Supporting Information

Studies on the reactivity of group 15 Zintl ions with carbodiimides: synthesis and characterization of a heptaphosphaguanidine dianion.

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1. Experimental Section

General synthetic methods. All reactions and product manipulations were carried out under an inert atmosphere using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at < 0.1 ppm H_2O and < 0.1 ppm O_2). The Zintl phase precursor K_3P_7 was synthesised according to a previously reported synthetic procedure from a mixture of the elements (K: 99.95%, Strem; P: 99.99%, Aldrich).[1] $[K(18\text{-crown-}6)]_2[HP_7]$ was synthesized according to the method reported by Dai and Xu.[2] Bis(2,6-diisopropylphenyl)carbodiimide was synthesized according to the method reported by Findlater, Hill and Cowley.[3] 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane; 99%, Alfa Aesar) was used as received after careful drying under vacuum. Toluene (tol; 99.9%, Rathburn), hexanes (hex; +99%, Rathburn) and dimethylformamide (DMF; 99.9%, Rathburn) were purified using an MBraun SPS-800 solvent system. Ethylenediamine (en; 99%, Aldrich) and tetrahydrofuran (THF; 99.9%, Rathburn) were distilled over sodium metal and a sodium metal/benzophenone mixture, respectively. d_7-DMF (99.5%, Cambridge Isotope Laboratories, Inc.) and d_5-pyridine (99.5%, Cambridge Isotope Laboratories, Inc.) were dried over CaH_2 and vacuum distilled. D_2O (>99.92%, Apollo Scientific) was used as received. All dry solvents were stored under argon in gas-tight ampoules.

Synthesis of [K(18-crown-6)]$_2$[HP$_7$]: K$_3$P$_7$ (500 mg, 1.50 mmol) and 18-crown-6 (872 mg, 3.30 mmol) were dissolved in approximately 15 mL of ethylenediamine and left to stir under argon for 2 hours. The resultant red-brown solution was filtered, and 200 mL of toluene was added to precipitate the product as a bright yellow powder, which was collected by filtration. The filtrate was concentrated and further product precipitation induced by the addition of more toluene. The total yield of [K(18-crown-6)]$_2$HP$_7$ was 640 mg (66.7%). CHN Anal. Calcd for: C$_{24}$H$_{49}$K$_2$O$_{12}$P$_7$ Calcd: C 34.94, H 5.99. Found: C 34.49, H 5.43. ^{1}H NMR (500 MHz, d$_5$-pyridine, 20 ºC): δ (ppm) 3.49 (s, 48H, 18-crown-6), 0.47 (s, br, 1H, [*H*P$_7$]$^{2-}$, ^{1}*J*(P,H) = 159.7 Hz). ^{31}P NMR (202.4 MHz, d$_5$-pyridine, 20 ºC): δ (ppm) –18.4 (br, m), –112.4 (br, s), –117.8 (br, s). ^{31}P NMR (202.4 MHz, d$_5$-pyridine, –35 ºC): δ (ppm) –20.1(m, 1P, ^{1}*J*(P,P) = 292.3 Hz, ^{1}*J*(P,P) = 367.9 Hz, ^{1}*J*(P,H) = 159.7 Hz, P3), –52.2 (m, 1P, ^{1}*J*(P,P) = 360.8 Hz, P1), –77.4 (m, 1P, ^{1}*J*(P,P) = 452.3 Hz, P4), –112.2 (m, overlapping resonance, 1P, ^{1}*J*(P,P) = 451.0 Hz, P2), –113.0 (m, overlapping resonance, ^{1}*J*(P,P) = 220.0 Hz, P5), –126.5 (m, 1P, ^{1}*J*(P,P) = 177.7 Hz, P7), –232.8 (m, 1P, P6). ESI– MS (DMF): *m/z* 216.0 [HP$_7$]$^-$. ESI+ MS (DMF): *m/z* 1129.1 {[K(18-crown-6)]$_3$[HP$_7$]}$^+$.

Synthesis of [K(18-crown-6))]$_2$[P$_7$C(NDipp)(NHDipp)] (1): In an inert atmosphere glovebox [K(18-crown-6)]$_2$[HP]$_7$ (50 mg, 61 μmol) and bis(2,6-diisopropylphenyl)carbodiimide (22 mg, 61 μmol) were weighed out into an J. Young's NMR tube equipped with an air-tight valve. The contents of the NMR tube were dissolved in d$_7$-DMF and the reaction monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy which showed immediate quantitative conversion to **1**. The contents of the tube were filtered into a Schlenk tube under argon and the solvent removed under dynamic vacuum yielding an orange oil. Addition of 10 mL of diethyl ether and sonication precipitated a yellow powder that was isolated by filtration and re-dissolved in 5 mL of dry THF. The yellow solution was filtered, and layered with 20 mL of hexanes. After several days yellow block-like crystals suitable for single crystal X-ray diffraction formed (60 % yield). Elemental analyses were found to reproducibly give low values of C, H, and N, presumably due to the formation of non-volatile products on heating. Anal. Calcd for C$_{49}$H$_{83}$K$_2$N$_2$O$_{12}$P$_7$: C, 49.77; H, 7.05; N, 2.36. Found: C, 43.52; H, 5.46; N, 2.07. ^{1}H NMR (500 MHz, d$_7$-DMF, 20 ºC): δ (ppm) 6.93 (overlapping multiplets, 3H, Ar*H*), 6.81 (d, 2H, ^{3}*J*(H,H) = 5 Hz, Ar*H*), 6.64 (t, 1H, ^{3}*J*(H,H) = 5 Hz, Ar*H*), 6.29 (br, s, 1H, N*H*), 3.58 (s, 48H, 18-crown-6), 3.38 (sep, 2H, ^{3}*J*(H,H) = 5 Hz, C*H*(CH$_3$)$_2$), 3.21 (sep, 2H, ^{3}*J*(H,H) = 5 Hz, C*H*(CH$_3$)$_2$), 1.42 (d, 6H, ^{3}*J*(H,H) = 5 Hz, CH(C*H*$_3$)$_2$), 1.18 (d, 6H, ^{3}*J*(H,H) = 5 Hz, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, ^{3}*J*(H,H) = 5 Hz, CH(C*H*$_3$)$_2$), 0.86 (d, 6H,

^{3}J(H,H) = 5 Hz, CH(CH_3)$_2$). ^{31}P NMR (202.4 MHz, d$_7$-DMF, 20 ºC): δ (ppm) –6.4 (m, P3), –83.2 (br), –111.9 (br). ^{31}P NMR (202.4 MHz, d$_7$-DMF, –50 ºC): δ (ppm) –6.3 (m, 1P, ^{1}J(P,P) = 337.5 Hz, ^{1}J(P,P) = 393.5 Hz, ^{2}J(P,P) = –29.3 Hz, ^{2}J(P,P) = –6.0 Hz, ^{2}J(P,P) = –11.7 Hz, ^{2}J(P,P) = –15.6 Hz, P3), –28.3 (m, 1H, ^{1}J(P,P) = 365.7 Hz, ^{1}J(P,P) = 351.1 Hz, ^{2}J(P,P) = –21.2 Hz, ^{2}J(P,P) = 64.8 Hz, ^{2}J(P,P) = 48.4 Hz, P1), –68.7 (m, 1P, ^{1}J(P,P) = 420.2 Hz, ^{1}J(P,P) = 225.8 Hz, ^{1}J(P,P) = –178.1 Hz, ^{2}J(P,P) = 16.6 Hz, P5), –91.6 (m, 1P, ^{1}J(P,P) = 425.2 Hz, ^{2}J(P,P) = –19.7 Hz, ^{2}J(P,P) = 16.6, P4), –100.0 (m, 1P, ^{2}J(P,P) = 33.4 Hz, ^{2}J(P,P) = 21.9 Hz, P2), –134.1 (m, 1P, ^{1}J(P,P)= 187.5 Hz, P7), –211.7 (m, 1P, P6). ^{13}C{^{1}H} NMR (500 MHz, d$_7$-DMF, 20 ºC): 165.7 (^{1}J(C,P) = 81.7 Hz, P*C*N$_2$), 149.1, 148.2, 139.5, 139.1, 125.7, 122.3, 121.6, 120.6 (Ar*C*), 28.7, 27.7 (C*H*(CH$_3$)$_2$), 27.4, 24.9, 24.3, 22.6 (CH(CH_3)$_2$). ESI– MS (DMF): *m/z* 581.3 [M+H]$^{-}$, 379.5 [HP$_7$Dipp]$^{-}$. No evidence of the [P$_7$C(NDipp)(NHDipp)]$^{2-}$ cluster anion was observed in the positive ion mode ES-MS spectrum of **1**.

Synthesis of [K(18-crown-6)]$_2$[DP$_7$]: K$_3$P$_7$ (100 mg, 0.30 mmol) was dissolved in pyridine (3 mL) in the presence of D$_2$O (13 μL, 0.60 mmol) and the mixture stirred under argon for 1 hour yielding a brown solution. 18-crown-6 (158 mg, 0.60 mmol) was added, and the mixture stirred for a further 5 minutes and subsequently filtered. The resultant bright orange filtrate was concentrated to approximately half of the original volume after which 20 mL of toluene were added to precipitate the product as a bright yellow powder. The resultant product was isolated by filtration and dried under dynamic vacuum. Yield 135 mg (55%). ^{1}H NMR (500 MHz, DMF, 20 °C): δ 3.60 (s, 18-crown-6). ^{2}H NMR (76.7 MHz, DMF, 20 °C): δ 0.33 (br, DP$_7^{2-}$). ^{2}H NMR (76.7 MHz, DMF, –50 °C): δ 0.35 (d, $^{1}J_{\mathrm{P-D}}$ = 22.3 Hz). ^{31}P NMR (202.4 MHz, DMF, 20 °C): δ –24.4 (br, t), –110.8 (br). ^{31}P NMR (202.4 MHz, DMF, –50 °C) δ –24.9 (1P, m), –51.0 (1P, m), –78.0 (1P, m), –111.1 (2P, overlapping resonances, m), –124.1 (1P, m), –233.1 (1P, m). Judging by the NMR spectra of this sample there is less than 10% of the protic species, HP$_7^{2-}$, present in solution (presumably arising due to adventitious moisture from the solvent or 18-crown-6.

Synthesis of [K(18-crown-6)]$_2$[P$_7$C(NDipp)(NDDipp)]: C(DippN)$_2$ (18 mg, 49 μmol) was added to a solution of [K(18-crown-6)]$_2$[DP$_7$] (40 mg, 49 μmol) in protic DMF (0.5 mL). ^{2}H NMR (76.7 MHz, DMF, 20 °C): δ 6.23 (br, s), 4.53 (br, s). ^{2}H NMR (76.7 MHz, DMF, –50 °C): δ 6.92 (very broad). ^{31}P NMR (202.4 MHz, DMF, 20 °C): δ –6.5 (t), –82.4 (br), –111.2 (br). ^{31}P NMR (202.4 MHz, DMF, –50 °C): δ –8.7 (1P, m), –29.4 (1P, m), –69.4 (1P, m), –91.6 (1P, m), –99.7 (1P, m), –132.7 (1P, m), –208.9 (1P, m).

Single crystal X-ray structure determination: Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[4] Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å) and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[5] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro. The structure was subsequently solved using direct methods, and refined on F^2 using the SHELXL 97-2 package.[6]

1: Formula: $C_{49}H_{83}K_2N_2O_{12}P_7$; Mr = 1187.16; crystal colour and morphology: small yellow blocks; crystal size: 0.32 × 0.22 × 0.08 mm; monoclinic; space group: *P*2(1)/*c*; a = 14.1477(1) Å; b = 19.1536(2) Å; c = 69.3584(8) Å; β = 92.246(1)°; V = 18780.3(3) $Å^3$; Z = 12; ρ_{calcd} = 1.260 g cm^{-3}; μ = 3.477 mm^{-1}; T = 150(2) K; 168980 reflections collected; 33114 independent reflections; R_{int} = 0.0427; R1 = 6.47 and R2 = 14.43 for $I \geq 2\sigma(I)$; R1 = 6.81 and R2 = 14.59 for all data.

Other characterization techniques: Positive and negative ion mode electrospray mass spectra were recorded on DMF solutions (10–20 mm) on a Masslynx LCT Time of Flight mass spectrometer with a Z-spray source (150°C source temperature, 200°C desolvation temperature, 2.4 kV capillary voltage and 25 V cone voltage). The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe. Samples were introduced directly with a 1 mL SGE syringe and a syringe pump at 0.6 mL h^{-1}.

^1H and ^{31}P NMR spectra were acquired at 500.0 and 202.4 MHz, respectively, on a Varian Unity-plus 500 NMR spectrometer. ^1H spectra were referenced to the most downfield residual protic solvent resonance (d_7-DMF δ 8.03 ppm; d_5-pyridine δ 8.74 ppm). ^{31}P spectra were externally referenced to H_3PO_4 (δ 0 ppm). Spectral simulations were carried out using the program gNMR.[7]

Elemental analyses were carried out by Stephen Boyer of the London Metropolitan University. Samples (approx. 5 mg) were submitted in sealed Pyrex ampoules.

2. Computed structure and analysis of electronic structure

2.1 Computational details

All calculations described in this paper were performed using the Amsterdam Density Functional package (ADF2007.01).[8] A triple-ζ Slater-type basis set, extended with a single polarization function, was used to describe all atoms. The local density approximation was employed for the optimizations,[9] along with the local exchange-correlation potential of Vosko, Wilk and Nusair[10] and the gradient corrections to exchange and correlation proposed by Becke and Perdew (BP86).[11] Relativistic effects were incorporated using the Zeroth Order Relativistic Approximation (ZORA).[12] The presence of cations in the crystal lattice of **1** was modelled by surrounding the anion with a continuum dielectric using COSMO.[13] The chosen dielectric constant ε = 16.9 corresponds to that of ammonia, although structural parameters are not strongly dependent on this choice. All structures were optimized using the gradient algorithm of Versluis and Ziegler.[14]

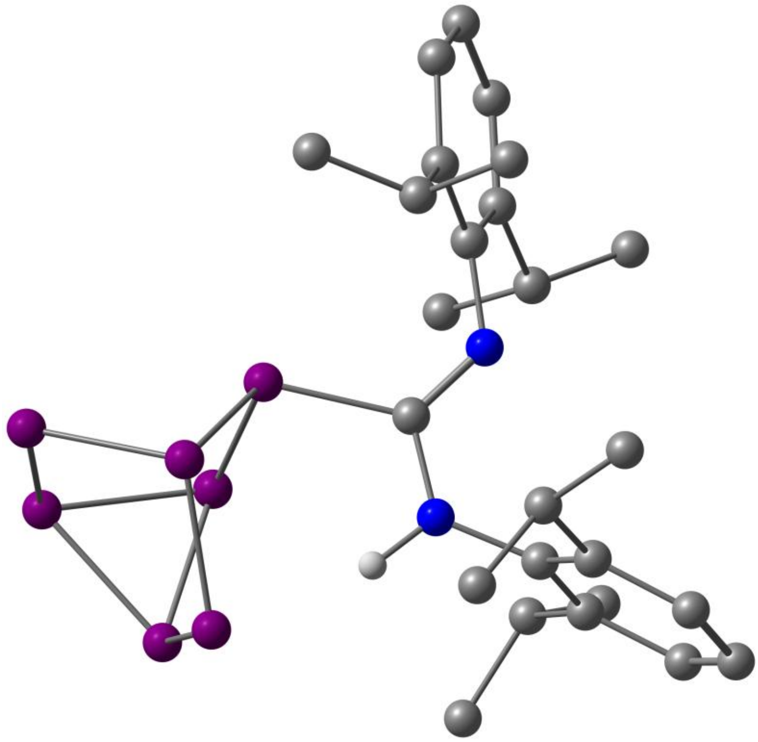

Figure S1. Optimized geometry of the $[P_7C(NDipp)(NHDipp)]^{2-}$ cluster anion from DFT calculations.

Cartesian coordinates [Å] for the optimized structure of $[P_7C(NDipp)(NHDipp)]^{2–}$

Atom	x	y	z (Å)
1. C	–0.002178	–0.002790	–0.032571
2. C	0.684367	–0.829177	0.889368
3. C	1.675037	–1.695570	0.397726
4. H	2.213484	–2.344913	1.089521
5. C	1.983009	–1.741421	–0.963512
6. H	2.753667	–2.422787	–1.327172
7. C	1.305199	–0.910669	–1.857343
8. H	1.554403	–0.951786	–2.919027
9. C	0.307116	–0.027049	–1.413653
10 .C	0.335426	–0.819294	2.373836
11. H	–0.102446	0.165298	2.591788
12. C	–0.735740	–1.881930	2.696971
13. H	–0.997326	–1.847105	3.765690
14. H	–0.360843	–2.893288	2.470373
15. H	–1.654994	–1.710989	2.116746
16. C	1.561771	–1.002020	3.283899
17. H	1.270492	–0.859381	4.334230
18. H	2.354089	–0.277346	3.048100
19. H	1.987204	–2.013171	3.198263
20. C	–0.452496	0.840617	–2.411278
21. H	–0.876828	1.684415	–1.849305
22. C	–1.634041	0.062684	–3.024896
23. H	–2.190411	0.702456	–3.726003
24. H	–2.335793	–0.274305	–2.248040
25. H	–1.273598	–0.819223	–3.578626
26. C	0.444815	1.414413	–3.520223
27. H	–0.131481	2.118378	–4.137917
28. H	0.823684	0.627591	–4.189295
29. H	1.308665	1.952931	–3.106049
30. C	0.336923	4.016177	1.398577
31. C	0.310858	4.320742	2.792775
32. C	0.665179	5.613804	3.209928
33. H	0.643519	5.850419	4.276221
34. C	1.045213	6.604695	2.301869
35. H	1.307470	7.604076	2.651463
36. C	1.094472	6.292518	0.940191
37. H	1.402853	7.059019	0.225937
38. C	0.761171	5.014550	0.471383
39. C	–0.022775	3.270246	3.849413
40. H	–0.403249	2.382726	3.327689
41. C	1.246400	2.846385	4.617319
42. H	1.012135	2.056221	5.346874
43. H	1.673987	3.699680	5.167734
44. H	2.016602	2.461751	3.932975
45. C	–1.117077	3.732503	4.828023
46. H	–1.351371	2.927457	5.540667
47. H	–2.042101	3.991508	4.292284
48. H	–0.794813	4.609070	5.411359

49. C	0.838171	4.698631	–1.018312
50. H	0.820849	3.601855	–1.099114
51. C	2.137088	5.205680	–1.670463
52. H	2.191238	4.870768	–2.716883
53. H	3.026751	4.827311	–1.145266
54. H	2.189620	6.305615	–1.674587
55. C	–0.393491	5.238066	–1.773597
56. H	–0.340575	4.972638	–2.840955
57. H	–0.447154	6.336828	–1.699101
58. H	–1.326755	4.819813	–1.366746
59. C	–1.018020	2.101948	0.857625
60. N	–1.098383	0.811108	0.418197
61. N	0.122625	2.715328	0.918177
62. P	–3.855359	1.378505	2.558717
63. P	–5.673413	2.614061	2.481438
64. P	–2.676644	2.923374	1.384112
65. P	–4.196185	–0.239694	1.102753
66. P	–5.876614	2.816191	0.310379
67. P	–3.760724	2.906549	–0.561862
68. P	–4.917448	0.926824	–0.581803
69. H	–2.035888	0.360910	0.484729

Table S1: Comparison of bond metric data for the three crystallographically unique cluster anions in the asymmetric unit of **1** and of the optimized computed structure for the $[P_7C(NDipp)(NHDipp)]^{2-}$ dianion.

Distance	**Cluster 1**	**Cluster 2**	**Cluster 3**	**Computed geometry**
P1-P2	2.162(1)	2.165(2)	2.164(2)	2.200
P1-P3	2.217(1)	2.234(1)	2.237(1)	2.271
P1-P4	2.164(1)	2.165(2)	2.164(2)	2.203
P2-P5	2.158(2)	2.150(2)	2.164(2)	2.190
P3-P6	2.188(1)	2.180(2)	2.195(1)	2.228
P4-P7	2.137(2)	2.130(2)	2.138(2)	2.172
P5-P6	2.242(1)	2.260(2)	2.229(1)	2.290
P5-P7	2.256(1)	2.242(2)	2.239(1)	2.299
P6-P7	2.237(1)	2.248(2)	2.237(1)	2.293
P3-C1	1.895(3)	1.885(4)	1.898(4)	1.924
C1-N1	1.356(4)	1.358(4)	1.355(4)	1.366
N1-H1	fixed	fixed	fixed	1.042
C1-N2	1.286(4)	1.284(4)	1.277(5)	1.297
N1-C2	1.436(4)	1.427(5)	1.433(4)	1.438
N2-C14	1.403(4)	1.404(4)	1.404(5)	1.403
Angle				
C1-P3-P1	106.96(10)	104.69(11)	107.95(11)	107.37
P1-P3-P6	101.02(5)	101.20(6)	100.56(5)	101.19
P6-P3-C1	99.03(10)	100.67(12)	98.17(11)	100.21
N1-C1-P3	116.0(2)	116.4(3)	115.0(3)	116.15
N1-C1-N2	119.3(3)	118.3(3)	119.6(3)	120.92
N2-C1-P3	124.7(2)	125.3(2)	125.3(3)	122.93

3. NMR spectra

3.1 NMR spectra of $[HP_7]^{2-}$

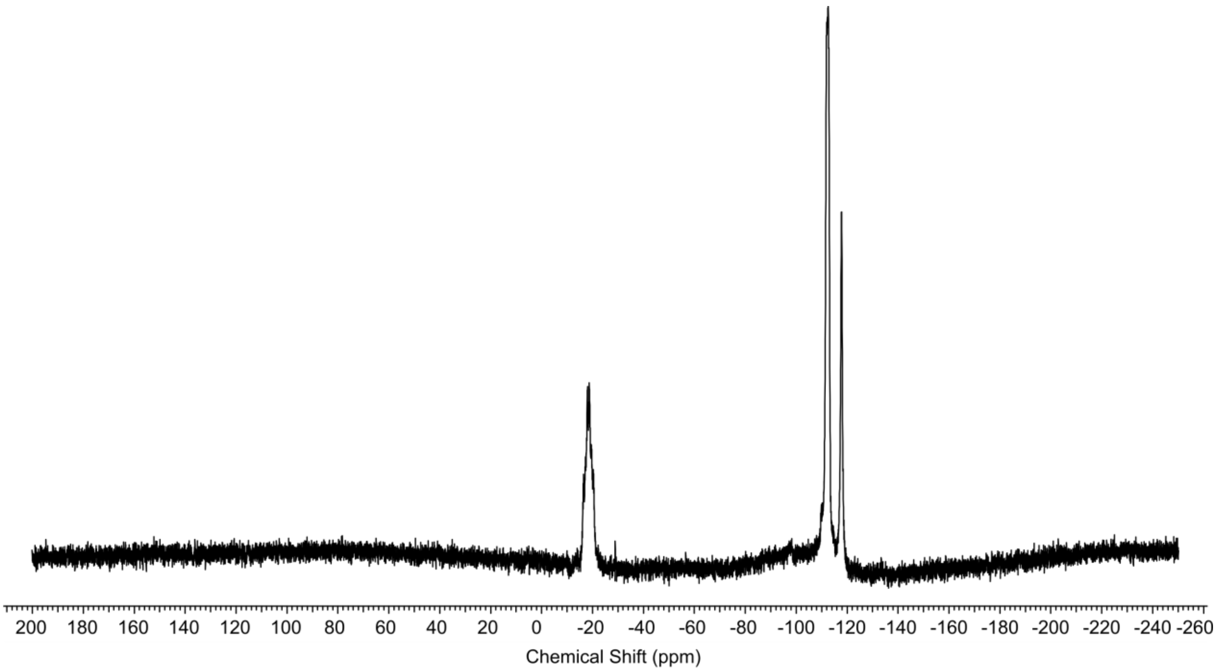

Figure S2. Room temperature $^{31}P\{^1H\}$ NMR spectrum of a d_5-pyridine solution of $[K(18\text{-crown-6})]_2[HP_7]$.

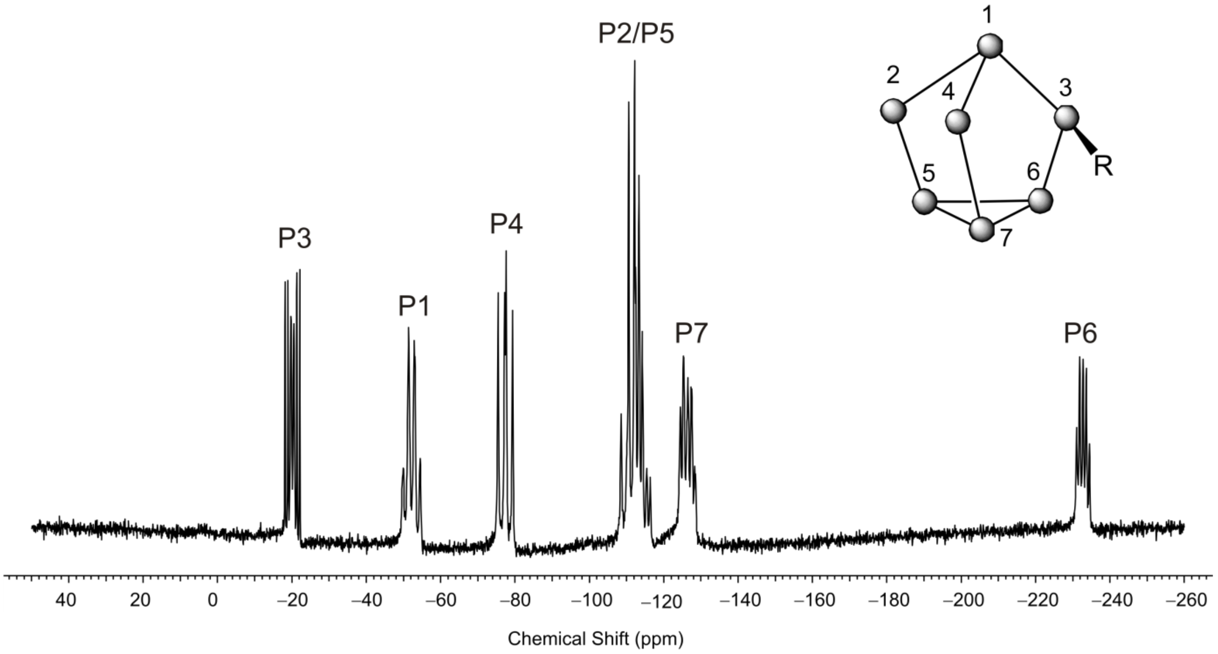

Figure S3. ^{31}P NMR spectrum of a d_5-pyridine solution of $[K(18\text{-crown-6})]_2[HP_7]$ collected at –35 ºC.

Table S2. ^{31}P-^{31}P NMR coupling constants [Hz] taken from the ^{31}P{^{1}H} NMR spectrum of the $[HP_7]^{2-}$ dianion.

δ(ppm)		–52.2	–112.2	–20.1	–77.4	–113.0	–232.8	–126.5
		P1	***P2***	***P3***	***P4***	***P5***	***P6***	***P7***
–52.2	***P1***		360.8	292.3	368.2	-	-	-
–112.2	***P2***	360.8		-	-	451.0	-	-
–20.1	***P3***	292.3	-		-	-	367.9	-
–77.4	***P4***	368.2	-	-		-	-	452.3
–113.0	***P5***	-	451.0	-	-		180.2	220.0
–232.8	***P6***	-	-	367.9	-	180.2		177.7
–126.5	***P7***	-	-	-	452.3	220.0	177.7	

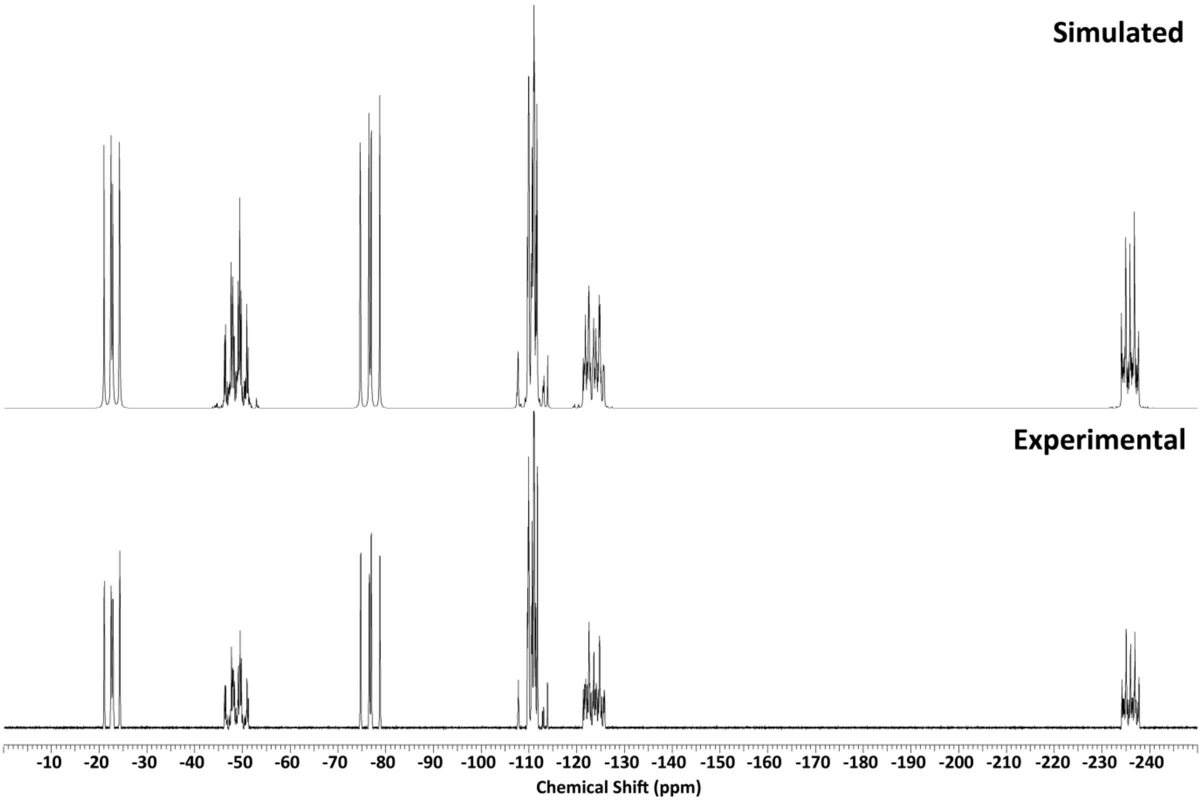

Figure S4. Simulated (top) and experimentally determined (bottom) ^{31}P{^{1}H} NMR spectra of $[K(18\text{-crown-6})]_2[HP_7]$.

3.2 NMR spectra of $[P_7C(NDipp)(NHDipp)]^{2-}$

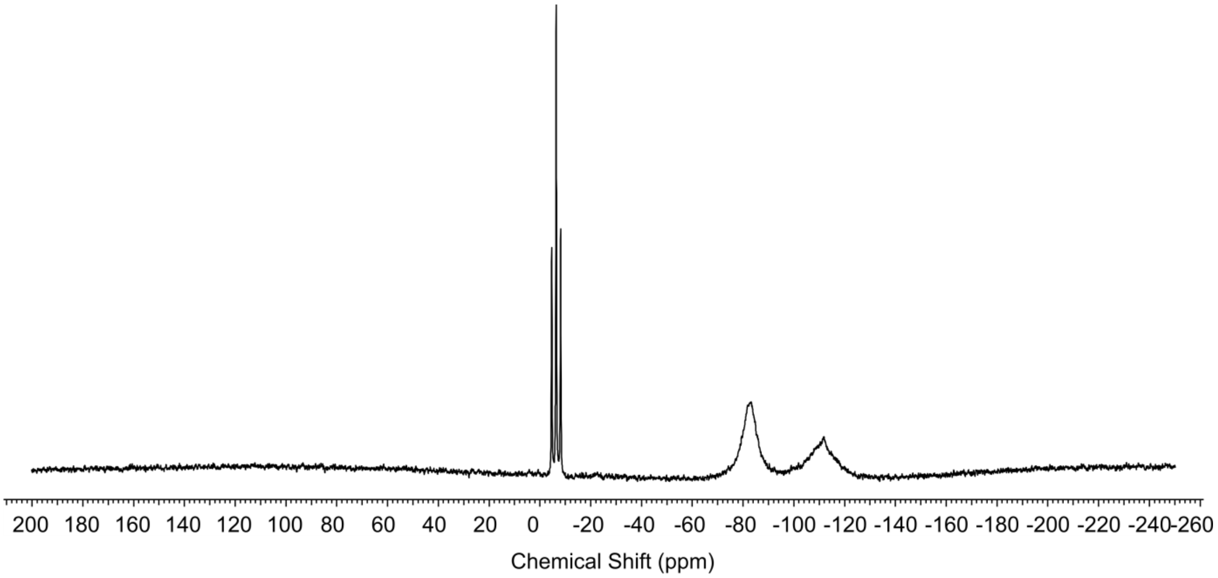

Figure S5. Room temperature $^{31}P\{^1H\}$ NMR spectrum of a d_7-DMF solution of **1**.

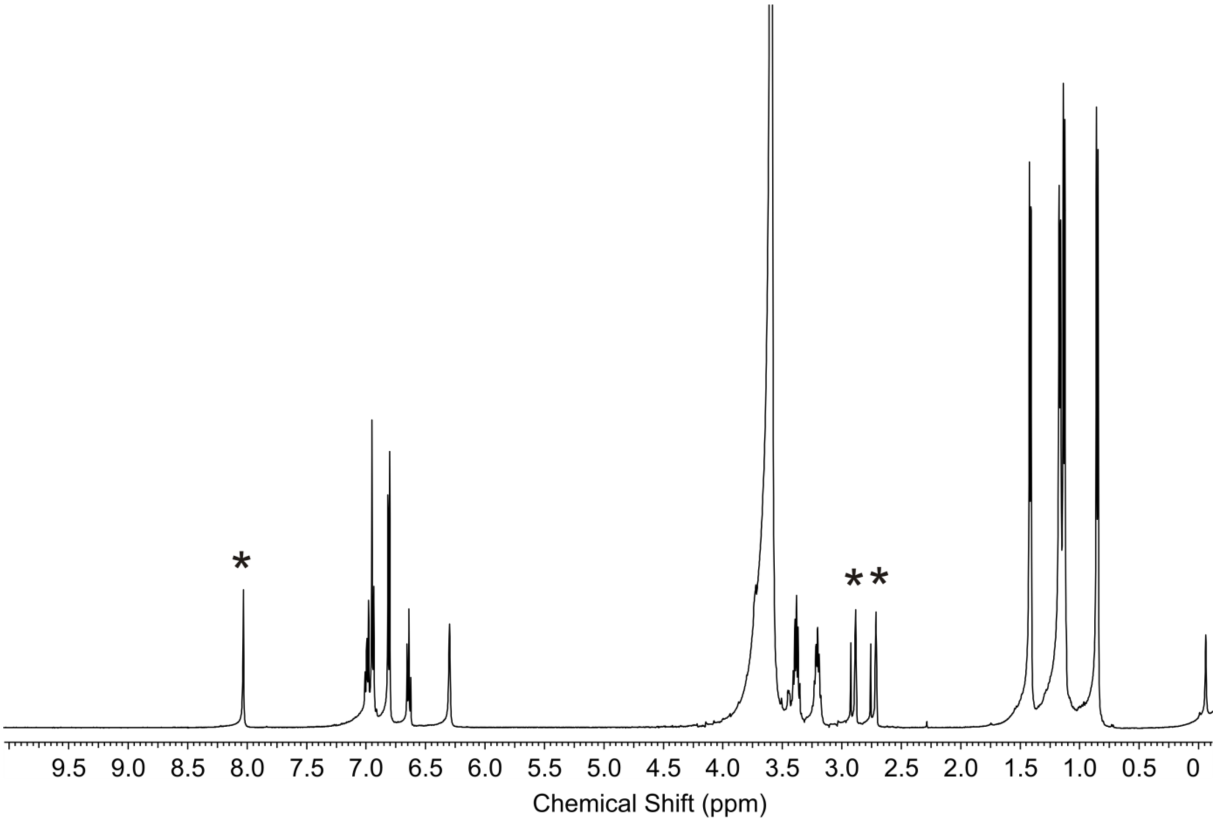

Figure S6. Room temperature ^1H NMR spectrum of a d_7-DMF solution of **1**. Resonances labelled with an asterisk correspond to DMF.

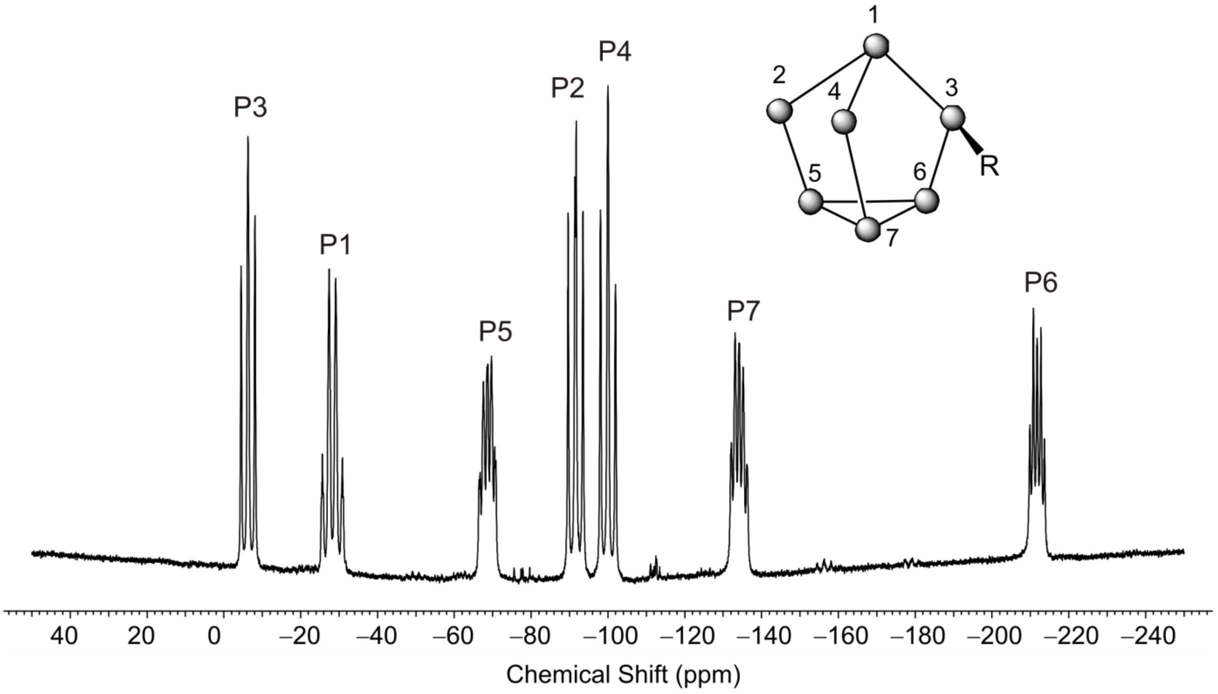

Figure S7. ^{31}P NMR spectrum of a d$_7$-DMF solution of **1** collected at –50 ºC.

Table S3. ^{31}P-^{31}P NMR coupling constants [Hz] taken from the ^{31}P{^{1}H} NMR spectrum of the [$P_7C(NDipp)(NHDipp)]^{2-}$ anion.

δ(ppm)		–28.3	–100.0	–6.3	–91.6	–68.7	–211.7	–134.1
		P1	***P2***	***P3***	***P4***	***P5***	***P6***	***P7***
–28.3	***P1***		351.1	337.5	365.7	64.8	48.4	–21.2
–100.0	***P2***	351.1		–15.6	–19.7	420.2	21.9	33.4
–6.3	***P3***	337.5	–15.6		–11.7	–29.3	393.5	–6.0
–91.6	***P4***	365.7	–19.7	–11.7		16.6	-	425.2
–68.7	***P5***	64.8	420.2	–29.3	16.6		–178.1	225.8
–211.7	***P6***	48.4	21.9	393.5	-	–178.1		187.5
–134.1	***P7***	–21.2	33.4	–6.0	425.2	225.8	187.5	

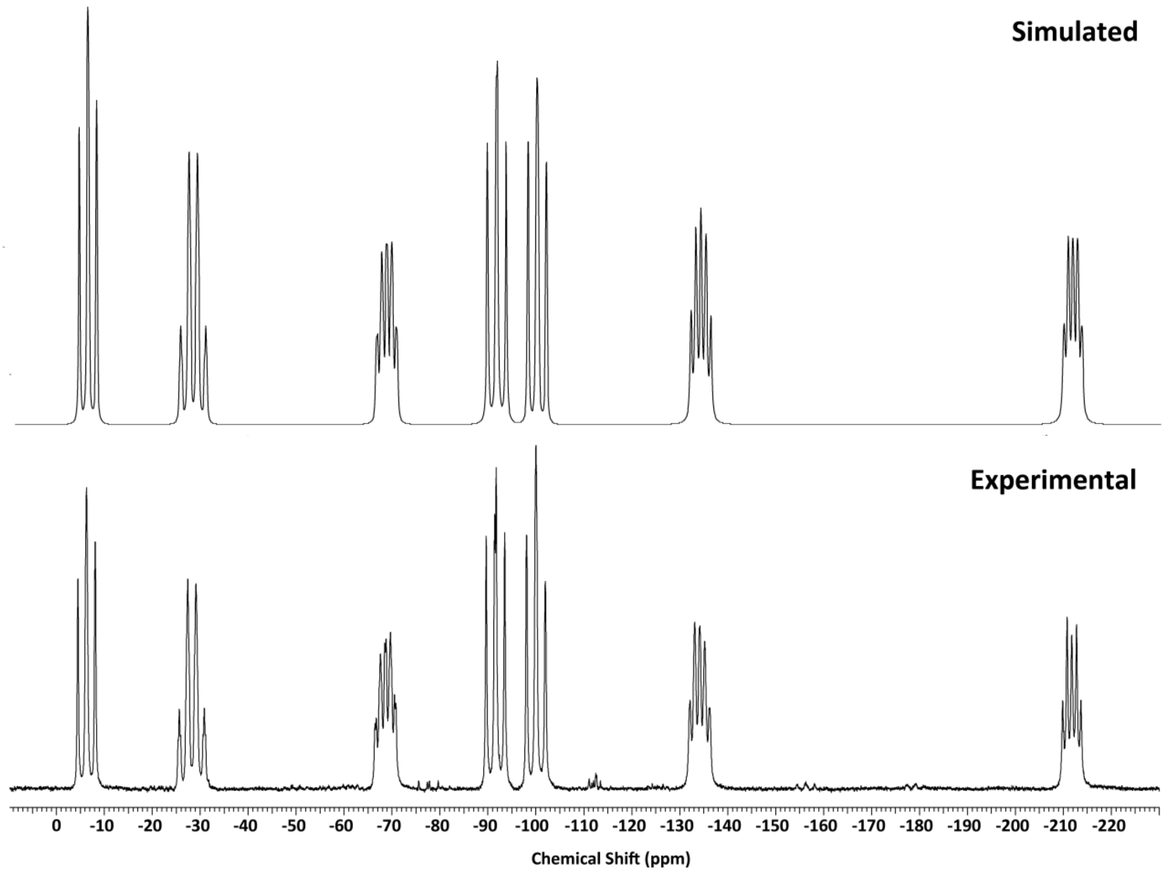

Figure S8. Simulated (top) and experimentally determined (bottom) ^{31}P NMR spectra of **1**.

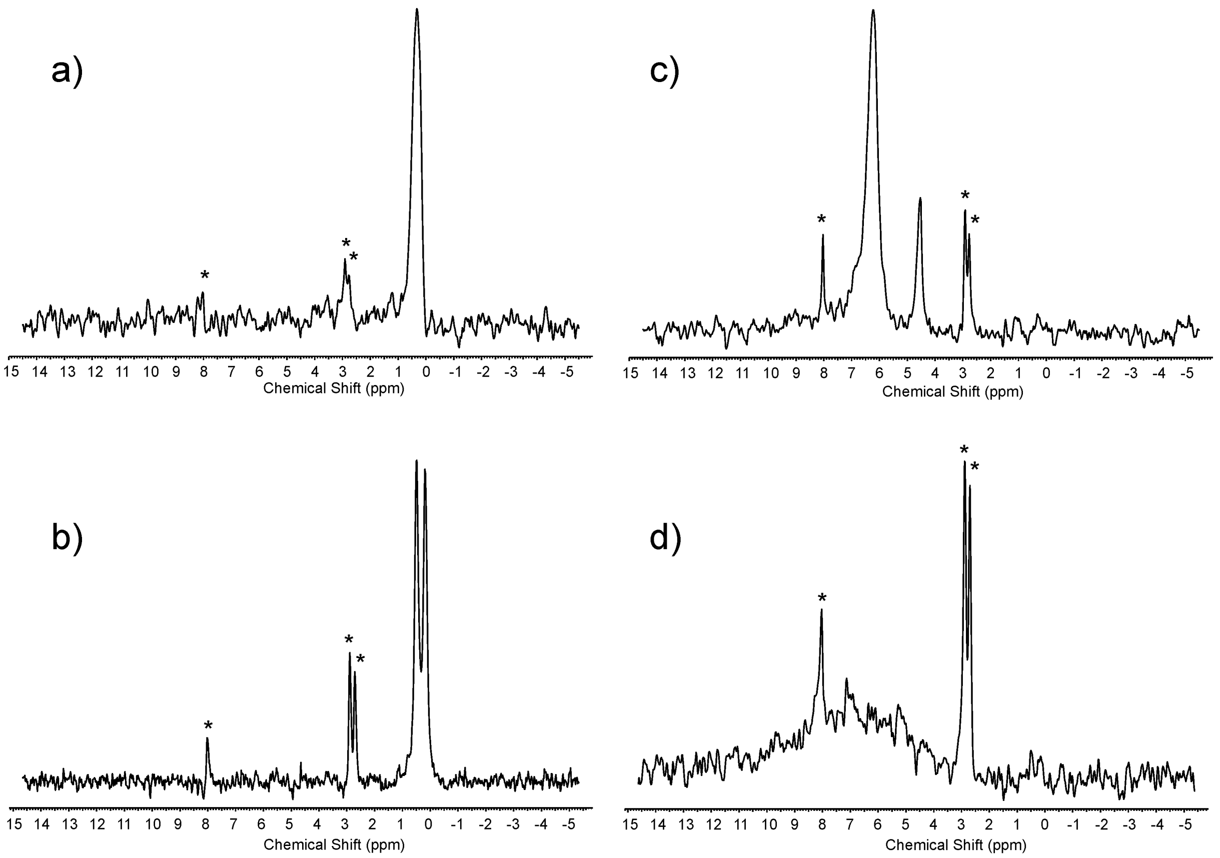

Figure S9. a) ^{2}H NMR spectrum of $[DP_7]^{2-}$ collected at 20 °C. b) ^{2}H NMR spectrum of $[DP_7]^{2-}$ collected at –50 °C ($^1J_{D\text{-}P}$ = 22.3 Hz). c) ^{2}H NMR spectrum of $[K(18\text{-crown-}6)]_2[P_7C(NDipp)(NDDipp)]$ collected at 20 °C. The two resonances at 6.23 and 4.53 ppm arise from the cluster anion, presumably due a dynamic exchange process observed due to the kinetic isotope effect. No evidence of this process is visible in the ^{1}H NMR spectrum of **1**. At –50 °C both resonances coalesce into a broad resonance centred at 6.92 ppm. d) ^{2}H NMR spectrum of $[K(18\text{-crown-}6)]_2[P_7C(NDipp)(NDDipp)]$ collected at –50 °C. Resonances labelled with as asterisk correspond to the naturally occurring deuterated DMF solvent present in the protic solvent.

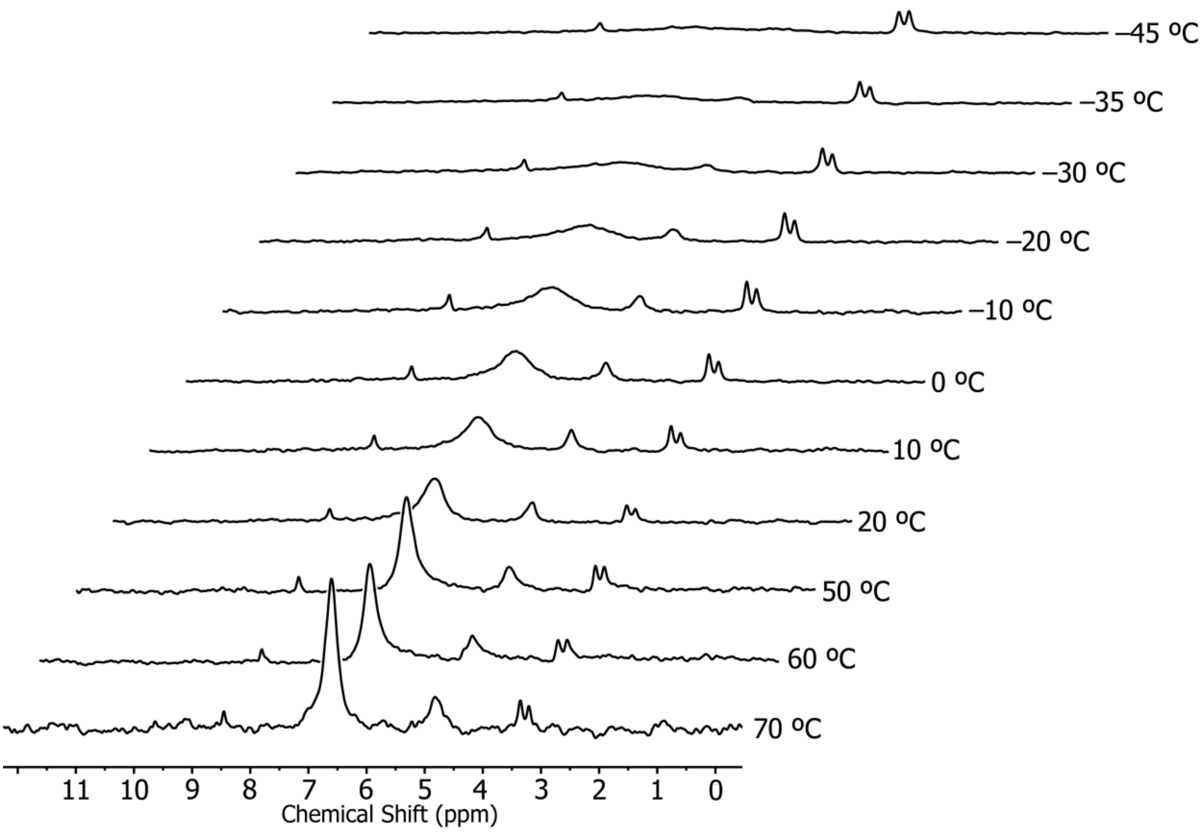

Figure S10. Variable temperature ^{2}H NMR spectra of $[K(18\text{-crown-}6)]_2[P_7C(NDipp)(NDDipp)]$.

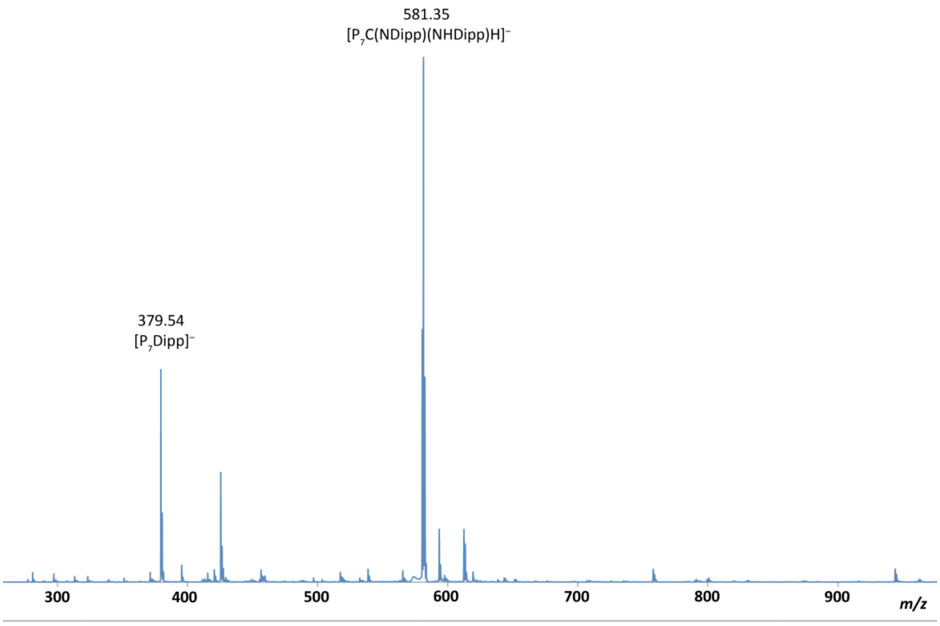

Figure S11. Negative ion-mode electrospray mass-spectrum of a DMF solution of **1**.

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