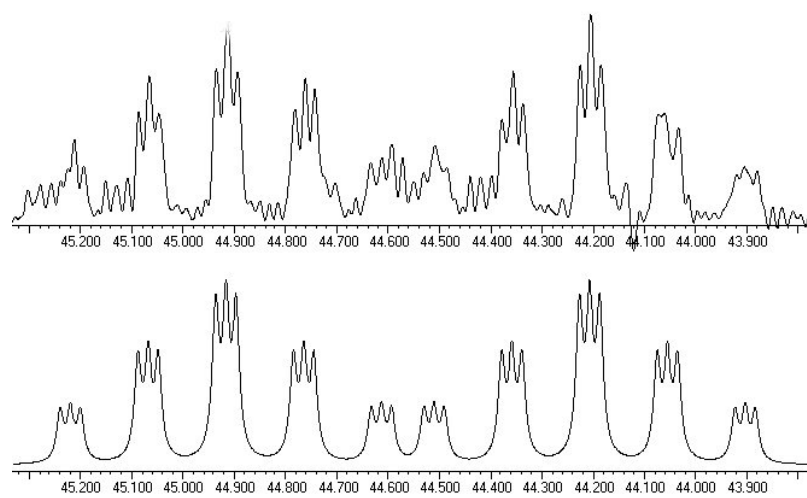
The [$CD_2P(O)D$] portion of the spectrum has been simulated using gNMR version 4.1.2 (Adept Scientific, UK) assuming that the CD_2 deuterons are equivalent. A full lineshape analysis was performed; with ^{13}C chemical shifts and all related coupling constants allowed to vary. The ^{13}C spectrum was referenced to an external TSP (trimethylsilylproprionate-d[4] - the methyl signals as 0 ppm); the ^{31}P was referenced to 85% aqueous orthophosphoric acid as 0 ppm. Spectra were recorded at 300 K on a Bruker DRX 500 with ^{13}C and ^{31}P operating frequencies of 125.762 and 202.466 MHz respectively. [13]C spectra were recorded with a spectral width of 3800 Hz in 16k of data points and ^{1}H decoupled using the Waltz-16 sequence. Almost 30000 transients were acquired. Following the application of a trapezoidal then exponential window function the fid was zero filled 8 times prior to Fourier transformation. [31]P spectra were recorded using a spectral width of 40.5k Hz in 64k of data points, over 156 transients. Again ^{1}H decoupling was achieved using the Waltz-16 sequence. An exponential window function was applied prior to Fourier transformation. It should be noted that the two geminal deuterium atoms in $^tBuCD_2P(O)D(OD)$ are strictly speaking diastereotopic but appear to model as though their coupling to carbon is essentially the same.

SM1.6 Preparation of 2,2-Dimethylpropylphosphinic acid, calcium salt

In a dry Schlenk tube under nitrogen, magnesium turnings (75mmol, 1.8g) were stirred overnight until the surface of the metal appeared black; this being indicative of activated magnesium. Dried, distilled THF (30 mls) was added and the suspension cooled in an ice bath. To this was added by syringe neopentyl bromide (1-bromo-2,2-dimethylpropane, 15

mmol, 2.26g). The mixture was allowed to warm to room temperature and stirred until visible reaction ceased after about 2 hours. The solution was then transferred by cannula filter to a second Schlenk vessel containing a solution of PCl_3 (15 mmol, 2.06g) in dry THF (30 mls) and stirring was continued overnight. The reaction was monitored at regular intervals by $^{31}P\{^1H\}$-NMR for the disappearance of PCl_3. When this was judged to be largely complete the solution was opened to the air and deionised water (20 mls) added. The solvent was removed on a rotary evaporator and the solids re-dissolved in fresh deionised water (30 mls). A saturated solution of calcium hydroxide was added to remove any phosphonic acid as the insoluble calcium salt which forms on standing and is removed by filtration. The remaining water was removed subsequently removed by evaporation to leave a white crystalline powder of 2,2-dimethylpropylphosphinic acid as the calcium salt.

$^{31}P\{^1H\}$-NMR (D_2O; 101.26 MHz; 298K) δ 28.1 (dt, $^1J_{PH}$ = 501Hz, $^2J_{PH}$ = 15.7Hz). ^1H-NMR (D_2O; 250.13 MHz; 298K) δ 0.89 ppm (s, 9H, CH_3); δ 1.39 ppm (d, 2H, $^2J_{PH}$ = 15.7Hz, PCH_2) δ 6.93ppm (d, 1H, $^1J_{PH}$ = 501Hz). $^{13}C\{^1H\}$-NMR (D_2O; 62.9 MHz; 298K) δ 44.75 (d, $^1J_{PC}$ = 89Hz, CH_2P), δ 30.67 (d, $^3J_{PC}$ = 8.7Hz, CH_3); δ = 29.62 (d, $^2J_{PC}$ = 3.1Hz, $C(CH_3)_3$). IR (KBr Disc) υ 2955 cm^{-1}, methyl C-H stretch, υ 2346 cm^{-1}, P- H stretch.

SM1.6 Image 1. ^1H-NMR (250MHz; 300K; D_2O) of 2,2-dimethylpropylphosphinic acid as the calcium salt.
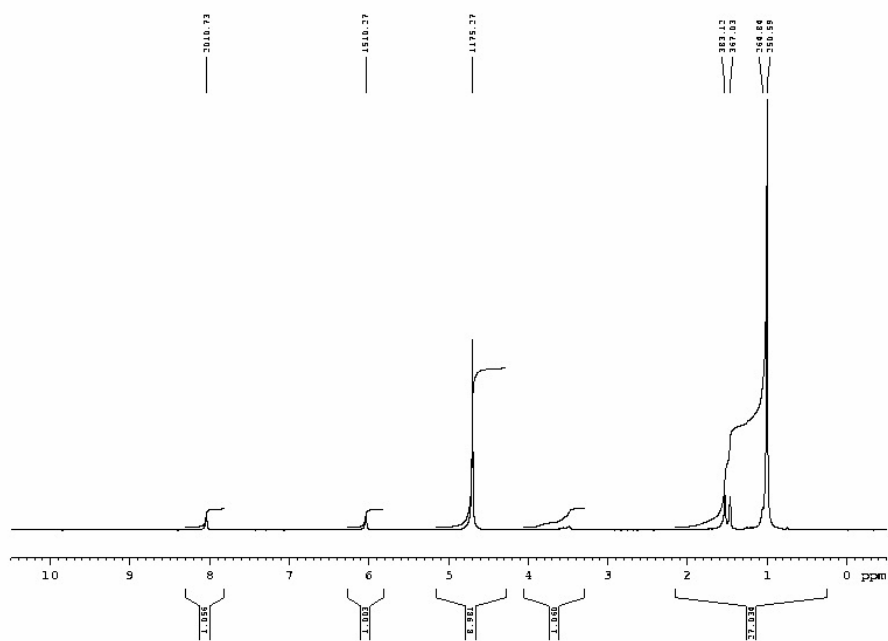
SM1.6 Image 2. ^{31}***P-NMR (101MHz; 300K; D$_2$O) of 2,2-dimethylpropylphosphinic acid as the calcium salt.***
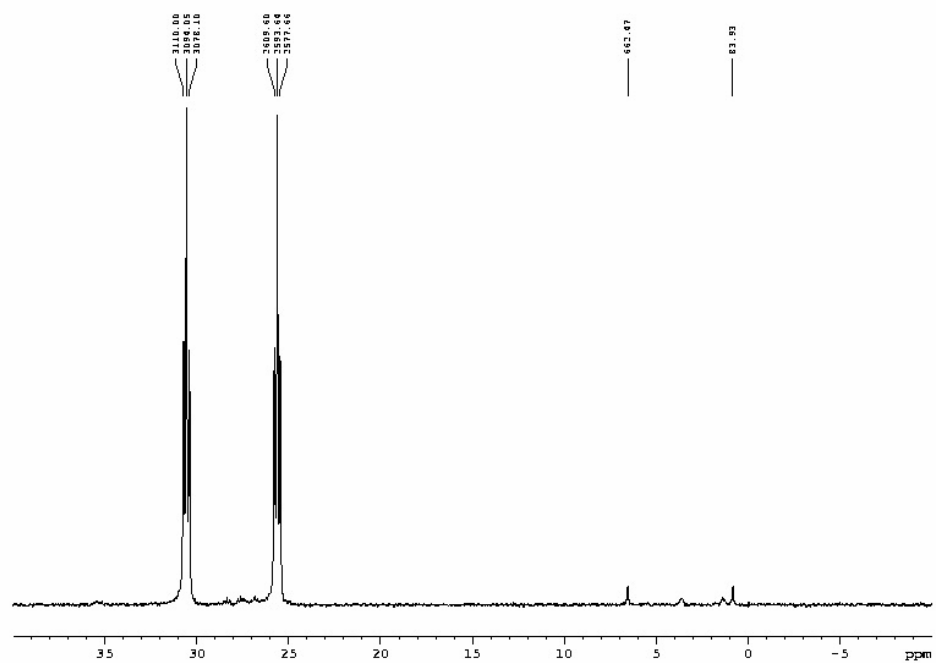
SM1.6 Image 3. *$^{13}C\{^1H\}$-NMR (63MHz; 300K; D_2O) of 2,2-dimethylpropylphosphinic acid as the calcium salt.*
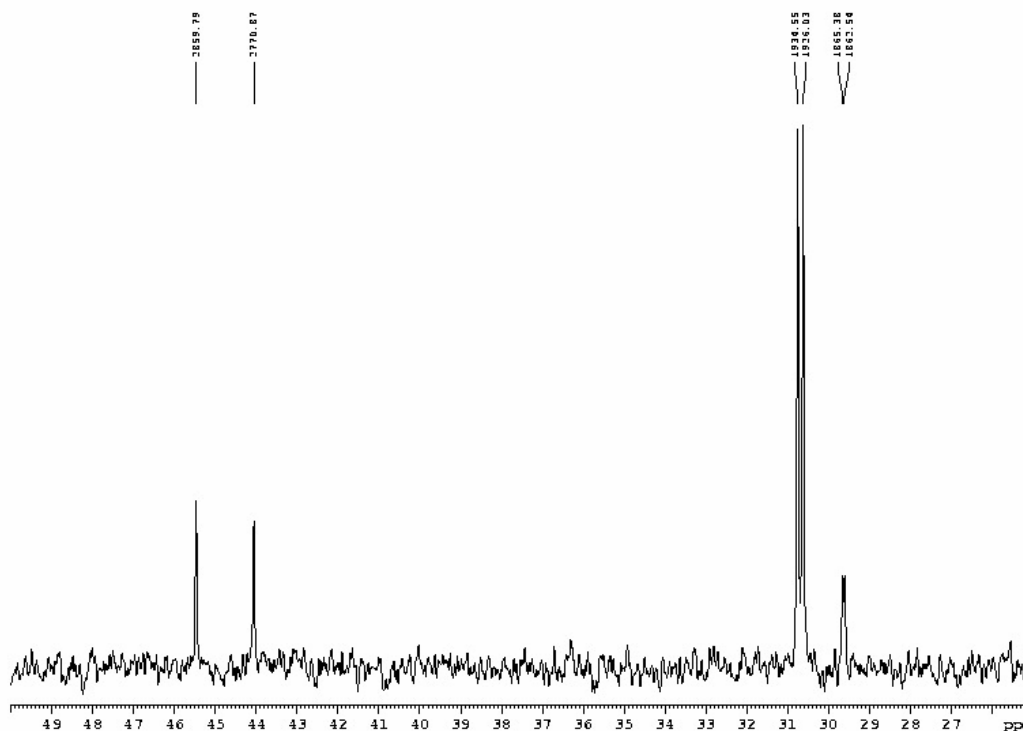
SM2. Computational Analyses on the Hydrolysis of HCP

All calculations were carried out using the Gaussian 03 suite of programs [M. J. Frisch, *et al*, Gaussian 03, Revision B.05 (Wallingford CT, 2004)]. Geometry optimisations and vibrational frequency calculations were performed at B3LYP/6-311+G(3df,2p) level. Scale factor of 0.9854 was used for zero-point energy corrections. The accurate energetic parameters were evaluated using G3X model chemistry, which approximates the electron correlation level of QCISD(T,Full)/G3XLarge [L. A. Curtiss, P. C. Redfern, K. Raghavachari, J. A. Pople, *J. Chem. Phys.,* **114**, 108 (2001)].

Table SM2. The zero-point energies and G3X electronic energies (all in Hartree)

Molecules	ZPE	G3X [*]	Molecules	ZPE	G3X [*]
H_2	0.01003	-1.17724	H_2O	0.02105	-76.40430
HCP	0.01380	-379.85085	CH_3PO	0.03841	-456.30945
$H_2C=POH$	0.03912	-456.30149	$CH_3P(OH)_2$	0.06539	-532.76930
$HP(O)(OH)_2$	0.04253	-568.71911	$CH_3P(O)(H)OH$	0.06483	-532.78719
HCOOH	0.03321	-189.69376	$CH_3P(O)(OH)_2$	0.07007	-608.03952
TS1	0.03344	-456.19788	TS3	0.05996	-532.66923
TS2	0.03356	-456.21841	TS4	0.06046	-532.68446

[*] ZPE not included

Calculation Level: G3X ~ QCISD(T,FU)/G3XLarge **Geometry:** B3LYP/6-311+G(3df,2p)

HCP + H2O

Energy Relative to HCP + H2O

	G3X DH(0 K)	G3X DH(298 K)		G3 DH(0 K)	B3LYP/3+	ZPE	ZPE+H	B3LYP 6-311+G(3df,2p)	MP2 6-31G(d)	MP4 6-31G(d)	QCISD(T) 6-31G(d)	MP2 6-31+G(d)	MP4 6-31+G(d)	MP2 6-31G(2df,p)	MP4 6-31G(2df,p)	MP2=Full G3Large	HF G3Large	HF G3XLarge	Spin-Orbital	Na	Nb	# H	# C	# O	# P
H2O	-237.627	-240.513	(kJ/mol)	-237.700	-231.376317	0.021360	0.025139	-76.463325	-76.1967	-76.2071	-76.2077	-76.2096	-76.2201	-76.2672	-76.2819	-76.3618	-76.0568	-76.0568	0.0000	4	4	2		1	
HCP	216.883	215.478		217.112	229.004704	0.014000	0.017519	-380.041461	-379.3445	-379.3741	-379.3729	-379.3483	-379.3782	-379.4044	-379.4396	-379.7826	-379.1494	-379.1495	0.0000	5	5	1	1		1
HCP + H2O	-20.743			-20.588	-2.372																			
CH2=POH (CPOH-Cis)	-129.816	-140.229	-109.07	-127.763	-124.327	0.039365	0.044332	-456.555183	-455.5814	-455.6226	-455.6234	-455.5958	-455.6375	-455.7142	-455.7651	-456.1866	-455.2574	-455.2583	0.0000	9	9	3	1	1	1
CH2=POH (CPOH-Trans)	-131.194	-141.577	-110.45	-129.128	-125.216	0.039700	0.044678	-456.555852	-455.5814	-455.6228	-455.6237	-455.5966	-455.6386	-455.7142	-455.7652	-456.1870	-455.2575	-455.2583	0.0000	9	9	3	1	1	1
CH2=P(=O)H	-91.998	-102.819	-71.25	-90.099	-88.088	0.037899	0.042710	-456.539936	-455.5620	-455.6010	-455.5993	-455.5766	-455.6161	-455.6995	-455.7483	-456.1753	-455.2400	-455.2407	0.0000	9	9	3	1	1	1
CH3PO (C1 ~ Cs)	-153.944	-163.293	-133.20	-152.333	-147.472	0.038984	0.044356	-456.563623	-455.5983	-455.6397	-455.6376	-455.6106	-455.6528	-455.7267	-455.7784	-456.1973	-455.2645	-455.2652	0.0000	9	9	3	1	1	1
Transistion States																								
HCP + H2O - H2C=POH (CPOH-Trans)	125.947	115.154	146.69	127.574	130.745	0.033938	0.038760	-456.452684	-455.4769	-455.5186	-455.5199	-455.4927	-455.5350	-455.6127	-455.6643	-456.0827	-455.1291	-455.1297	0.0000	9	9	3	1	1	1
CH2=POH (CPOH-Cis) - CH3PO	72.339	60.779	93.08	74.101	75.590	0.034053	0.038583	-456.473805	-455.4994	-455.5398	-455.5369	-455.5133	-455.5544	-455.6366	-455.6864	-456.1090	-455.1504	-455.1511	0.0000	9	9	3	1	1	1
or																								
CH2POH - CH2=P(=O)H	134.072	124.500	154.82	136.084	133.961	0.033210	0.038497	-456.450742	-455.4686	-455.5111	-455.5045	-455.4861	-455.5292	-455.6087	-455.6608	-456.0860	-455.1190	-455.1198	0.0000	9	9	3	1	1	1
CH2=P(=O)H - CH3PO	45.027	33.738	65.77	46.925	49.283	0.034796	0.039429	-456.484557	-455.5015	-455.5479	-455.5469	-455.5155	-455.5625	-455.6382	-455.6937	-456.1126	-455.1697	-455.1705	0.0000	9	9	3	1	1	1

Calculations above show that once HCP + H2O gets over the first energy barrier (146.7 kJ/mol) to H2C=POH, the isomerization towards CH3PO will be straight

CH3PO + H2O

Energy Relative to CH3PO + H2O

	G3X DH(0 K)	G3X DH(298 K)		G3 DH(0 K)	B3LYP/3+	ZPE	ZPE+H	B3LYP 6-311+G(3df,2p)	MP2 6-31G(d)	MP4 6-31G(d)	QCISD(T) 6-31G(d)	MP2 6-31+G(d)	MP4 6-31+G(d)	MP2 6-31G(2df,p)	MP4 6-31G(2df,p)	MP2=Full G3Large	HF G3Large	HF G3XLarge	Spin-Orbital	Na	Nb	# H	# C	# O	# P
H2O	-237.627	-240.513	(kJ/mol)	-237.700	-231.376317	0.021360	0.025139	-76.463325	-76.1967	-76.2071	-76.2077	-76.2096	-76.2201	-76.2672	-76.2819	-76.3618	-76.0568	-76.0568	0.0000	4	4	2		1	
CH3PO (C1)	-153.944	-163.293		-152.333	-147.472	0.038984	0.044356	-456.563623	-455.5983	-455.6397	-455.6376	-455.6106	-455.6528	-455.7267	-455.7784	-456.1973	-455.2645	-455.2652	0.0000	9	9	3	1	1	1
CH3PO + H2O	-391.570			-390.033	-378.848																			
Three conformers for CH3P(OH)2. The difference is in the dihedral angle of CPOH.																								
CH3P(OH)2 POH-OutOut Cs	-521.850	-540.377	-130.280	-517.797	-497.751	0.066569	0.073324	-533.078370	-531.8478	-531.8964	-531.8972	-531.8703	-531.9204	-532.0522	-532.1154	-532.6144	-531.3797	-531.3813	0.0000	13	13	5	1	2	1
CH3P(OH)2 POH-InOut C1	-521.851	-540.606	-130.281	-517.845	-498.044	0.066358	0.073026	-533.078274	-531.8487	-531.8974	-531.8983	-531.8703	-531.9204	-532.0525	-532.1157	-532.6141	-531.3803	-531.3819	0.0000	13	13	5	1	2	1
CH3P(OH)2 POH-InIn Cs	-511.262	-529.809	-119.692	-507.244	-488.199	0.065769	0.072516	-533.073944	-531.8435	-531.8923	-531.8932	-531.8638	-531.9142	-532.0484	-532.1116	-532.6093	-531.3759	-531.3775	0.0000	13	13	5	1	2	1
CH3P(O)(H)OH HOPO~Cis	-570.288	-589.625	-178.718	-566.482	-540.899	0.065786	0.072232	-533.094033	-531.8651	-531.9104	-531.9094	-531.8842	-531.9310	-532.0724	-532.1326	-532.6367	-531.4026	-531.4041	0.0000	13	13	5	1	2	1
CH3P(O)(H)OH is more stable than CH3P(OH)2. This may imply that the final product from CH3PO + H2O is CH3P(O)(H)OH, instead of CH3P(OH)2.																								
Transition States																								
CH3PO + H2O - CH3P(OH)2	-348.004	-367.701	43.566	-344.475	-331.290	0.061375	0.067684	-533.009851	-531.7812	-531.8295	-531.8288	-531.8013	-531.8512	-531.9861	-532.0492	-532.5446	-531.2879	-531.2893	0.0000	13	13	5	1	2	1
CH3P(OH)2 -- CH3P(O)(H)OH	-312.026	-331.141	79.544	-307.598	-290.510	0.061357	0.067888	-532.994301	-531.7578	-531.8055	-531.8017	-531.7822	-531.8314	-531.9672	-532.0297	-532.5342	-531.2674	-531.2692	0.0000	13	13	5	1	2	1
or directly																								
CH3PO + H2O - CH3P(O)(H)OH	-273.382	-292.047	118.188	-269.722	-262.528	0.060844	0.067546	-532.983137	-531.7503	-531.7982	-531.7947	-531.7733	-531.8228	-531.9553	-532.0182	-532.5187	-531.2479	-531.2494	0.0000	13	13	5	1	2	1
CH3P(O)(OH)2 Cs	-887.563	-907.517		-882.188	-833.811	0.071113	0.078978	-608.396119	-606.9501	-606.9986	-606.9971	-606.9757	-607.0263	-607.2120	-607.2784	-607.8618	-606.3470	-606.3492	0.0000	16	16	5	1	3	1