Directing alendronate structures into 2-D layers with bulky quaternary phosphonium cations.

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Supporting Information

Syntheses and Characterisation of $[Ag(LH_4)(H_2O)].2H_2O$

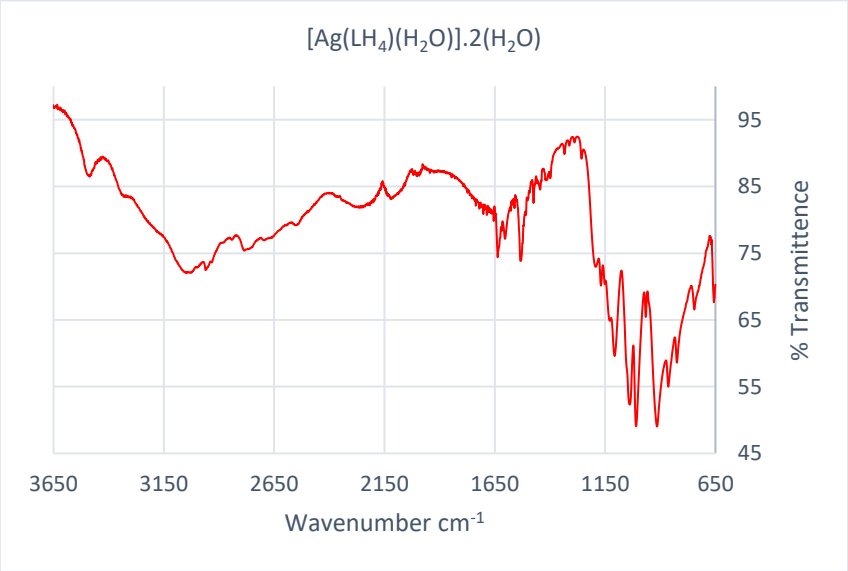
Syntheses and Characterisation of $[Ph_3PR][LH_4].xH_2O$ 1-5

Dehydration of $[Ph_4P][LH_4].6H_2O$ and $[Ph_3PEt][LH_4].4H_2O$

Supramolecular Interactions in the Structures of 1 to 5

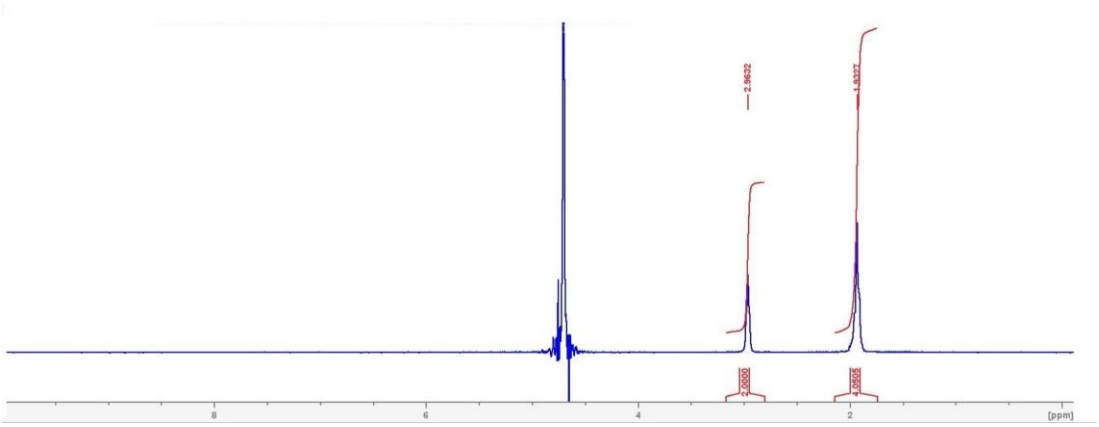
S1. Spectroscopic. PXRD and Crystal Data for $[Ag(LH_4)(H_2O)].2H_2O$

S1.1 AT-FTIR spectrum of crystalline $[Ag(LH_4)(H_2O)].2H_2O$

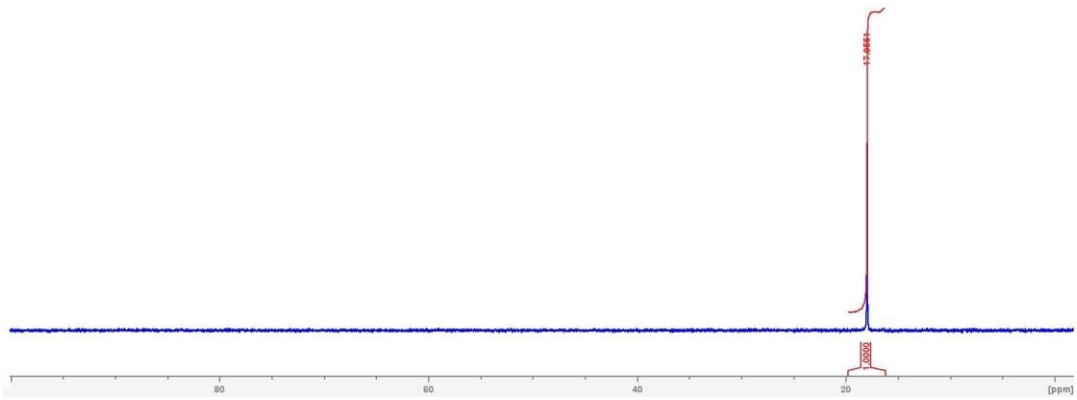


S1.2 NMR data for $[Ag(LH_4)(H_2O).2H_2O$.

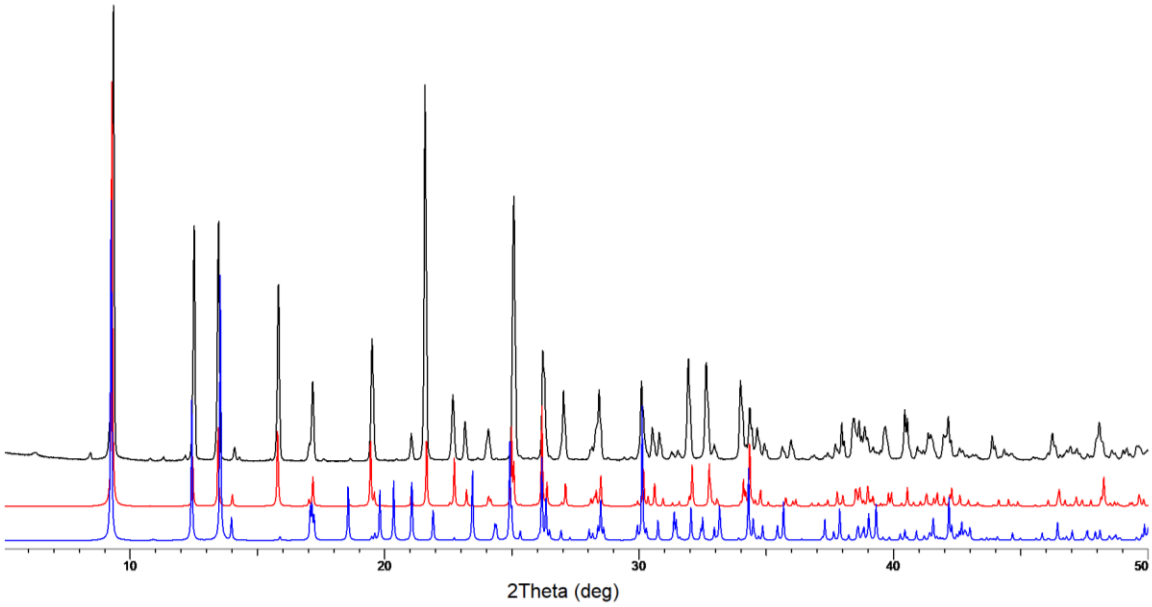
(a) ^{1}H, 400.13 MHz, D_2O



(b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O



S1.3 Experimental PXRD of bulk crystallised $[Ag(LH_4)(H_2O)].2H_2O$ (black) and simulated PXRD data calculated from the crystal structures of $[Ag(LH_4)(H_2O)].2H_2O$ (see below) (red) and $[Na(LH_4)(H_2O)].2H_2O$ (TEHWOS01) (blue).



S1.4 Crystal Structure of $[Ag(LH_4)(H_2O)].2H_2O$

Crystal and refinement data.

Formula: $C_4H_{18}AgNO_{10}P_2$, MW 410.00. Unit cell parameters, *a* 7.2368(2), *b* 9.0908(2), *c* 19.3367(5) Å; β = 100.219(2)°, *V* 1251.95(6) Å^3, monoclinic, $P2_1/n$. N_t 14668, *N* (R_{int}) 3281 (0.035), $N_o(I>2\sigma I)$ 2971. *R*1 ($I>2\sigma I$) 0.0227, w*R*2 (all data) 0.0539, GoF 1.068, $\Delta e_{min,max}$ _0.47, 0.51 eÅ^{-3}. Diffraction data were collected using Mo Kα radiation (λ = 0.71073 Å) at 123 K on a Rigaku Synergy S diffractometer fitted with a HYPIX 6000 hybrid photon counting detector. Data were collected and processed, including an empirical (multi-scan) absorption correction using the proprietary software package CrysAlisPro.[1] The structure was solved and refined by standard methods using the SHELX-2018 software suite,[2] in conjunction with the X-Seed400 graphical interface.[3] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms attached to carbon were placed in calculated positions using a riding model. The positions of hydrogen atoms attached to nitrogen or oxygen were obtained from the difference Fourier map and were freely refined (CCDC 2505719).

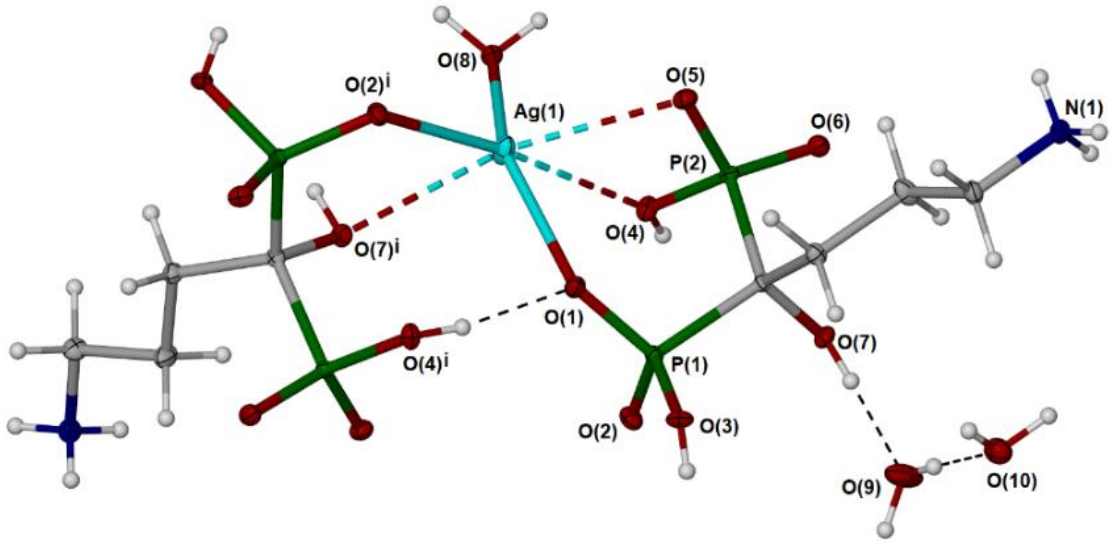
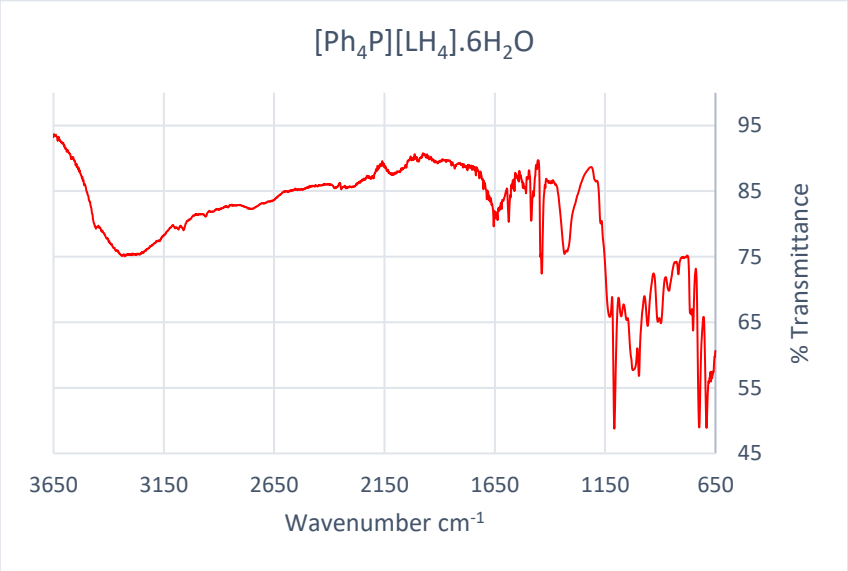


Figure S1.1 Molecular structure of $[Ag(LH_4)(H_2O)].2H_2O$ (**1**) showing the full Ag^+ coordination environment. The structure comprises a Ag^+ cation bound to two LH_4^- anions and one H_2O molecule through three shorter Ag-O distances (indicated by solid bonds) with an additional three longer interactions (indicated by dashed bonds) giving a pseudo six-coordinate octahedral coordination environment. Bond distances: Ag(1)-O(1) 2.408(1), Ag(1)-O(2)^i 2.370(1), Ag(1)-O(8) 2.343(1), Ag(1)-O(4) 2.744(1), Ag(1)-O(5) 2.620(1), Ag(1)-O(7)^i 2.662(1) Å. Symmetry operators for generated atoms: ^{i} 3/2-x,1/2+y,1/2-z.

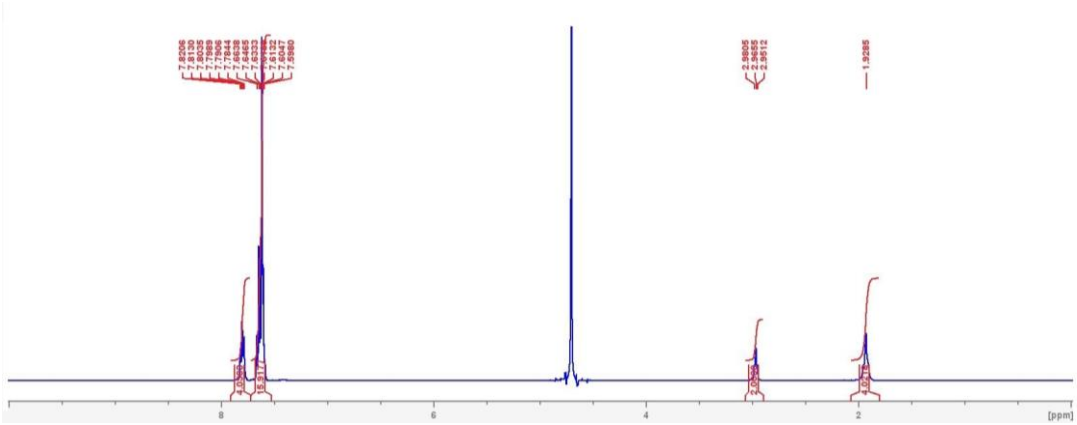
S2. Spectroscopic, PXRD and Crystal Structure of $[Ph_4P][LH_4].6H_2O$ 1.

S2.1 AT-FTIR spectrum of crystallised **1**.

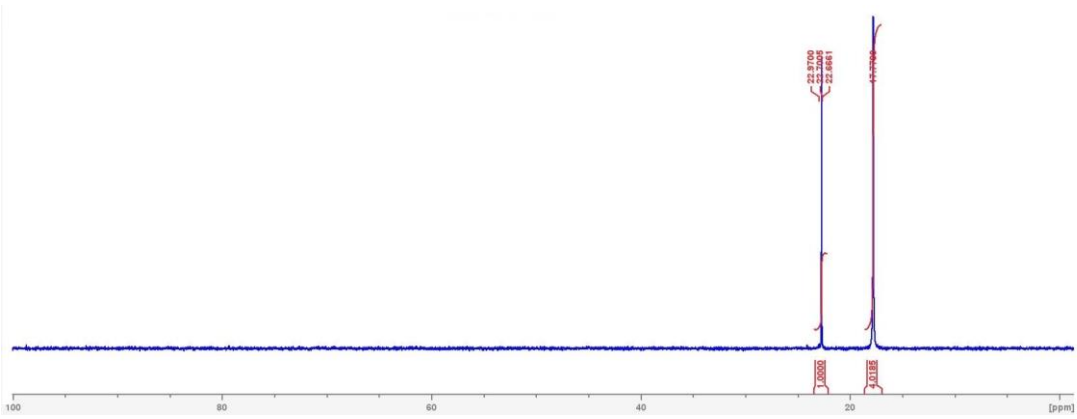


S2.2 NMR data for **1** (a) ^{1}H, 400.13 MHz, D_2O; (b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O.

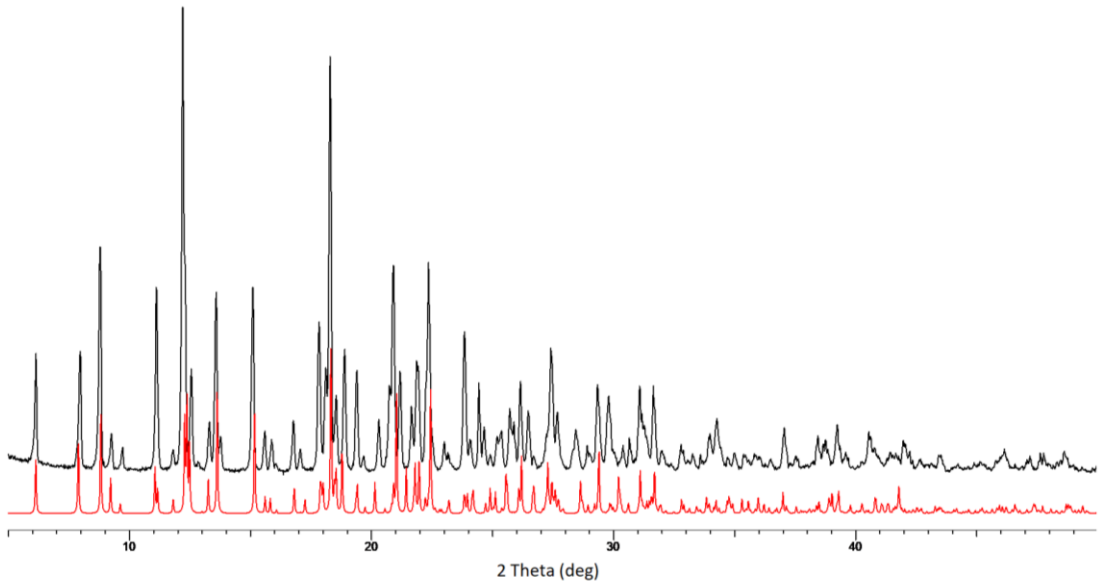
(a)



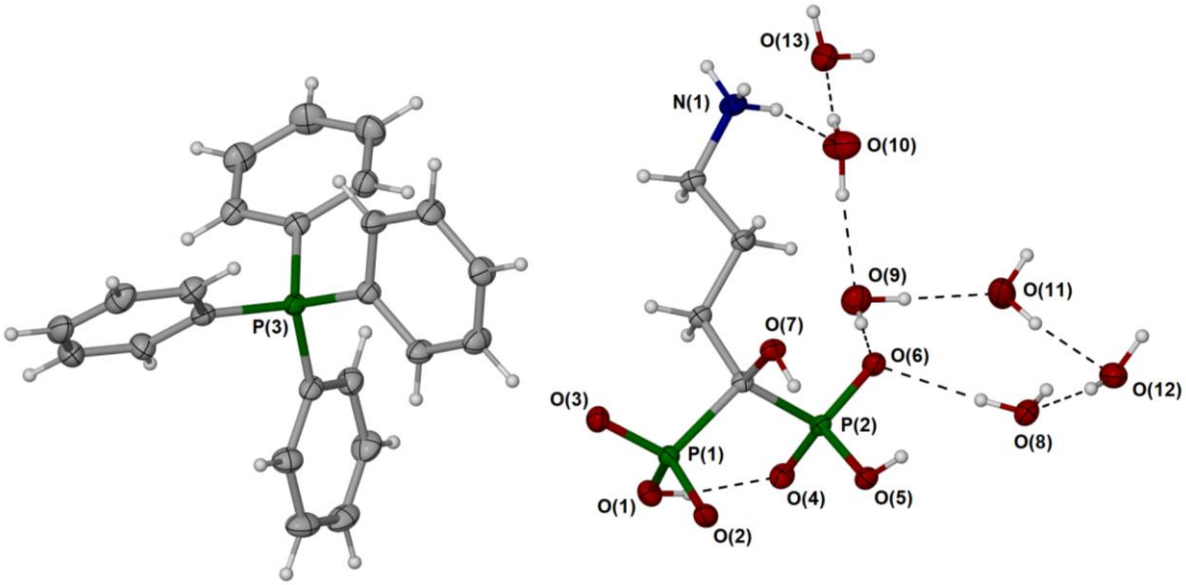
(b)



S2.3 Experimental PXRD of crystallised **1** (black) and simulated PXRD data calculated from the crystal structure of $[Ph_4P][LH_4].6H_2O$ (see below) (red).

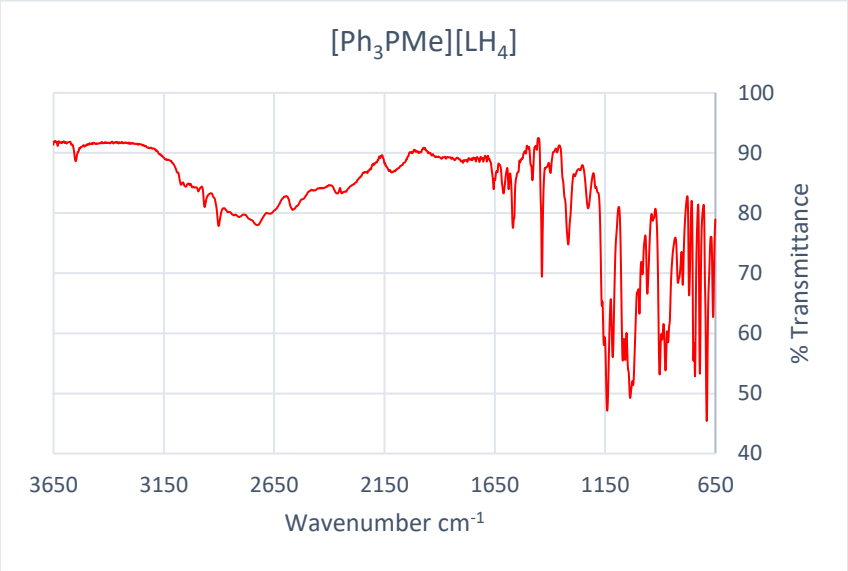


S2.4 Molecular diagram of $[Ph_4P][LH_4].6H_2O$ **1** with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.



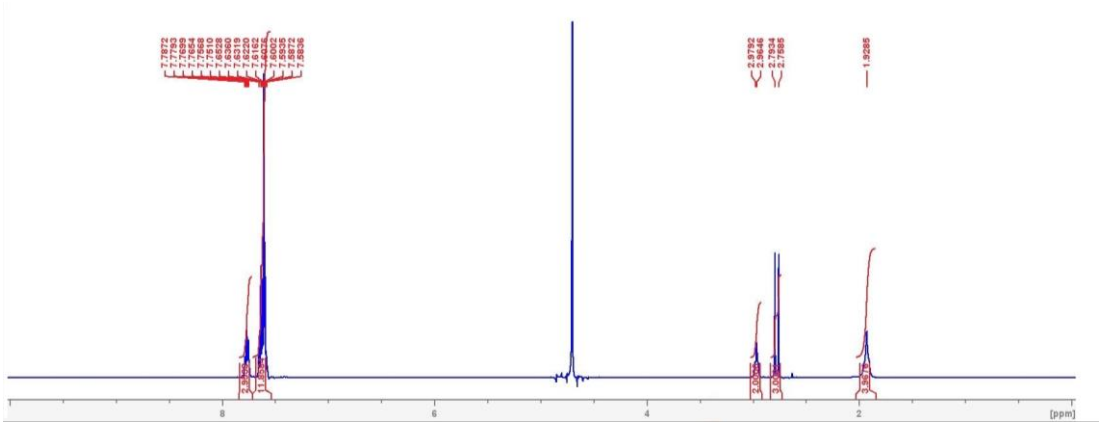
S3. Spectroscopic, PXRD and Crystal Structure of $[Ph_3PMe][LH_4]$ 2.

S3.1 AT-FTIR spectrum of crystallised **2**.

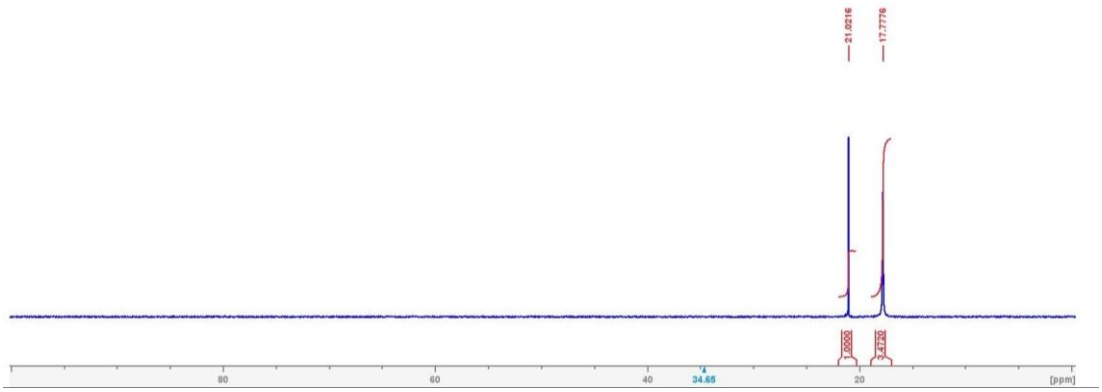


S3.2 NMR data for **2.**

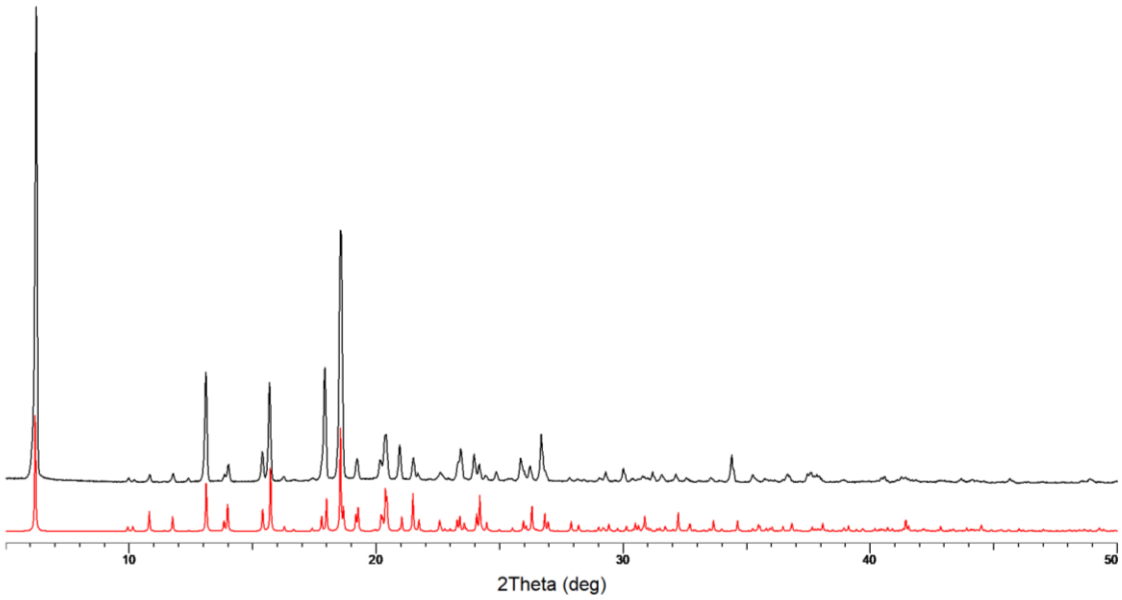
(a) ^{1}H, 400.13 MHz, D_2O



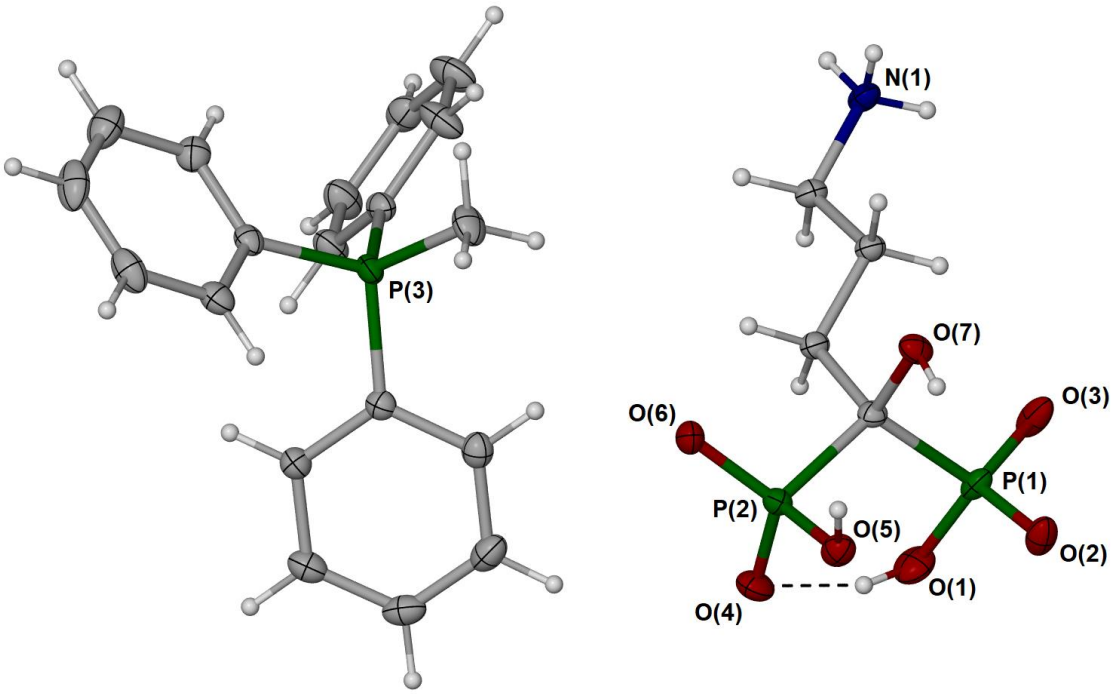
(b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O.



S3.3 Experimental PXRD of crystallised **2** (black) and simulated PXRD data calculated from the crystal structure of $[Ph_3PMe][LH_4]$ (see below) (red).

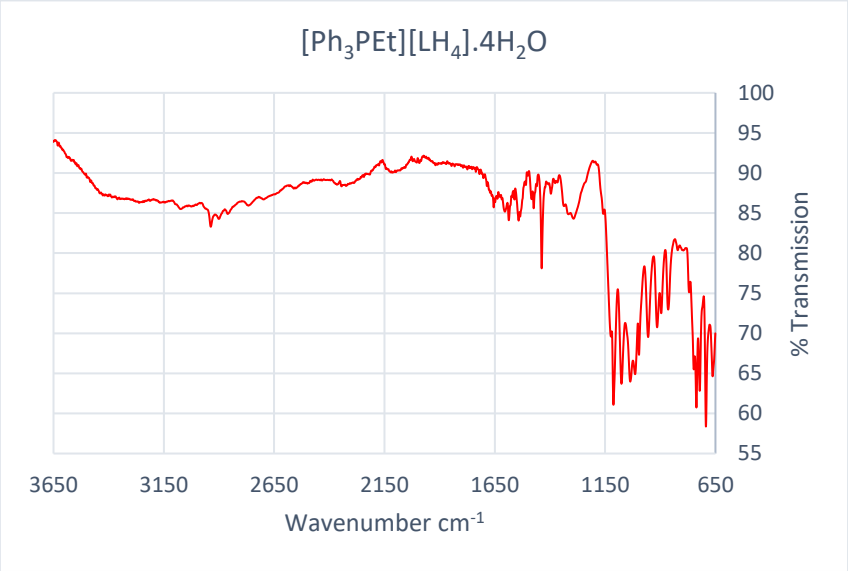


S3.4 Molecular diagram of $[Ph_3PMe][LH_4]$ **2** with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.



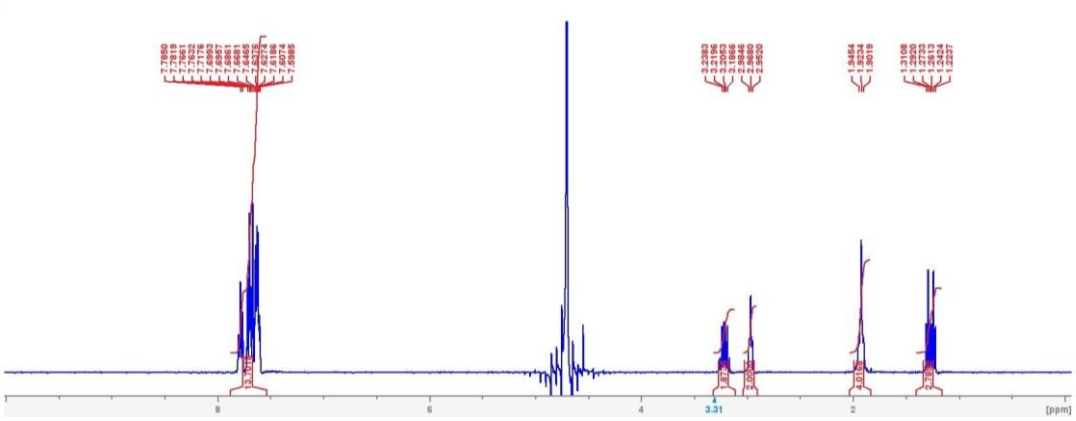
S4. Spectroscopic, PXRD and Crystal Structure of $[Ph_3PEt][LH_4].4H_2O$ 3.

S4.1 ATR-FTIR of crystallised **3**.

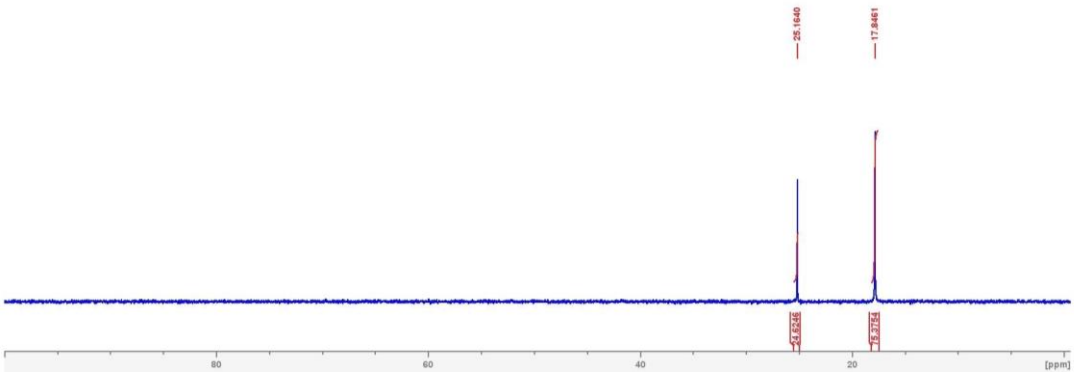


S4.2 NMR data of crystallised **3**.

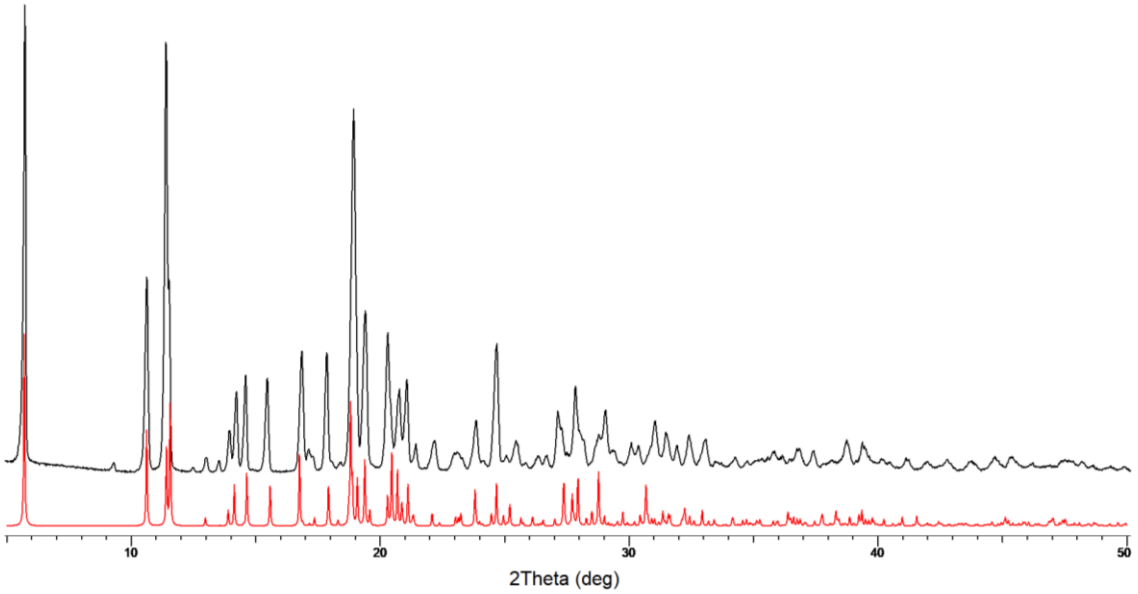
(a) ^{1}H, 400.13 MHz, D_2O;



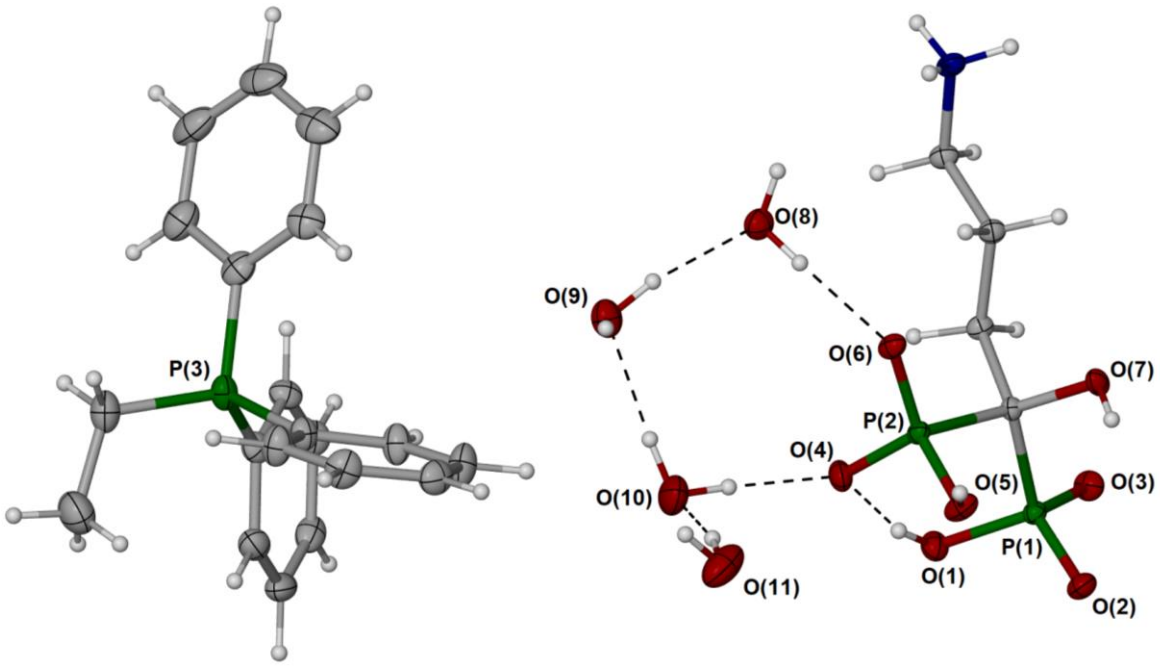
(b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O



S4.3 Experimental PXRD of crystallised **3** (black) and simulated PXRD data calculated from the crystal structure of $[Ph_3PEt][LH_4].4H_2O$ (see below) (red).

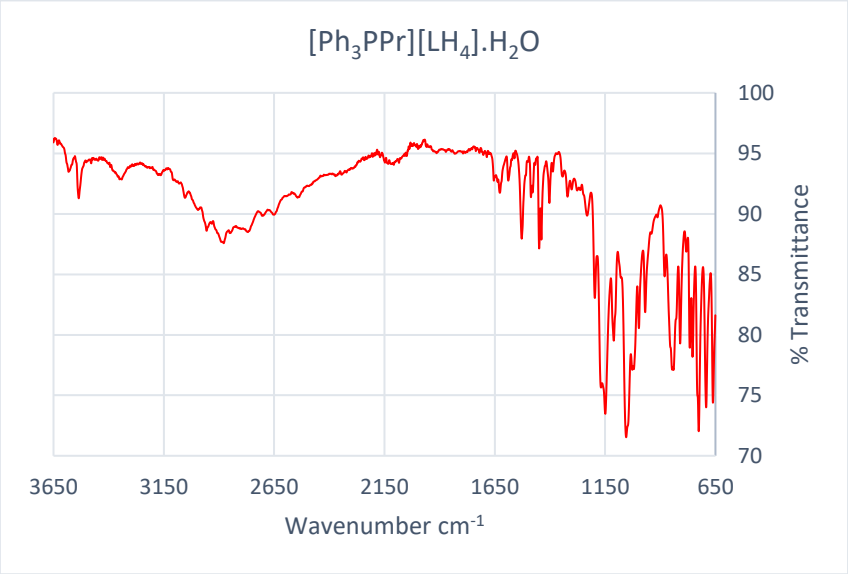


S4.4 Molecular diagram of $[Ph_3PEt][LH_4].4H_2O$ **3** with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.



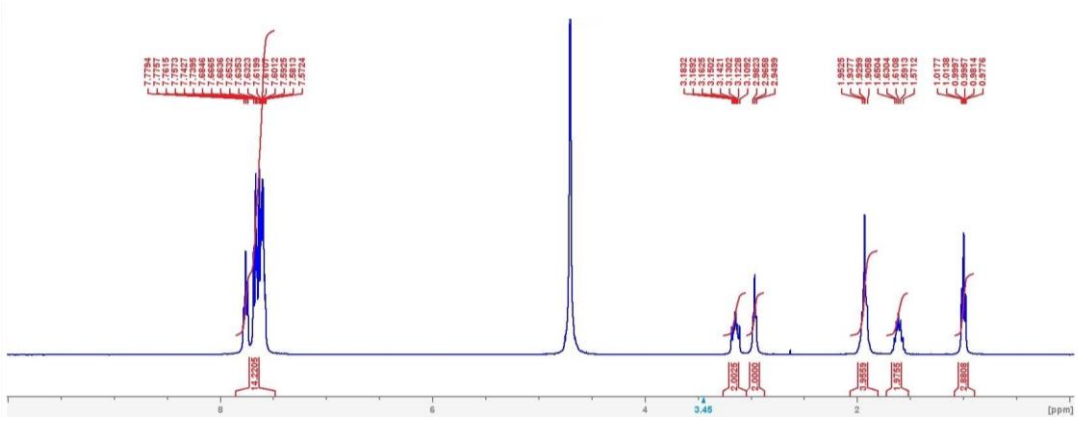
S5. Spectroscopic, PXRD and Crystal Structure of $[Ph_3PPr][LH_4].H_2O$ 4.

S5.1 AT-FTIR spectrum of crystallised **4**.

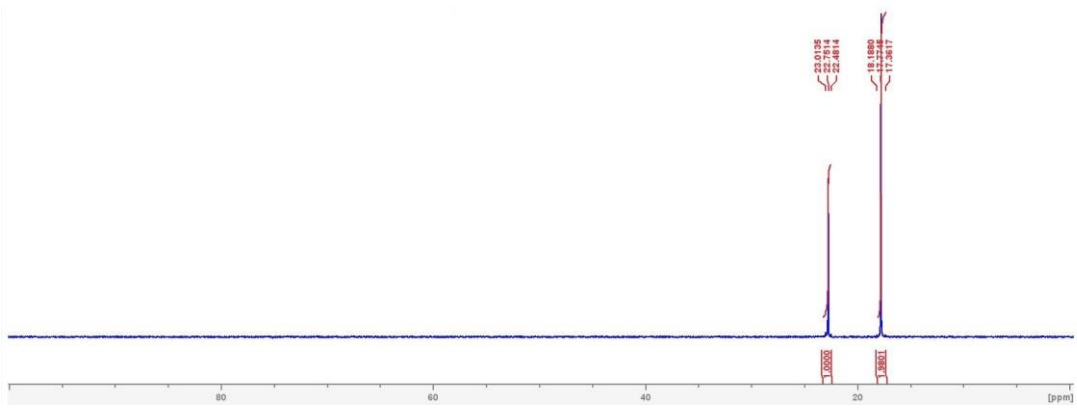


S5.2 NMR data for crystallised **4**.

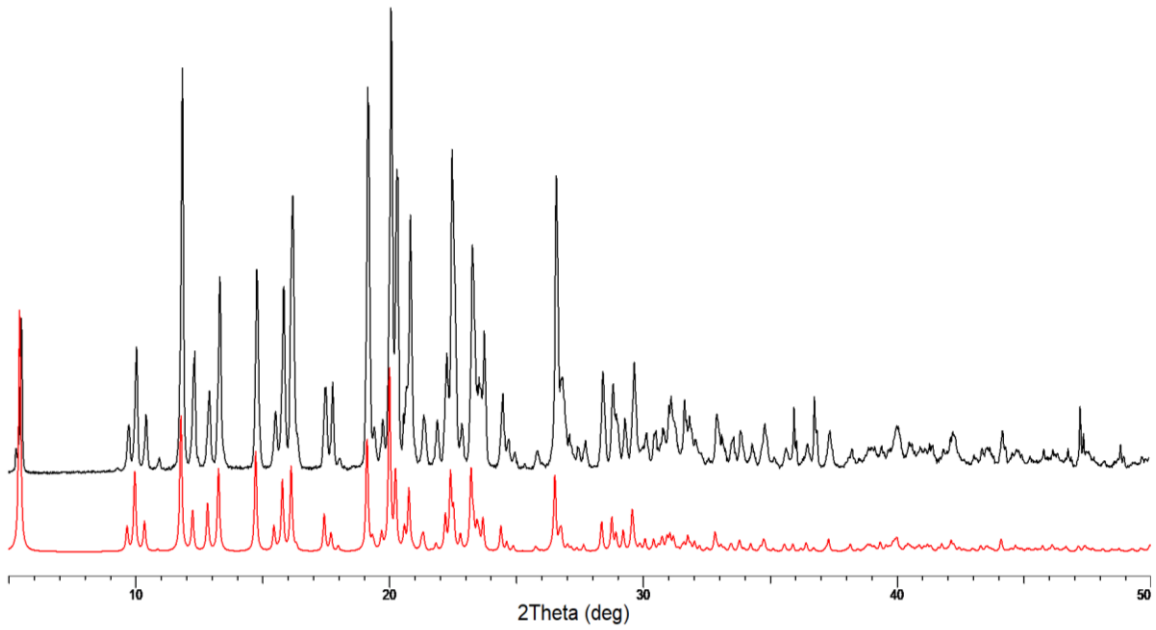
(a) ^{1}H, 400.13 MHz, D_2O



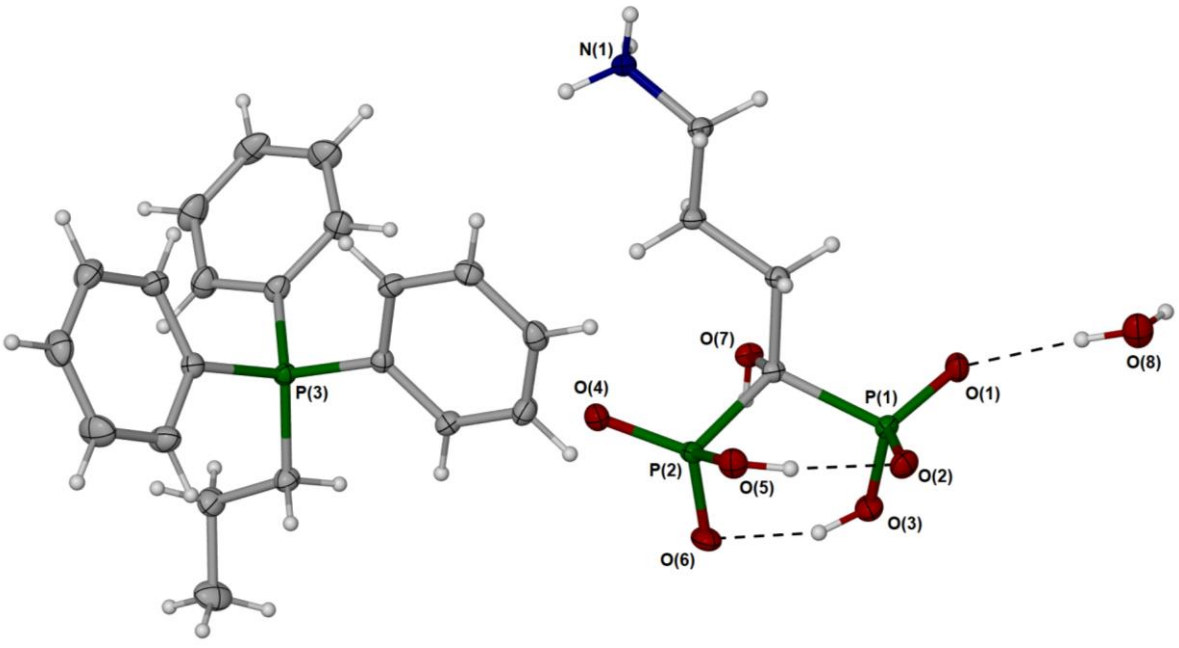
(b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O



S5.3 Experimental PXRD of crystallised **4** (black) and simulated PXRD data calculated from the crystal structure of $[Ph_3PPr][LH_4].H_2O$ (see below) (red).

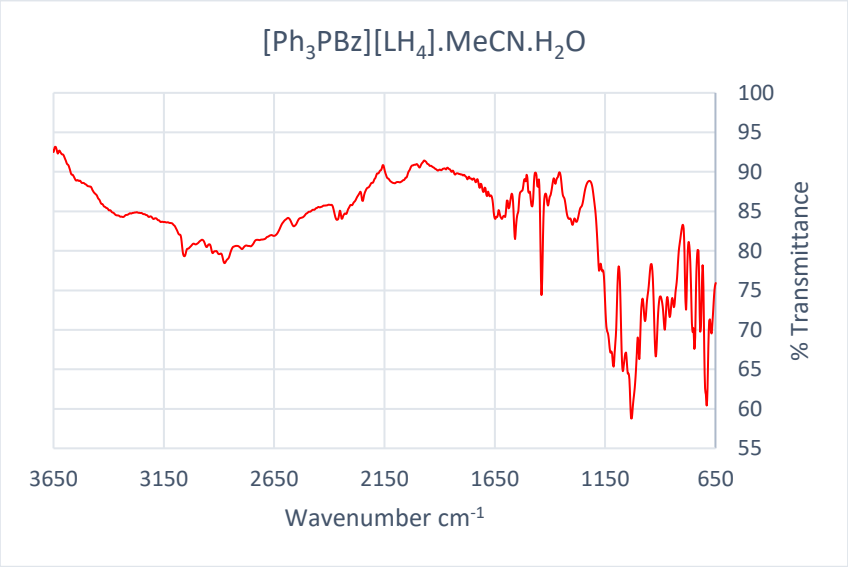


S5.4 Molecular diagram of $[Ph_3PPr][LH_4].H_2O$ **4** with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.



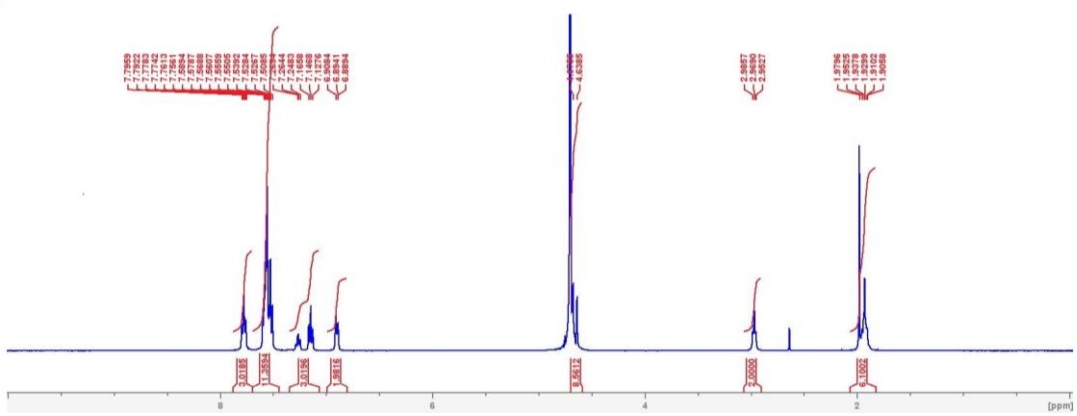
S6. Spectroscopic and PXRD Data for $[Ph_3PBn][LH_4].H_2O.MeCN$ 5.

S6.1 AT-FTIR spectrum of crystallised **5**.

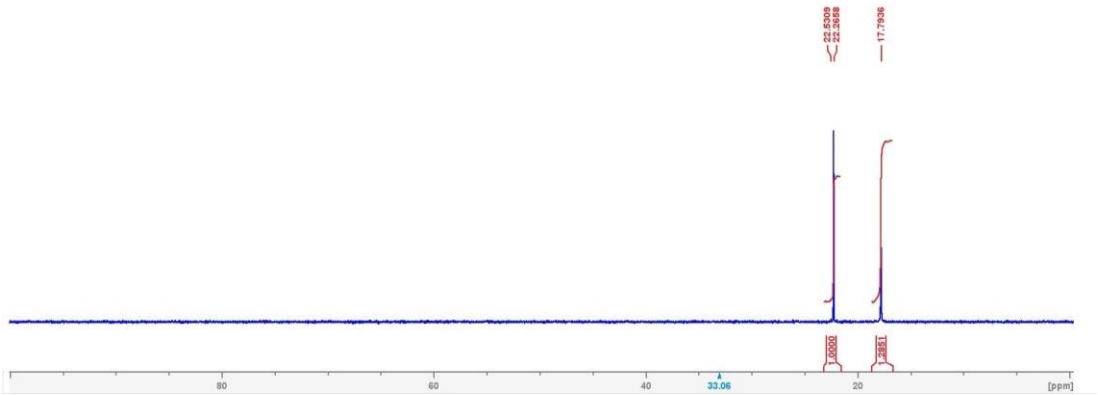


S6.2 NMR data for crystallised **5**.

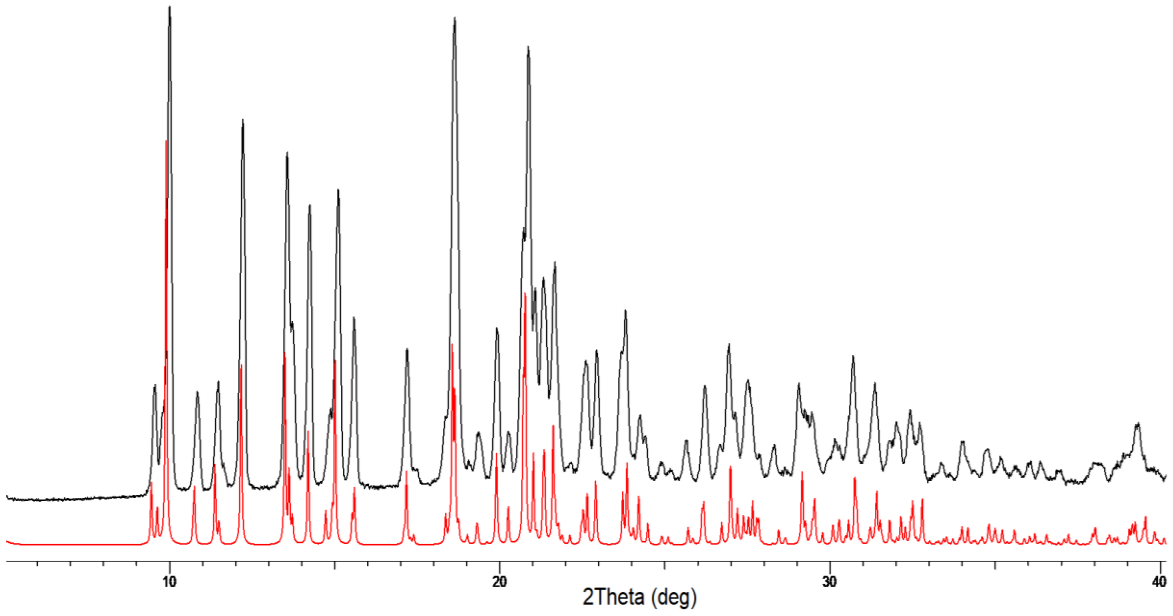
(a) ^{1}H, 400.13 MHz, D_2O



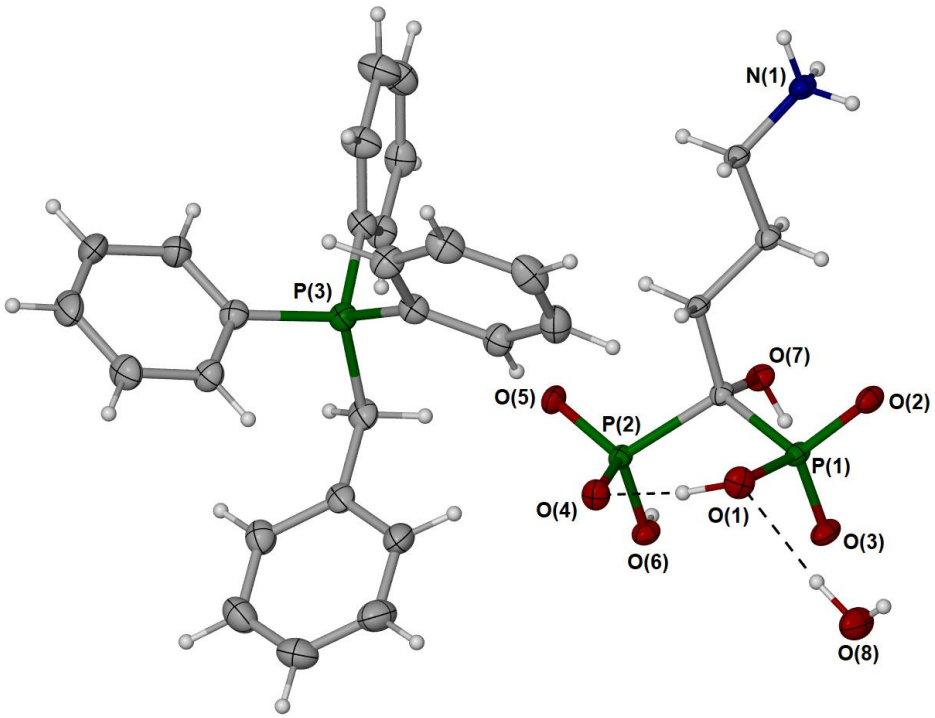
(b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O



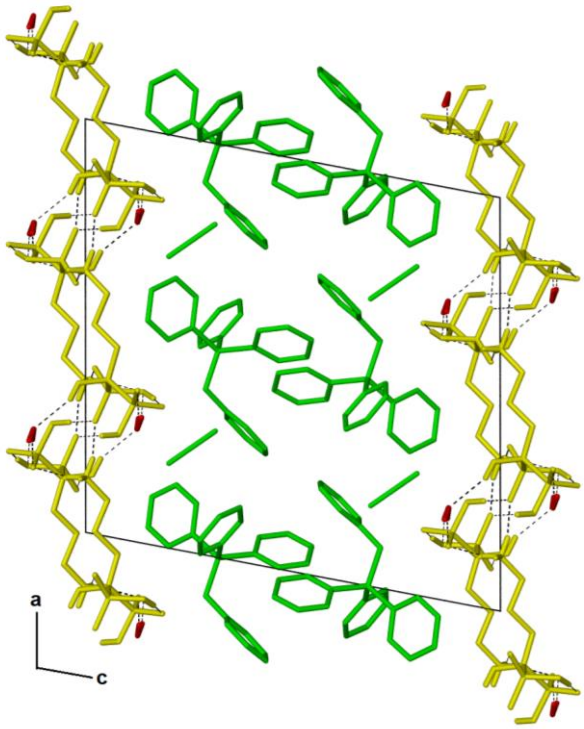
S6.3 Experimental PXRD of crystallised **5** (black) and simulated PXRD data calculated from the crystal structure of $[Ph_3PBn][LH_4].H_2O$ (see below) (red)).



S6.4 Molecular diagram of $[Ph_3PBn][LH_4].H_2O.MeCN$ **5** with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size. The water molecule O(8) is in a symmetry generated position (symmetry operator: x,1+y,z) and the MeCN solvent molecule has been omitted for clarity.

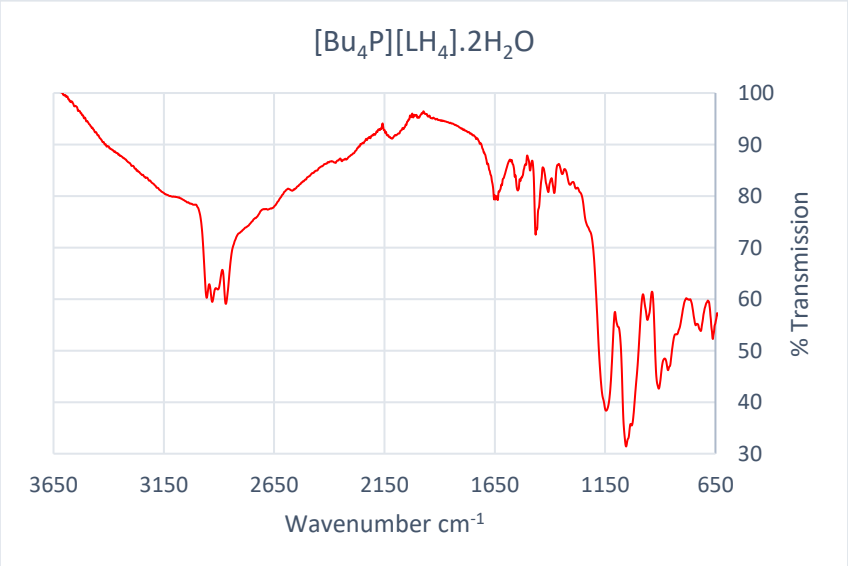


S6.5 Extended packing of compound **5** viewed along the *a*-axis. The $[LH_4]^-$ anions are depicted as yellow, the water molecules as red and the $[Ph_4P]^+$ cations and MeCN lattice solvent as green; some hydrogen atoms have been omitted for clarity.



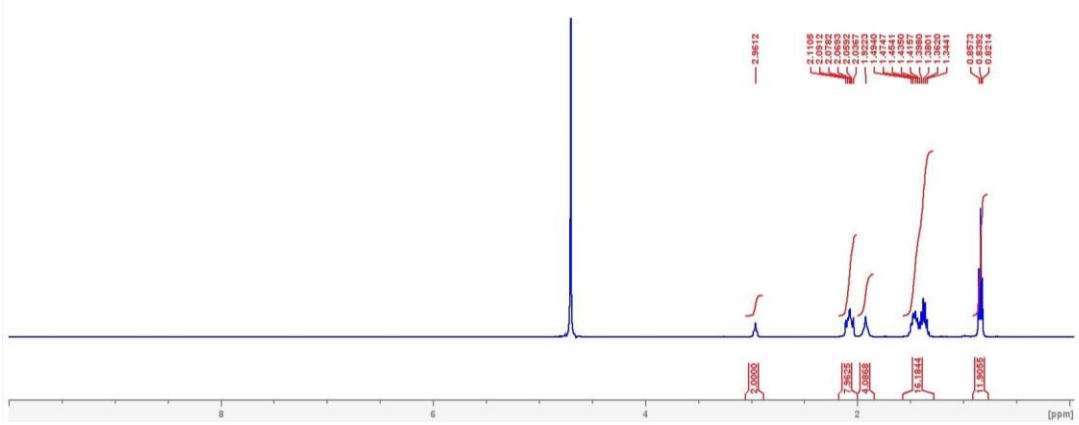
S7. Spectroscopic Data for $[Bu_4P][LH_4].2H_2O$ 6.

S7.1 AT-FTIR spectrum of amorphous $[Bu_4P][LH_4].2H_2O$.

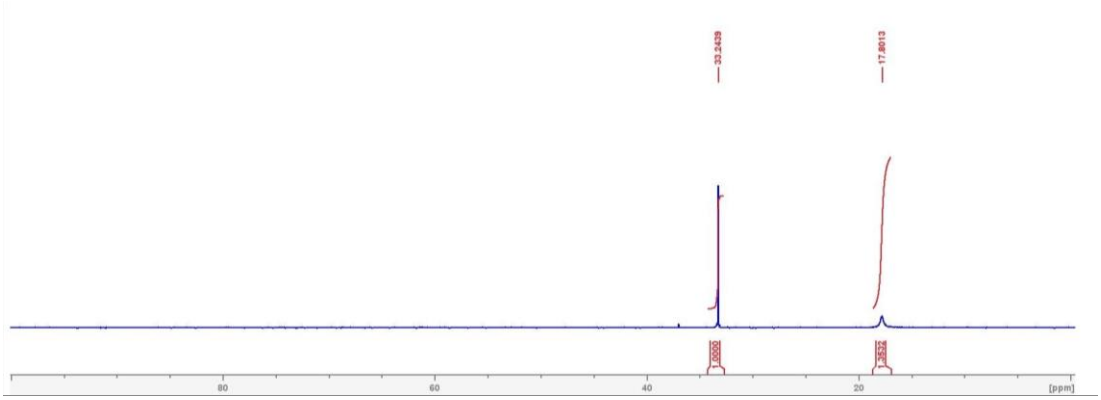


S7.2 NMR data for crude $[Bu_4P][LH_4].2H_2O$ **6**.

(a) ^{1}H, 400.13 MHz, D_2O



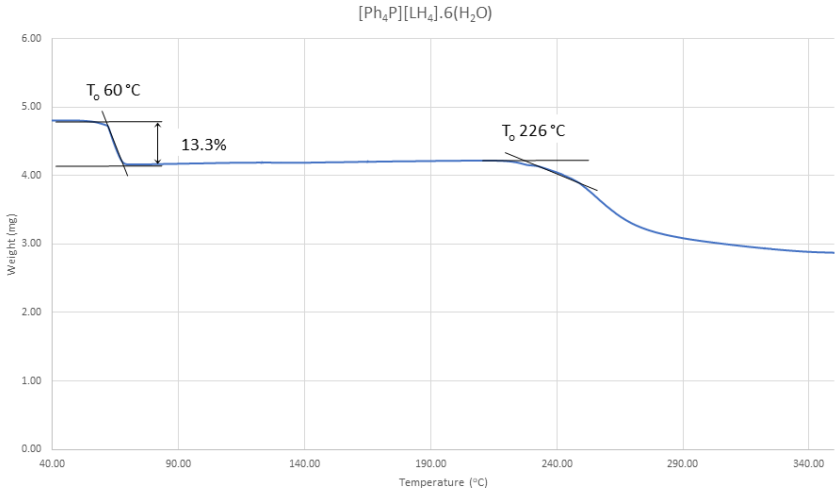
(b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O



S8. Dehydration of Compound 1: Spectroscopic, PXRD Data and Crystal Structures of $[Ph_4P][LH_4].0.5H_2O$ 1a and $[Ph_4P][LH_4][LH_5].H_2O.EtOH$ 1b.

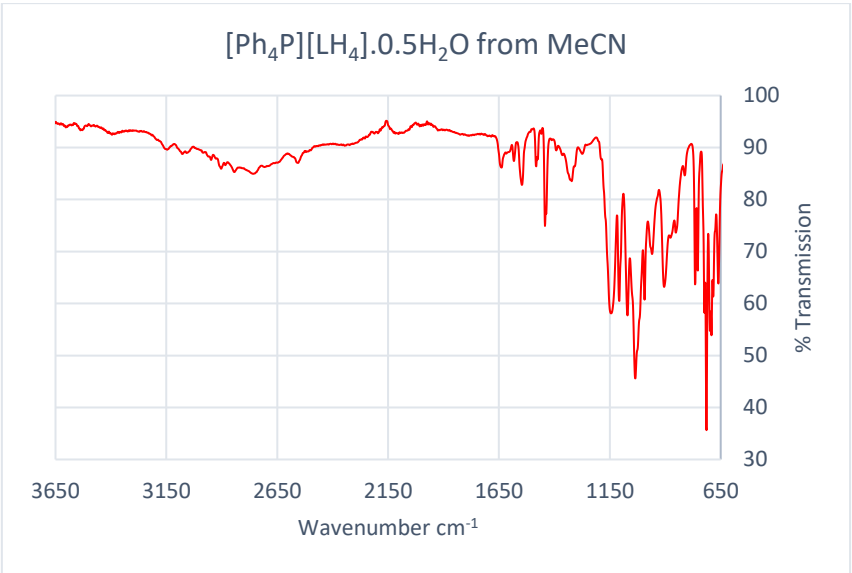
a) TGA of **1**.

S8.1 TGA trace of $[Ph_4P][LH_4].6H_2O$ **1**. Initial weight: 4.77 mg

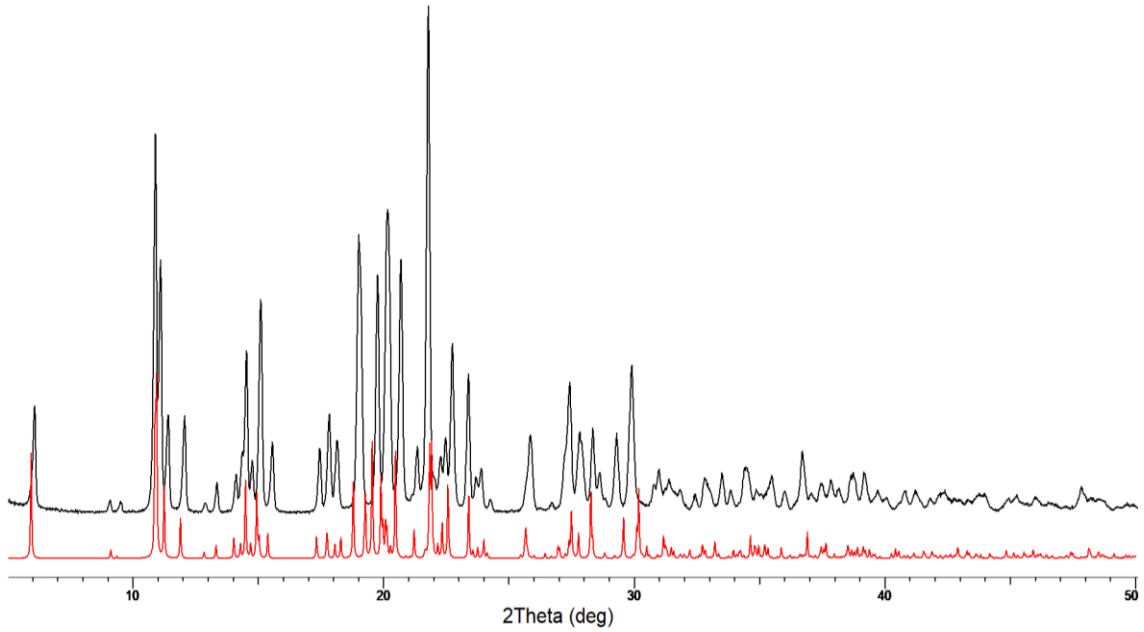


b) Bulk dehydration of **1** from heating in MeCN

S8.2 AT-FTIR spectrum of **1a**, prepared from heating **1** in MeCN.

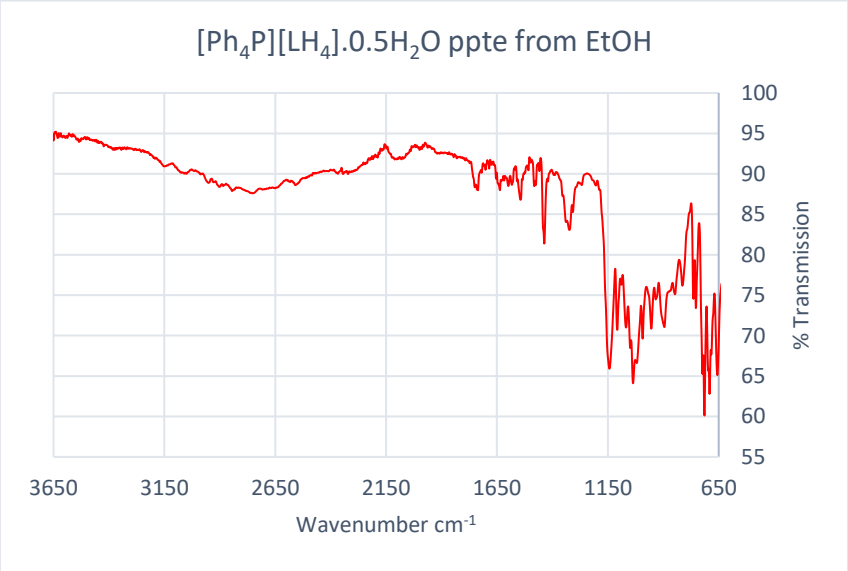


S8.3 Experimental PXRD of bulk **1a**, prepared from heating **1** in MeCN (black), and simulated PXRD data calculated from the crystal structure of **1a** (red).



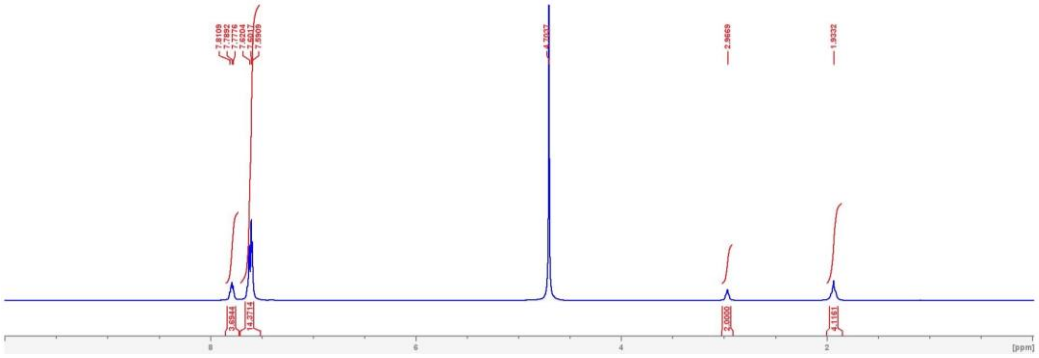
c) Dehydration of **1** from heating in EtOH

S8.4 AT-FTIR spectrum of **1a** isolated as a precipitate after heating **1** in EtOH.

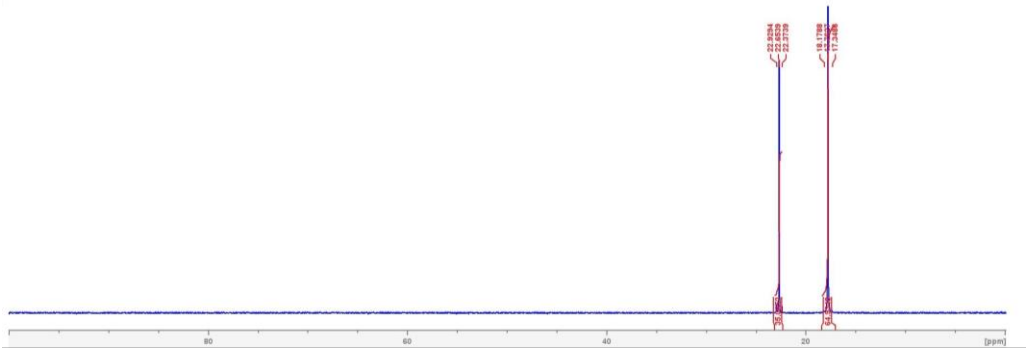


S8.5 NMR data for **1a** isolated as a precipitate after heating **1** in EtOH.

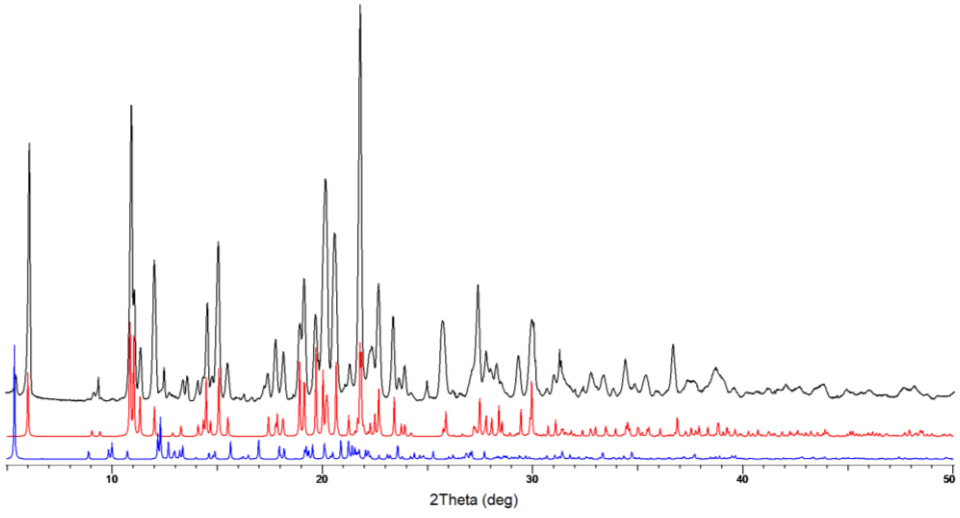
(a) ^{1}H, 400.13 MHz, D_2O;



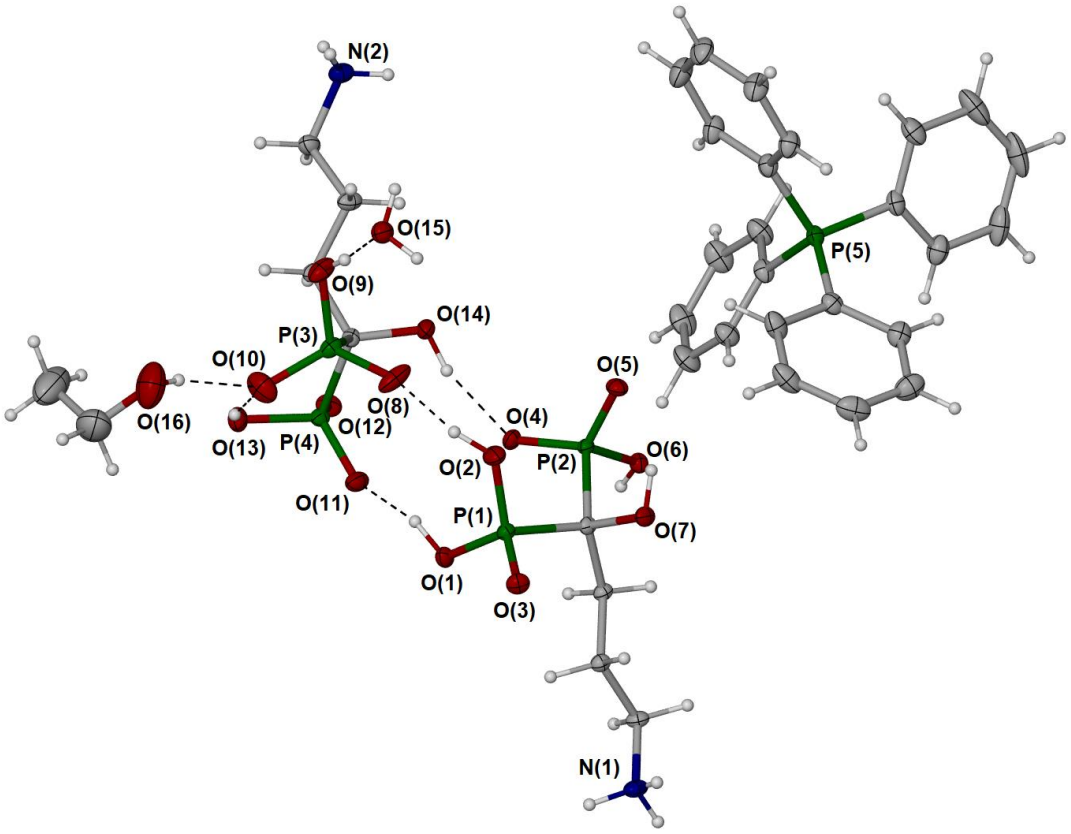
(b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O



S8.6 Experimental PXRD of bulk $[Ph_4P][LH_4].0.5H_2O$ **1a**, isolated as a precipitate from heating **1** in EtOH (black), and simulated PXRD data calculated from the crystal structures of $[Ph_4P][LH_4].0.5H_2O$ **1a** (red) and $[Ph_4P][LH_4][LH_5].H_2O.EtOH$ **1b** (blue).

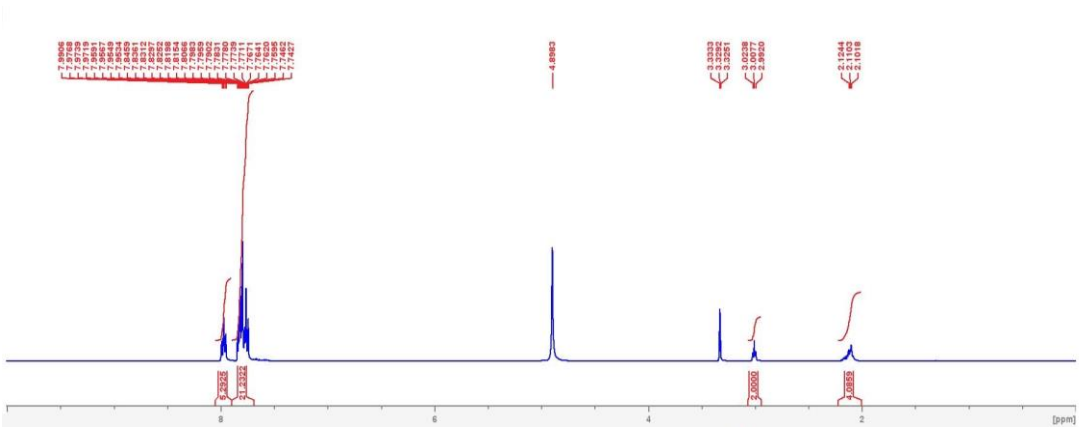


S8.7 Molecular diagram of $[Ph_4P][LH_4][LH_5]H_2O.EtOH$ **1b** with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size. Crystals were obtained by a second EtOH extraction of the solid precipitate resulting from heating of **1** in EtOH.

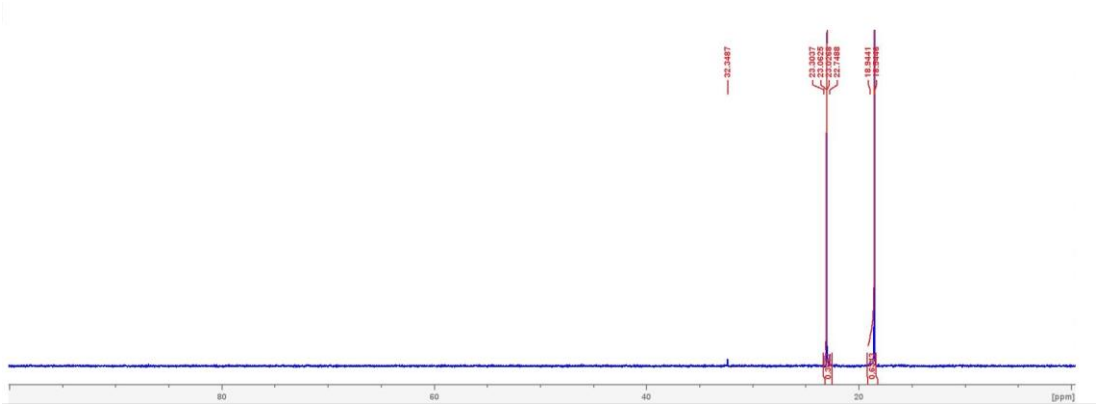


S8.8 NMR data for the solid obtained from evaporation of the EtOH filtrate after heating **1** in EtOH.

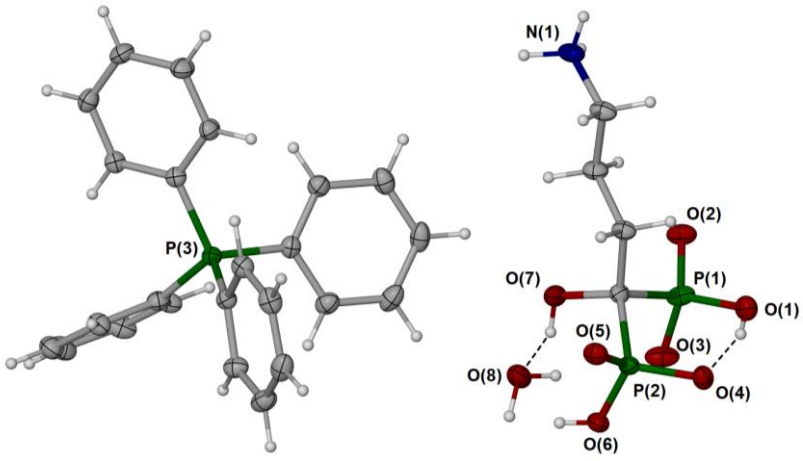
(a) ^{1}H, 400.13 MHz,CD_3OD;



(b) $^{31}P\{^{1}H\}$, 161.96 MHz, CD_3OD.



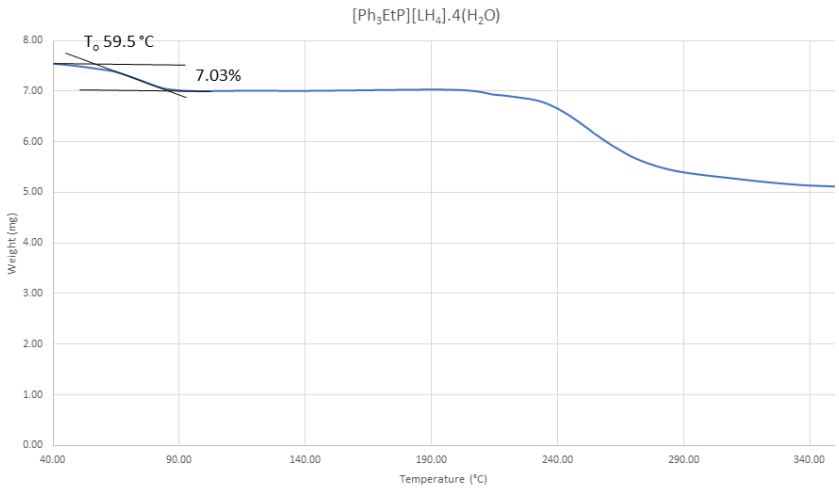
S8.9 Molecular diagram of $[Ph_4P][LH_4].0.5(H_2O)$ **1a** with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.



S9. Dehydration of compound 3. Spectroscopic and PXRD Data for $[Ph_3PEt][LH_4]$ 3a.

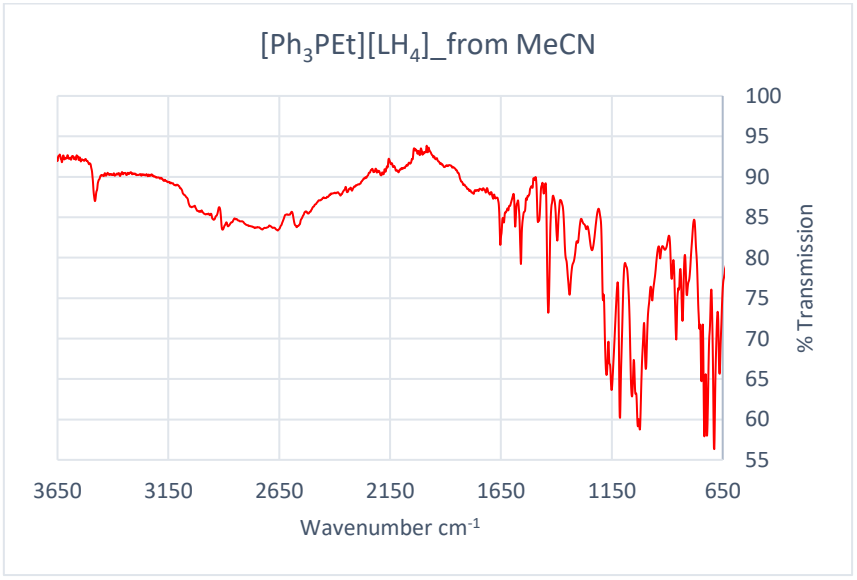
(a) TGA of **3**.

S9.1 TGA trace of $[Ph_3EtP][LH_4].4H_2O$ **3**. Initial weight: 7.56mg.

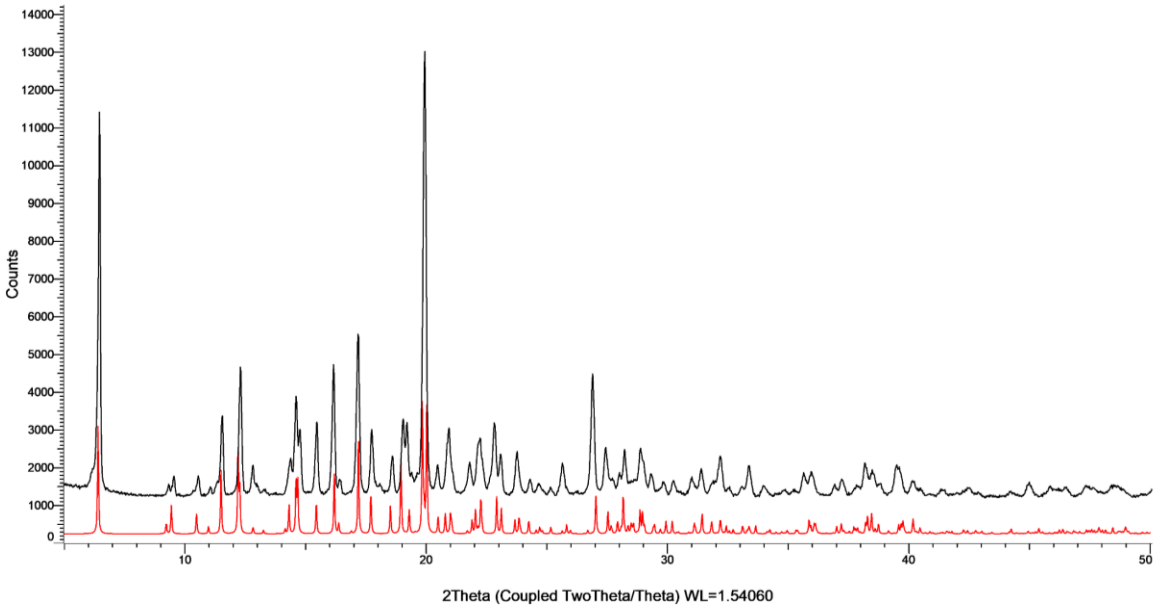


(b) Bulk dehydration of **3** in MeCN

S9.2 AT-FTIR spectrum of **3a** from MeCN.

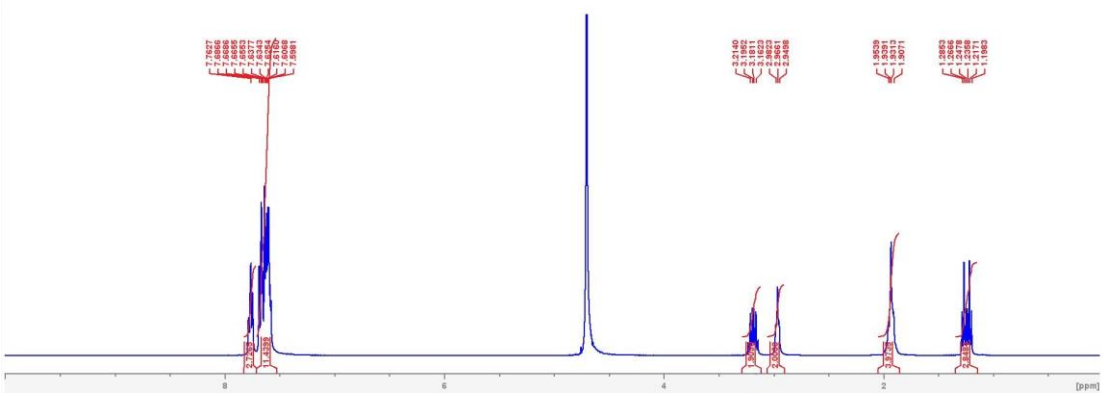


S9.3 Experimental PXRD of bulk $[Ph_3PEt][LH_4]$ **3a**, isolated from heating **3** in MeCN (black), and simulated PXRD data calculated from the crystal structures of **3a** (red).

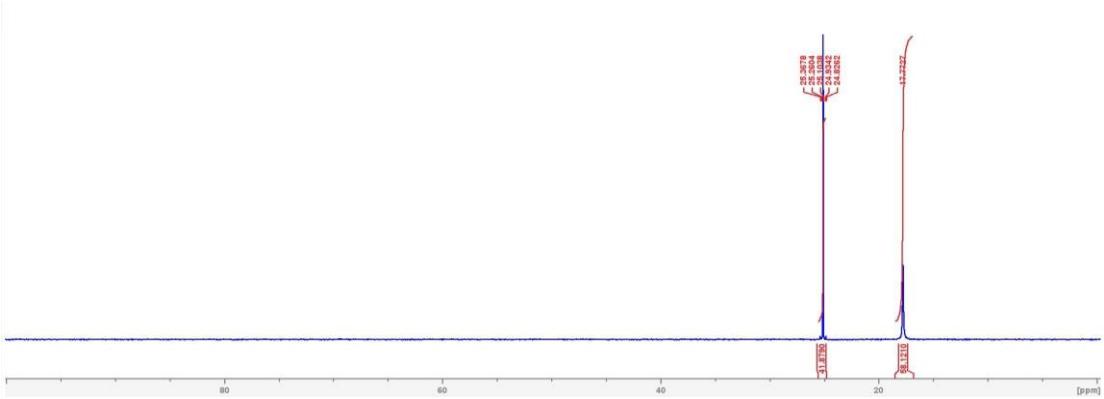


S9.4 NMR data for $[Ph_3PEt][LH_4]$ **3a** from MeCN.(a) ^{1}H, 400.13 MHz, D_2O; (b) $^{31}P\{^{1}H\}$, 161.96 MHz, D_2O.

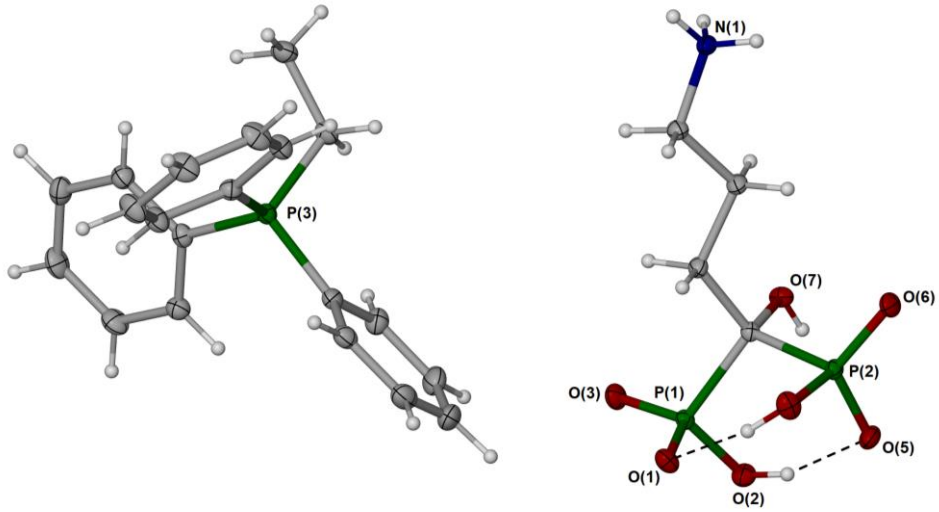
(a)



(b)



S9.4 Molecular diagram of $[Ph_3PEt][LH_4]$ **3a** with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.



S10. Supramolecular interactions in the structures 1-5.

S10.1 Standard hydrogen bond parameters for structure **1**-**5**.

Table 10.1a. Hydrogen bonds for $[Ph_4P][LH_4].6H_2O$ **1** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(4)	0.81(3)	1.76(3)	2.5447(14)	164(2)
N(1)-H(1A)...O(3)#1	0.92(2)	1.92(2)	2.8114(16)	162.8(18)
N(1)-H(1B)...O(8)#2	0.90(2)	2.09(2)	2.9249(16)	154.3(18)
N(1)-H(1C)...O(10)	0.89(2)	1.94(2)	2.7858(17)	157(2)
O(5)-H(5)...O(2)#4	0.87(3)	1.69(3)	2.5395(14)	164(3)
O(7)-H(7A)...O(5)#4	0.85(3)	2.07(3)	2.8906(13)	163(2)
O(8)-H(8A)...O(11)#5	0.89(3)	2.21(3)	3.0663(19)	161(2)
O(8)-H(8B)...O(6)	0.83(3)	1.97(3)	2.7922(15)	172(2)
O(9)-H(9A)...O(11)	0.91(3)	1.87(3)	2.7757(18)	178(3)
O(9)-H(9B)...O(6)	0.82(3)	2.03(3)	2.8410(15)	170(2)
O(10)-H(10A)...O(9)	0.89(3)	1.90(3)	2.7862(18)	172(2)
O(10)-H(10B)...O(13)	0.91(3)	1.84(3)	2.7409(17)	172(3)
O(11)-H(11A)...O(12)	0.85(3)	1.92(3)	2.7654(17)	169(2)
O(11)-H(11B)...O(2)#6	0.88(3)	1.88(3)	2.7455(16)	166(2)
O(12)-H(12A)...O(6)#5	0.89(3)	1.95(3)	2.8225(15)	167(2)
O(12)-H(12B)...O(8)	0.84(3)	1.97(3)	2.8063(16)	172(2)
O(13)-H(13A)...O(3)#6	0.82(3)	2.00(3)	2.7914(15)	165(2)
O(13)-H(13B)...O(12)#2	0.85(3)	2.00(3)	2.8432(16)	168(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z #2 x+1,y,z #3 -x+2,-y+2,-z #4 -x+1,-y+1,-z #5 -x+1,-y+2,-z #6 x,y+1,z
#7 -x+2,-y+1,-z+1

Table 10.1b. Hydrogen bonds for $[Ph_4P][LH_4].0.5H_2O$ **1a** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(5)#1	0.98(3)	1.81(3)	2.7813(19)	172(2)
N(1)-H(3N)...O(2)#2	0.91(3)	1.84(3)	2.7545(18)	175(2)
N(1)-H(2N)...O(3)#3	0.90(3)	2.27(3)	2.9869(18)	137(2)
N(1)-H(2N)...O(6)#3	0.90(3)	2.18(2)	2.8579(18)	131(2)
O(1)-H(1^a)...O(4)	0.856(19)	1.72(3)	2.5436(16)	161(5)
O(3)-H(3^b)...O(3)#4	0.88(5)	1.71(5)	2.571(2)	165(6)
O(4)-H(4^b)...O(1)	0.86(2)	1.70(2)	2.5436(16)	168(6)
O(6)-H(6A^a)...O(6)#5	0.80(4)	1.77(4)	2.560(2)	172(5)
O(7)-H(7A)...O(8)	0.83(4)	2.02(4)	2.725(3)	143(3)
O(8)-H(8B)...O(5)#5	0.872(19)	1.95(2)	2.812(3)	169(5)
O(8)-H(8A)...O(3)	0.87(2)	2.37(8)	2.989(3)	128(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x+1,-y+2,-z+1 #3 x+1,y,z
#4 -x,-y+2,-z+1 #5 -x,-y+1,-z+1 #6 x-1,y,z

Table 10.1c. Hydrogen bonds $[Ph_3MeP][LH_4]$ **2** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(4)	0.86(3)	1.77(3)	2.5944(18)	163(2)
O(5)-H(5)...O(2)#1	0.92(3)	1.70(3)	2.6166(16)	171(3)
O(7)-H(7A)...O(5)	0.79(3)	2.53(2)	2.9807(15)	118(2)
N(1)-H(3N)...O(3)#2	0.91(2)	1.83(2)	2.7418(18)	173(2)
N(1)-H(1N)...O(2)#3	0.90(2)	1.95(2)	2.7545(17)	148(2)
N(1)-H(2N)...O(6)#4	0.99(2)	1.77(2)	2.7492(17)	169.2(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y-1/2,-z+3/2 #2 -x,-y+2,-z+1 #3 x,-y+3/2,z-1/2
#4 -x,-y+1,-z+1 #5 x,y-1,z #6 -x+1,y-1/2,-z+3/2

Table 10.1d. Hydrogen bonds $[Ph_3EtP][LH_4].4H_2O$ **3** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(7)-H(7A)...O(11)#1	0.839(17)	1.951(18)	2.7537(19)	160(3)
O(8)-H(8A)...O(6)	0.838(16)	1.963(17)	2.7941(17)	171(3)
O(8)-H(8B)...O(6)#2	0.864(16)	2.080(18)	2.8999(17)	158(2)
O(9)-H(9A)...O(3)#3	0.850(17)	1.955(18)	2.7776(19)	163(3)
O(9)-H(9B)...O(8)	0.864(16)	2.018(18)	2.8365(19)	158(2)
O(10)-H(10A)...O(4)	0.897(17)	1.788(17)	2.6836(19)	177(3)
O(10)-H(10B)...O(9)	0.889(17)	1.885(18)	2.773(2)	176(3)
O(11)-H(11A)...O(10)	0.927(17)	1.782(19)	2.700(2)	170(3)
O(11)-H(11B)...O(2)#3	0.894(18)	2.63(2)	3.469(2)	156(3)
O(11)-H(11B)...O(3)#3	0.894(18)	2.32(3)	3.0654(19)	141(3)
N(1)-H(1N)...O(2)#4	0.86(3)	2.10(3)	2.8396(19)	144(2)
N(1)-H(1N)...O(5)#4	0.86(3)	2.37(3)	2.9473(19)	124(2)
N(1)-H(2N)...O(3)#5	0.89(3)	1.90(3)	2.777(2)	167(2)
N(1)-H(3N)...O(6)#2	0.92(3)	1.95(3)	2.8579(19)	170(2)
O(1)-H(1)...O(4)	0.837(17)	1.764(18)	2.5855(18)	167(3)
O(5)-H(5)...O(2)#6	0.848(18)	1.746(18)	2.5886(18)	173(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y-1/2,-z+3/2 #2 -x+2,-y+1,-z+1 #3 x,y+1,z
#4 x,-y+1/2,z-1/2 #5 -x+2,-y,-z+1 #6 -x+2,y+1/2,-z+3/2

Table 10.1e. Hydrogen bonds for $[Ph_3EtP][LH_4].H_2O$ **3a** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(5)#1	0.92(2)	1.88(2)	2.7912(14)	168.5(17)
N(1)-H(2N)...O(6)#2	0.89(2)	1.87(2)	2.7605(14)	178.0(18)
N(1)-H(3N)...O(3)#3	0.92(2)	1.78(2)	2.7032(15)	174.7(18)
O(2)-H(2)...O(5)	0.82(2)	1.87(2)	2.6533(13)	159(2)
O(4)-H(4)...O(1)	0.86(3)	1.80(3)	2.6239(13)	161(2)
O(7)-H(7A)...O(2)#4	0.82(2)	2.08(2)	2.8263(13)	151(2)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 -x+1,-y+2,-z+2 #3 -x+1,-y+1,-z+2
#4 -x,-y+1,-z+2

Table 10.1f. Hydrogen bonds for $[Ph_3PPr][LH_4].H_2O$ **4** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(4)#1	0.93(2)	1.84(2)	2.7625(14)	169.1(18)
N(1)-H(2N)...O(6)#2	0.90(2)	1.89(2)	2.7189(15)	153.0(17)
N(1)-H(3N)...O(1)#3	0.91(2)	1.89(2)	2.7923(15)	172.8(17)
O(5)-H(5)...O(2)	0.83(2)	1.82(2)	2.6098(14)	160(2)
O(3)-H(3)...O(6)	0.87(2)	1.84(2)	2.6543(14)	157(2)
O(7)-H(7A)...O(3)#4	0.80(2)	2.31(2)	2.9542(13)	137.4(19)
O(8)-H(8A)...O(5)#5	0.85(3)	2.15(3)	2.9834(15)	169(2)
O(8)-H(8B)...O(1)	0.87(3)	1.95(3)	2.8143(15)	175(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1 #2 x+1,y,z #3 -x+2,-y+2,-z+1
#4 -x+1,-y+2,-z+1 #5 x,y+1,z

Table 10.g. Hydrogen bonds for $[Ph_3BnP][LH_4].H_2O.MeCN$ **5** [Å and deg.].

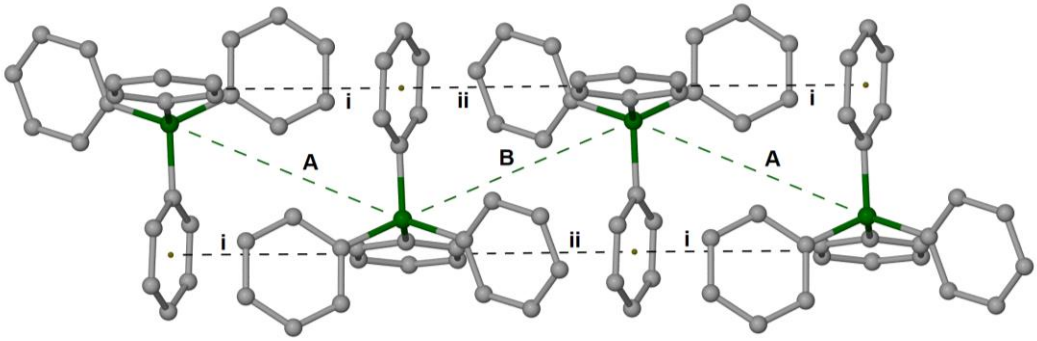
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(4)	0.95(5)	1.62(5)	2.543(2)	164(4)
O(6)-H(6A)...O(3)#1	0.98(5)	1.57(5)	2.554(2)	178(4)
O(7)-H(7A)...O(8)#2	0.84(4)	2.17(4)	2.958(2)	156(3)
O(8)-H(8A)...O(5)	0.81(4)	2.02(4)	2.822(2)	174(3)
O(8)-H(8B)...O(1)#3	0.91(5)	2.10(5)	2.997(2)	170(4)
N(1)-H(1N)...O(5)#4	0.89(3)	1.96(3)	2.839(2)	169(3)
N(1)-H(2N)...O(2)#5	0.91(3)	1.84(3)	2.733(2)	166(3)
N(1)-H(3N)...O(3)#6	0.90(3)	1.98(3)	2.815(2)	154(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y-1/2,-z+3/2 #2 -x+2,y+1/2,-z+3/2 #3 x,y-1,z
#4 -x+2,-y+1,-z+1 #5 -x+2,-y+2,-z+1 #6 x,-y+3/2,z-1/2

S10.2 Details of supramolecular structures of the $[Ph_4P]^+$ cations in DEMYEZ03, **1**, **1a**, **3** and **4**.

The closest intermolecular arrangements of the cations within the chain are indicated by green dashed lines with the P…P separations and P…P…P angles listed below. The **ef** phenyl-phenyl arrangements within the central embraces and parallel to the chain axis are represented by black dashed lines, with the closest C-H…*Cg* interactions listed below (*Cg* = phenyl ring centroid). Note phenyl-phenyl arrangements perpendicular to the chain axes are not indicated.

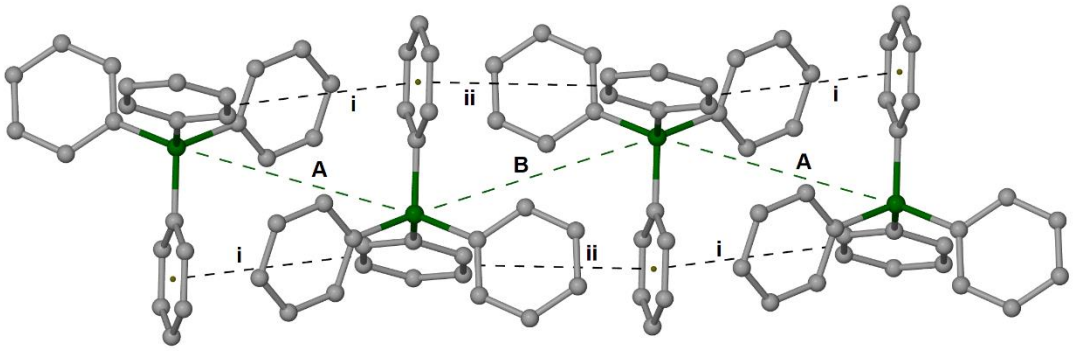
DEMYEZ03



P…P: A = 6.603 Å, B = 6.691 Å, P…P…P 115.9 °.

C-H…*Cg*: d(C…*Cg*) i = 4.53 Å (C14), ii = 4.36 Å (C18).

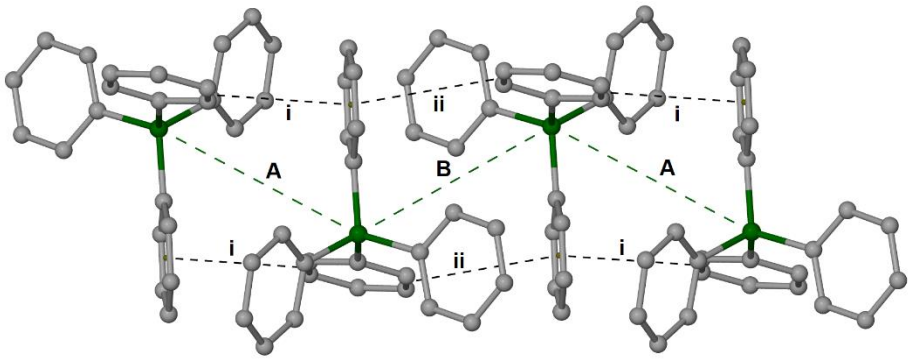
$[Ph_4P][LH_4].6(H_2O)$



P…P: A = 6.493 Å, B = 6.848 Å, P…P…P 120.8 °.

C-H…*Cg*: d(C…*Cg*) i = 4.64 Å (C10), ii = 4.63 Å (C7).

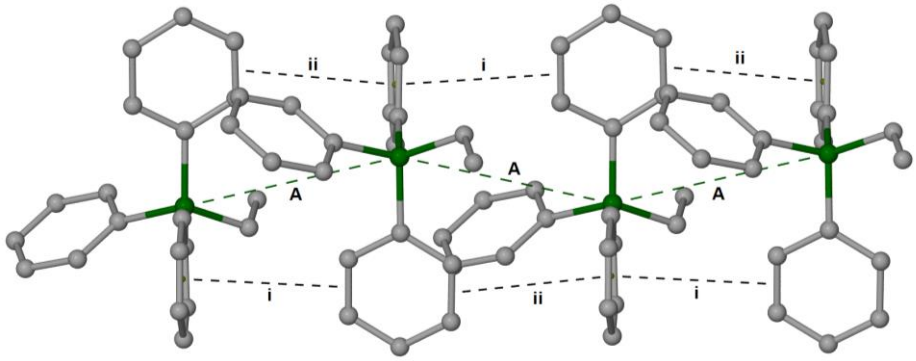
[Ph_4P][LH_4].0.5H_2O



P…P: A = 5.966 Å, B = 5.96 Å, P…P…P 109.6 °.

C-H…Cg: d(C…*C*g) i = 3.56 Å (C22), ii = 3.86 Å (C18).

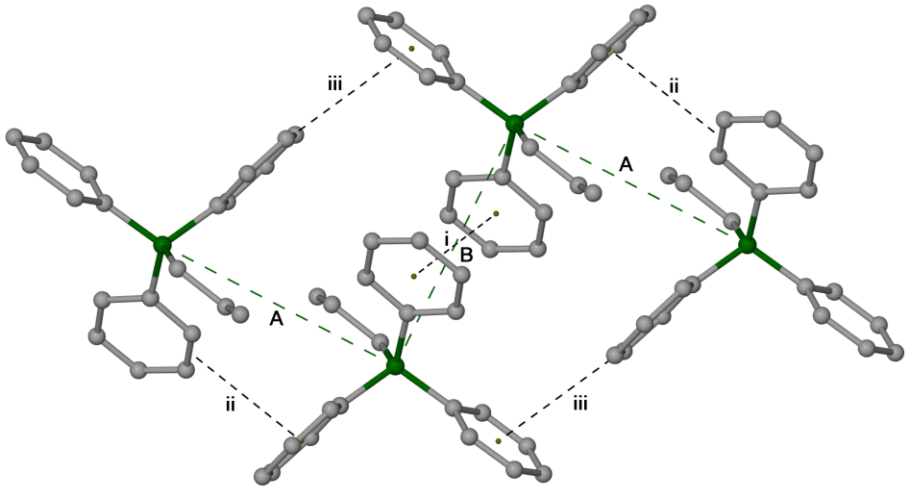
[Ph_3PEt][LH_4].4H_2O



P…P: A = 6.247 Å, P…P…P 104.8 °.

C-H…*C*g: i = 3.86 Å (C18), ii = 3.73 Å (C22).

[Ph_3PPr][LH_4].H_2O



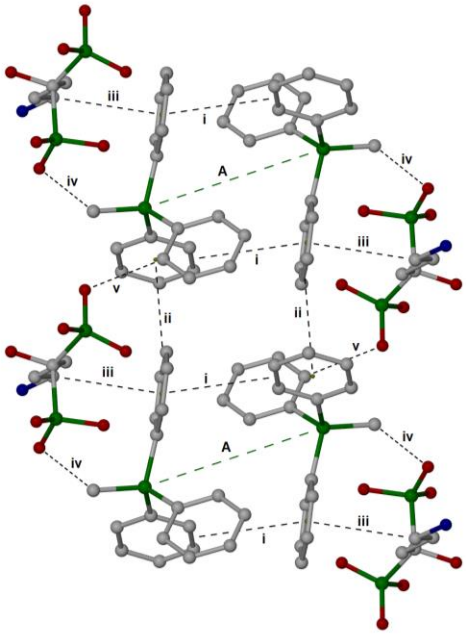
P…P: A = 6.579 Å, B = 6.779 Å, P…P…P 87.7 °.

Cg…*Cg*: i 4.32 Å, C-H…*Cg*: d(C…*Cg*) ii = 4.19 Å (C16), iii = 3.87 Å (C21).

S10.3 Details of supramolecular interactions in **2**, **3a** and **5**

The intermolecular arrangements of the cations with green dashed lines for P…P separations, black dashed lines for *Cg* …*Cg*, C-H…*Cg* and C-H…O interactions with d(C…Cg) and d(C…O) listed below.

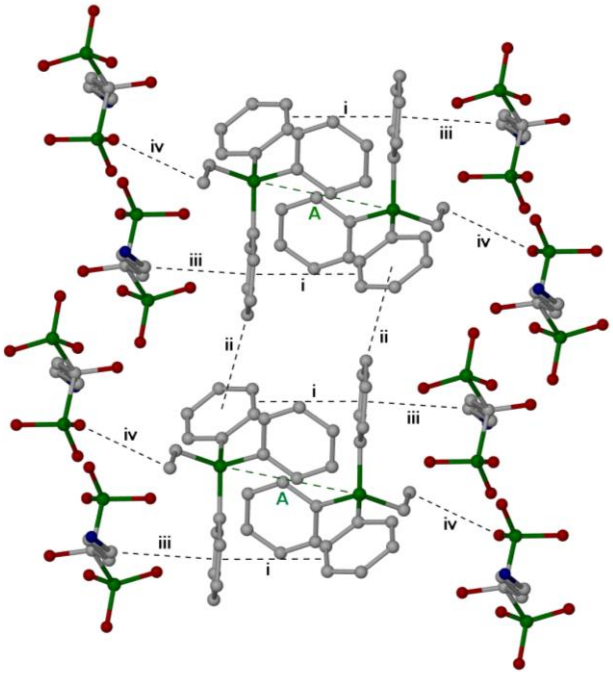
[Ph_3PMe][LH_4]



P…P: A = 6.629 Å. C-H…Cg: d(C…*Cg*) i = 3.88 Å (C19), ii = 3.69 Å (C15), iii 3.64 (C4).

C-H…O d(C…O): iv 3.217(2) Å (C5), v 3.156(2) (C7)

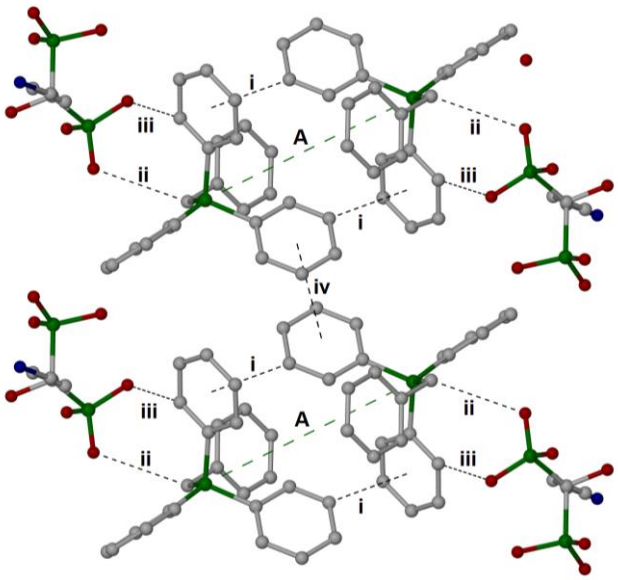
[Ph_3PEt][LH_4]



P…P: A = 6.016 Å. C-H…*Cg*: d(C…*Cg*) i = 3.75 Å (C15), ii = 4.22 Å (C19), iii 3.59 (C4).

C-H…O: d(C…O) iv 3.489(2) Å (C24). (note: a second C-H…O interaction from C24 - see table S10.3 - is not shown for clarity).

[Ph_3PBn][LH_4].H_2O.MeCN



P…P: A = 7.609 Å. C-H…*Cg*: d(C…*Cg*) i = 3.59 Å (C21). C-H…O: d(C…O) ii = 3.230(2) Å (C23), iii 3.240(3) Å (C29). *Cg*…*Cg* iv 4.01 Å.

S10.4 Cation-Anion Supramolecular Contacts.

Table 10.4 Calculated using PLATON (v270519);[5] C-H…O <<2.72 Å, C-H…*Cg* , <3.0 Å. Note: C-H entities are in idealised positions (riding on the C atom) with d(C-H) = 0.95-0.98 Å).

1	C-H…O	C…O (Å)	H…O (Å)	C-H…O (°)	π…π	Cg…Cg Å
	C4-H4B…O7	3.428(2)	2.52	153	*Cg*2…*Cg*2^{vi}	3.69
	C7-H7…O4	3.139(2)	2.50	125	*Cg*4…*Cg*4^{iii}	4.31
	C20_H20…O7	3.220(2)	2.52	130		
	C27-H27…O4	3.252(2)	2.41	148		

1a	C-H…O	C…O (Å)	H…O (Å)	C-H…O (°)		
	C8-H8…O7	3.100(2)	2.45	126		
	C20_H20…O8^{i}	3.199(3)	2.26	172		
	C21-H21…O1^{ii}	3.464(2)	2.56	159		
	C-H…π		H…*Cg* (Å)	C-H…*Cg* (°)		
	C4-H4B…*Cg*2^{iii}	3.716	2.78	158		
	C14-H14…*Cg*3^{iv}	3.602	2.67	167		
	C22-H22…*Cg*2^{v}	3.560	2.70	150		

Symmetry operators: i -x,1-y,2-z; ii x,y-1,1+z; iii 1-x,1-y,1-z; iv 1+x,y,z,; v 1-x,-y,2-z; vi 1-x,-y,1-z.

2	C-H…O	C…O (Å)	H…O (Å)	C-H…O (°)		
	C5-H5C…O3^{i}	3.217(2)	2.39	142		
	C7-H7…O6	3.156(2)	2.39	137		
	C10-H10…O4^{ii}	3.326(2)	2.38	176		
	C-H…π	C…*Cg* (Å)	H…Cg (Å)	C-H…Cg (°)		
	C4-H4A…*Cg*2^{iii}	3.64	2.81	142		
	C15-H15-*Cg*3^{i}	3.69	2.90	142		

Symmetry operators: i x,y-1,z; ii 1-x,y-½,1½-z; iii x,1+y,z.

3	C-H…O	C…O (Å)	H…O (Å)	C-H…O (°)	π…π	Cg…Cg Å
	C7-H7…O9^{i}	3.339(2)	2.45	156	*Cg*3…*Cg*3^{iii}	4.95
	C19-H19…O10	3.169(2)	2.40	138		
	C23-H23B…O8^{ii}	3.209(2)	2.34	146		
	C-H…π	C…*Cg* (Å)	H…Cg (Å)	C-H…Cg (°)		
	C4-H4B…*Cg*1^{i}	3.53	2.99	116		

Symmetry operators: i 1-x,y-½,½-z; ii 1-x,½+y,½-z; iii 1-x,2-y,1-z.

3a	C-H…O	C…O (Å)	H…O (Å)	C-H…O (°)	π…π	Cg…Cg Å
	C24-H24A…O5^{i}	3.387(2)	2.51	149	*Cg*3…*Cg*3^{iv}	5.35
	C24-H24B…O5^{ii}	3.489(2)	2.52	169		
	C-H…π	C…*Cg* (Å)	H…Cg (Å)	C-H…Cg (°)		
	C4-H4B…*Cg*1^{iii}	3.59	2.72	147		

Symmetry operators: i 1+x,y-1,1+z; ii 1-x,1-y,2-z; iii x,1-Y,z; iv 2-x,-y,1-z.

4	C-H…O	C…O (Å)	H…O (Å)	C-H…O (°)	π…π	Cg…Cg Å
	C4-H4A…O7[i]	3.347(2)	2.53	140	*Cg*2…*Cg*2[v]	4.32
	C8-H8…O7[ii]	3.269(2)	2.43	148		
	C9-H9…O4[iii]	3.294(2)	2.44	150		
	C14 H14…O8[iv]	3.252(2)	2.32	166		
	C-H…π	C…*Cg* (Å)	H…*Cg* (Å)	C-H…*Cg* (°)		
	C4-H4B…*Cg*1[iii]	3.61	2.74	146		

Symmetry operators: i 2-x,2-y,1-z; ii 1-x,2-y,1-z; iii 2-x,1-y,1-z; iv x,y-1,1+z; v 1-x,1-y,2-z.

5	C-H…O		H…O (Å)	C-H…O (°)	π…π	*Cg*…*Cg* Å
	C4-H4A…O7[i]	3.256(2)	2.46	137	*Cg*3…*Cg*3[v]	4.01
	C6-H6…O4	3.261(3)	2.42	147		
	C15-H15…O2[ii]	3.350(3)	2.48	153		
	C23-H23B…O5	3.230(2)	2.27	164		
	C29-H29…O4	3.240(3)	2.43	143		
	C-H…π	C…*Cg* (Å)	H…*Cg* (Å)	C-H…*Cg* (°)		
	C21-H21…*Cg*1[iii]	3.59	2.68	159		
	C31-H31B…*Cg*1[iv]	3.89	2.96	149		

Symmetry operators: i 2-x,1-y,1-z; ii x,y-1,z; iii 1-x,1-y,1-z; iv x, ½-y, ½+z; v 1-x,-y,1-z.

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