

Preparation and Structural Variety of Neutral Heptaphospha-Nortricyclane Derivatives of Zinc and the Coinage Metals

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1 NMR Spectroscopy

For experimental details see *Materials and Methods* section in the main manuscript.

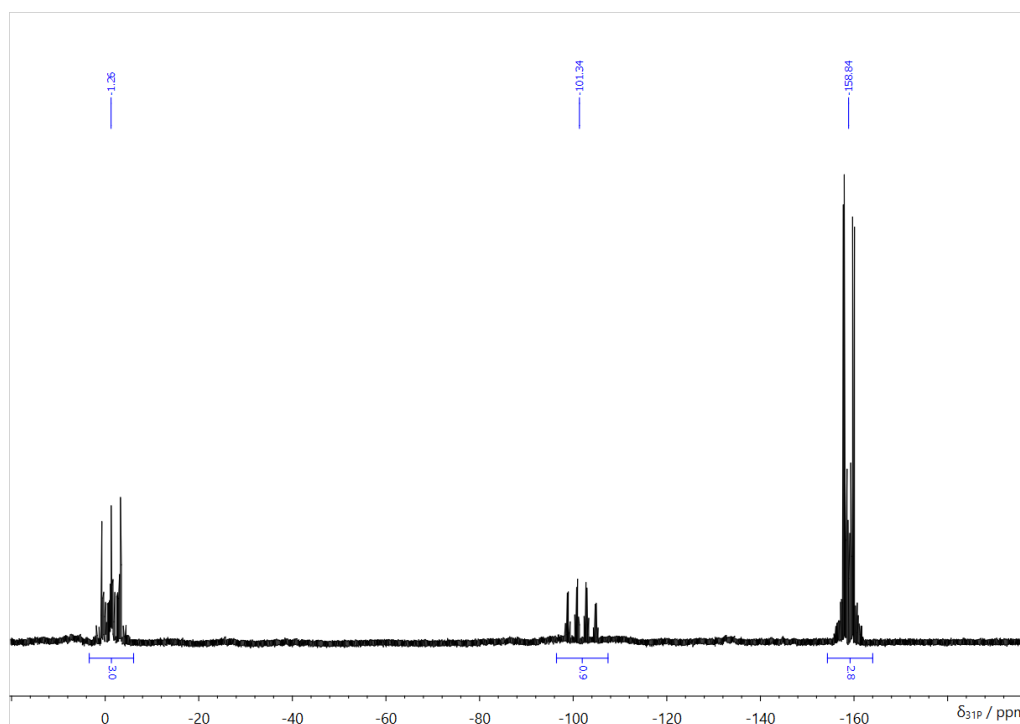


Figure S 1 ^{31}P decoupled NMR spectrum of $(\text{tms})_3\text{P}_7$ (1) in THF-d_8 .

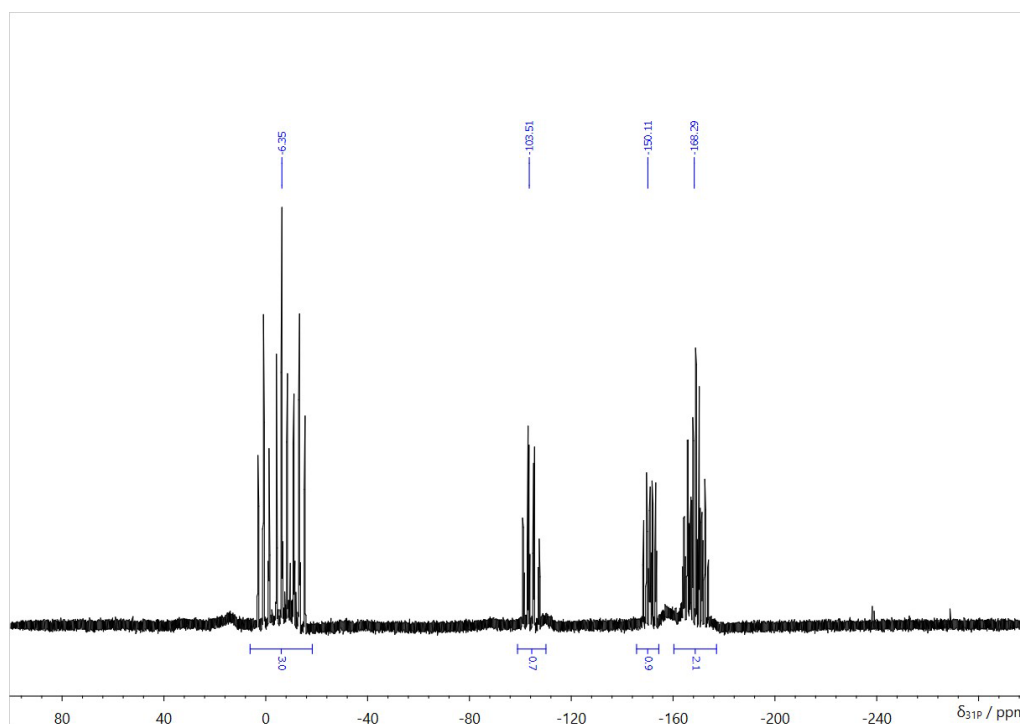


Figure S 2 ^{31}P decoupled NMR spectrum of $(\text{hyp})_2(\text{tms})\text{P}_7$ (3) in THF-d_8 .

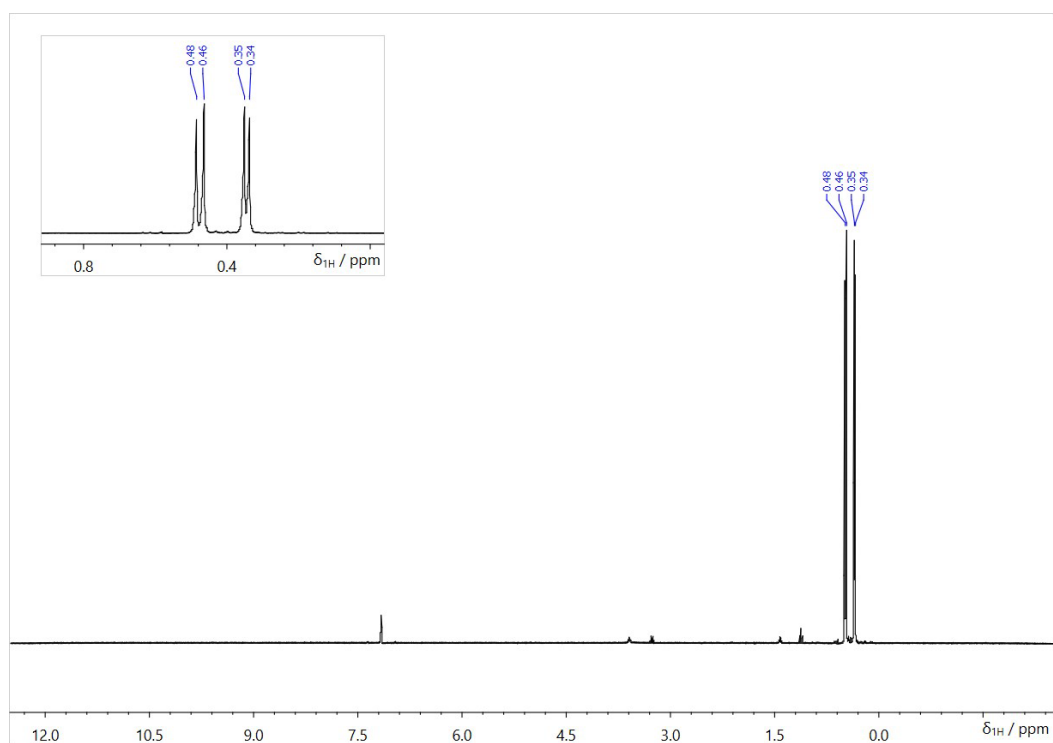


Figure S 3 ^1H NMR spectrum of $[(\text{hyp})_2\text{P}_7]_2\text{Zn}$ (7) in C_6D_6 .

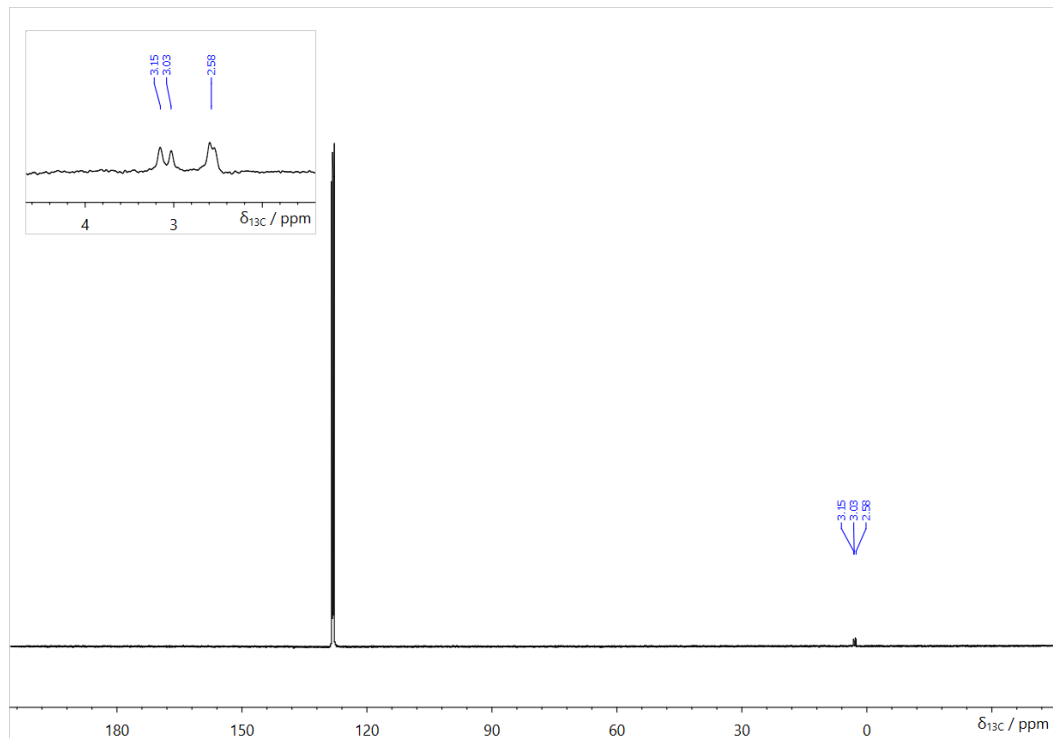


Figure S 4 ^{13}C NMR spectrum of $[(\text{hyp})_2\text{P}_7]_2\text{Zn}$ (7) in C_6D_6 .

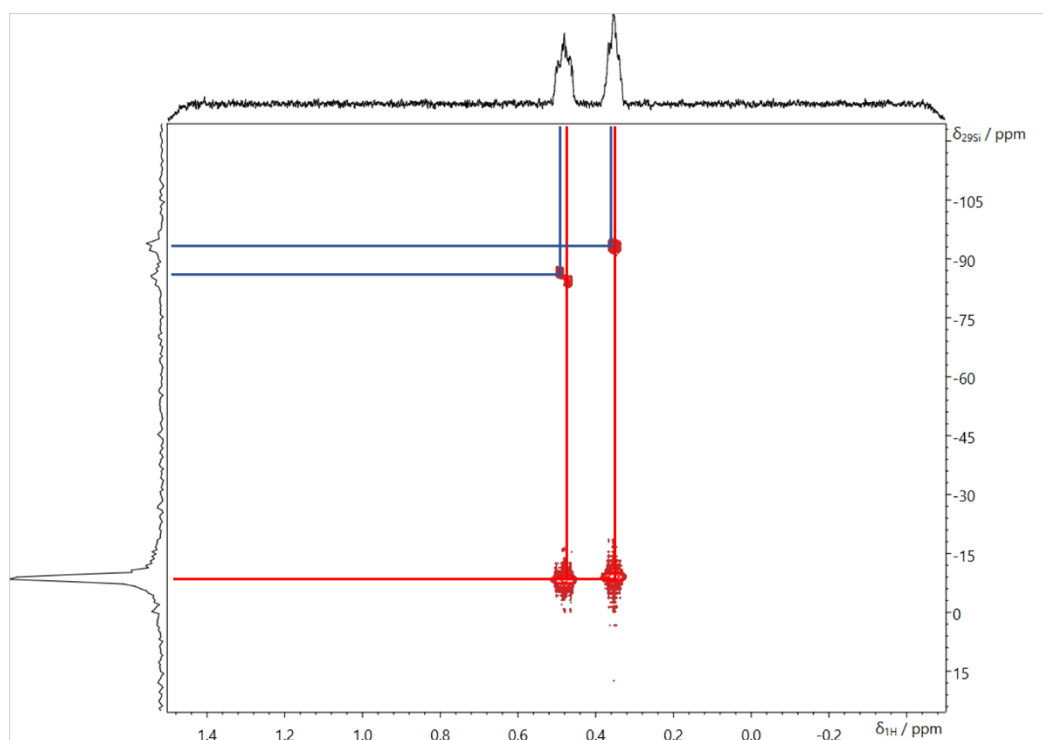


Figure S 5 ^{29}Si INEPT NMR spectrum of $[(\text{hyp})_2\text{P}_7]_2\text{Zn}$ (**7**) in C_6D_6 .

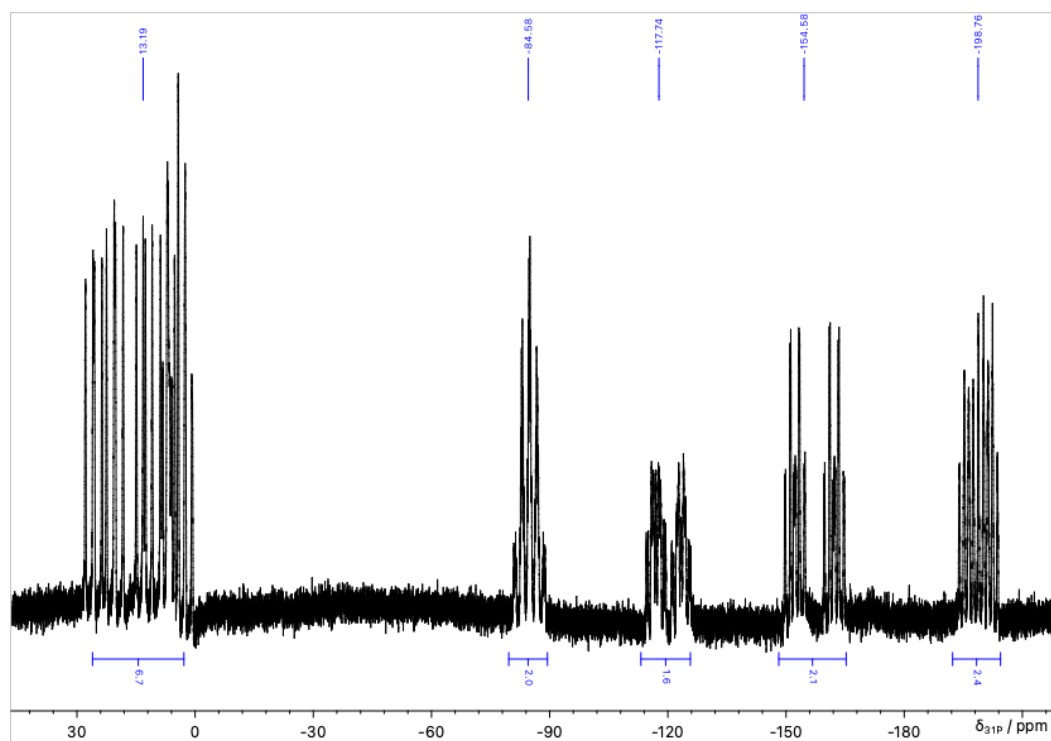


Figure S 6 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\text{hyp})_2\text{P}_7]_2\text{Zn}$ (**7**) in C_6D_6 .

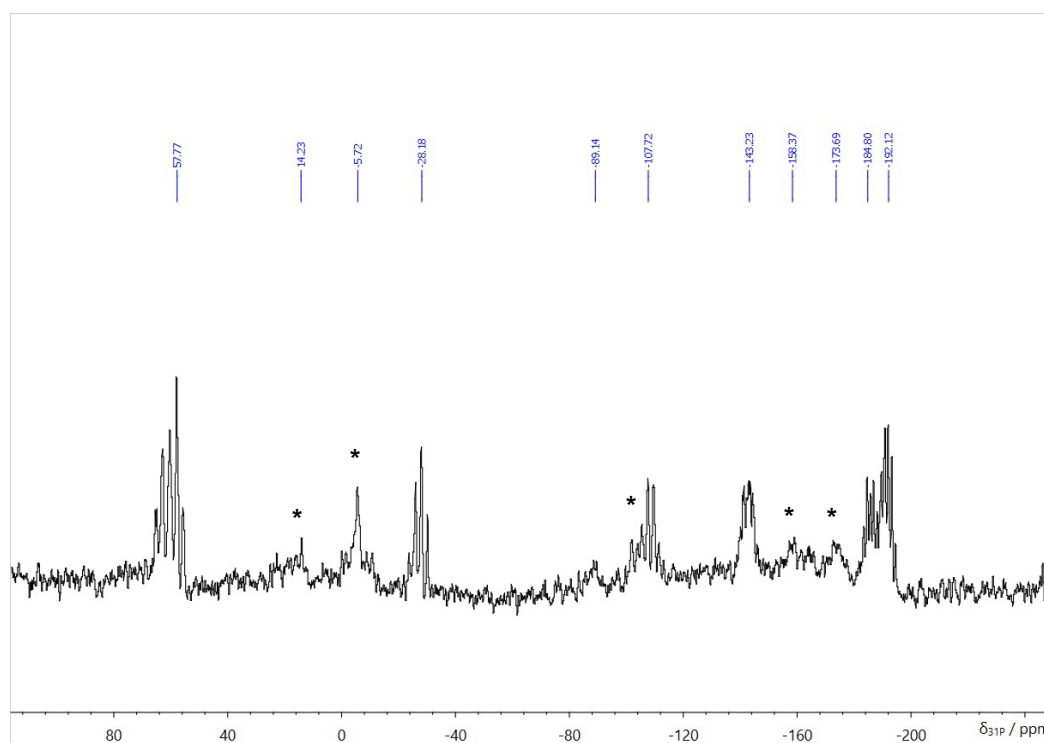


Figure S $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\text{hyp})_2\text{P}_7\text{Au}]_2$ (**4**) in THF-d_8 . Resonances likely originating from $(\text{hyp})_2\text{P}_7\text{H}$ or other decomposition products are marked with asterisks (*).

2 Raman Spectroscopy

For experimental details see *Materials and Methods* section in the main manuscript.

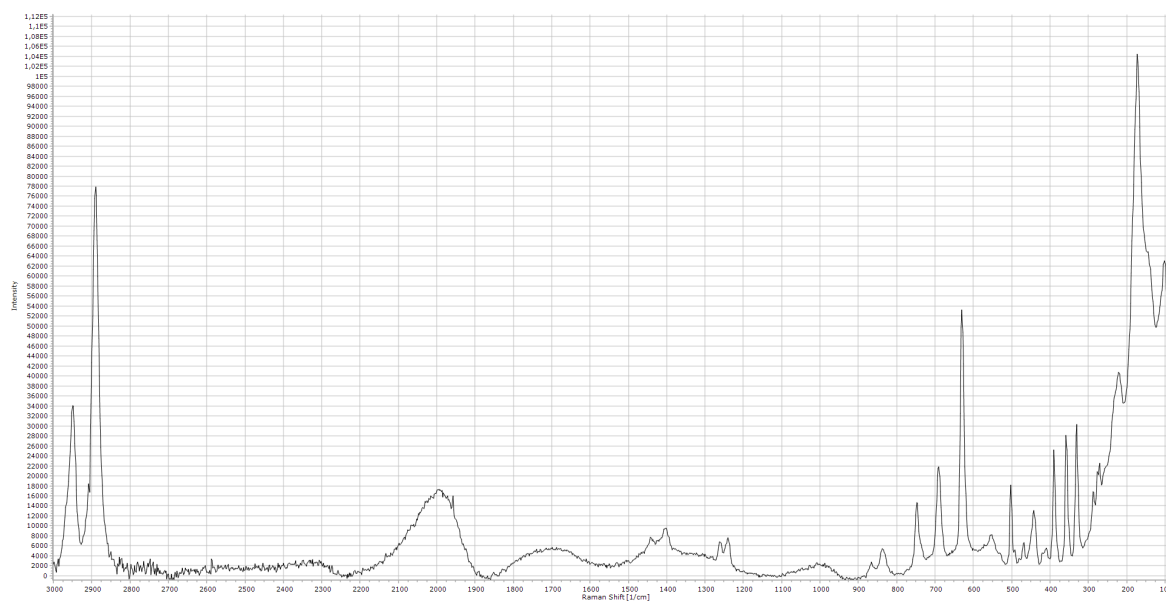


Figure S 8 Raman spectrum of (hyp)₂(tms)P₇ (**3**).

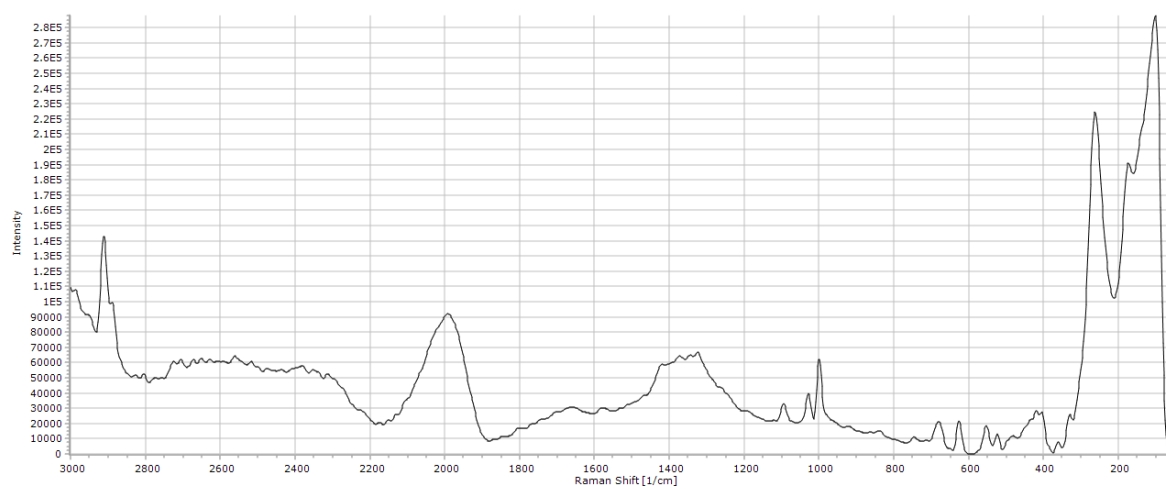


Figure S 9 Raman spectrum of (hyp)₂(tms)P₇ (**3**).

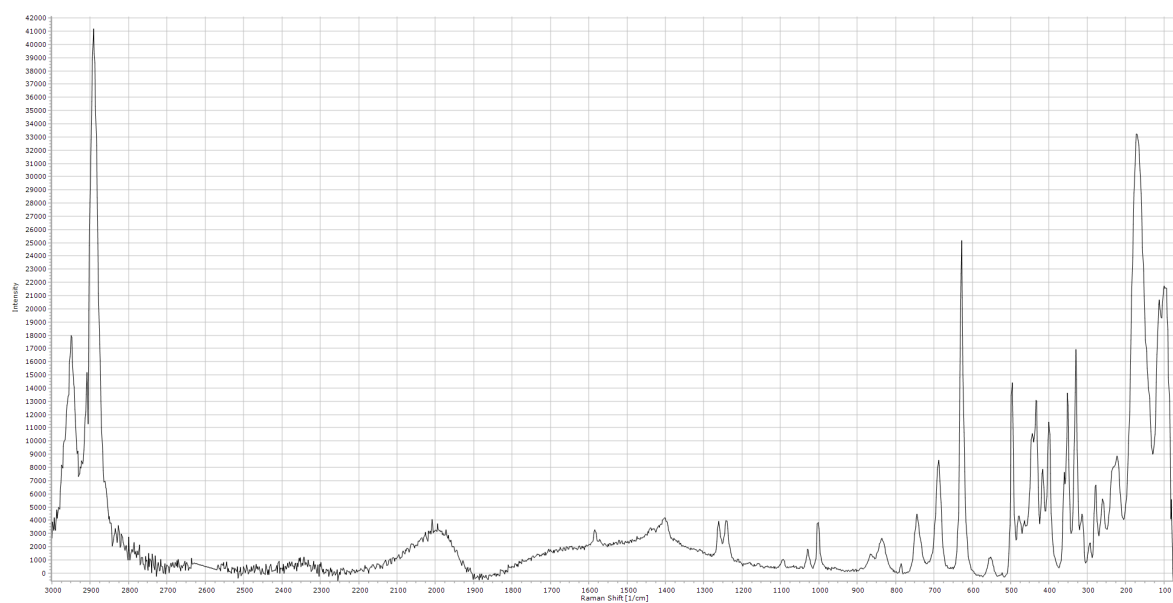


Figure S 10 Raman spectrum of $[(\text{hyp})_2\text{P}_7\text{Ag}]_4$ (5).

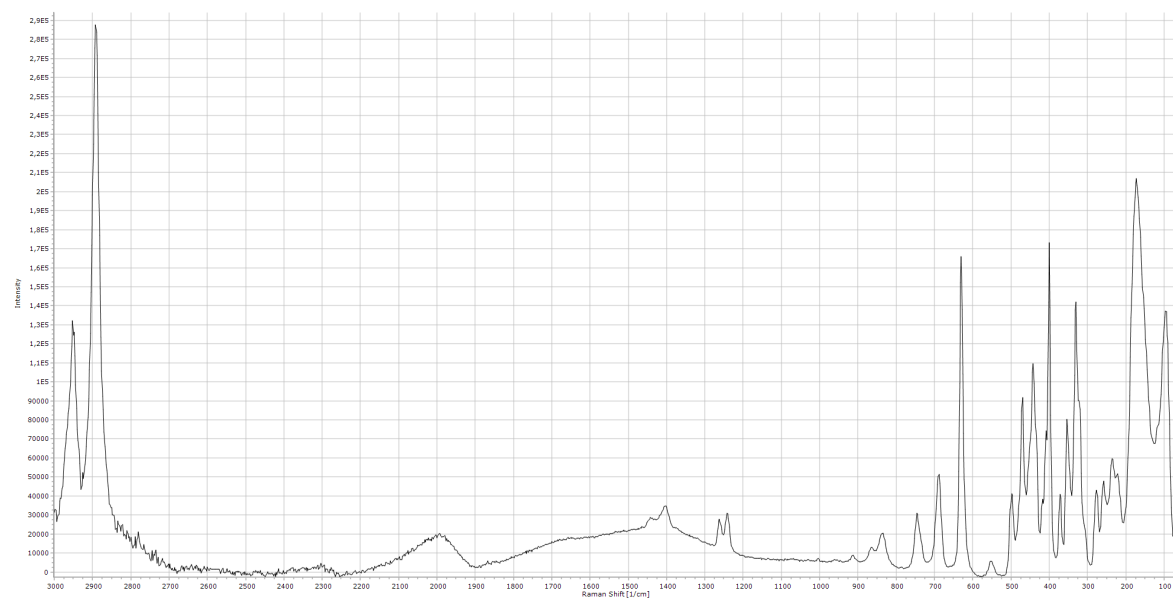


Figure S 11 Raman spectrum of $[(\text{hyp})_2\text{P}_7\text{Cu}]_4$ (6).

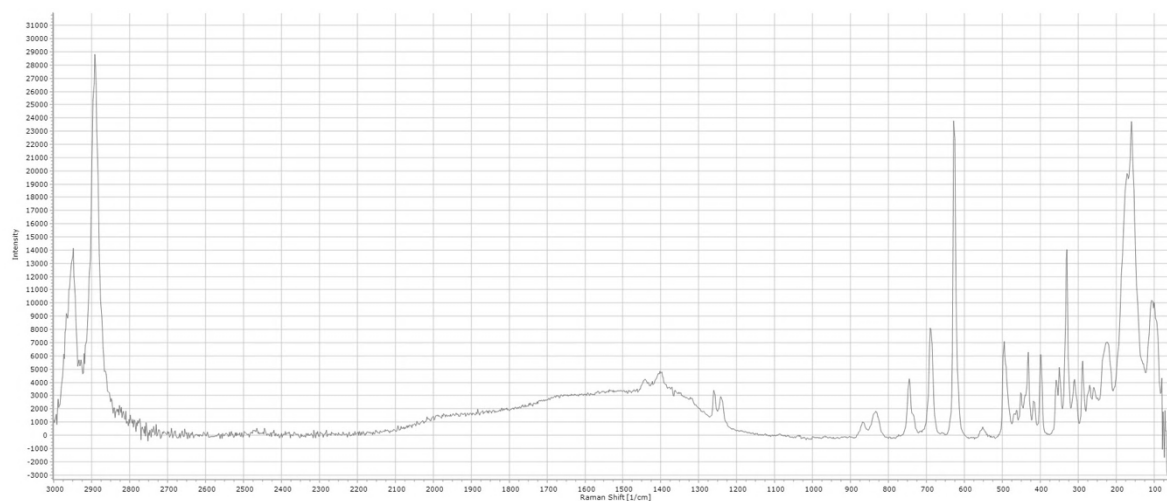


Figure S 12 Raman spectrum of $[(\text{hyp})_2\text{P}_7]_2\text{Zn}\cdot\text{Et}_2\text{O}$ (**7**).

3 Single Crystal X-Ray Diffraction

For experimental details see *Materials and Methods* section in the main manuscript.

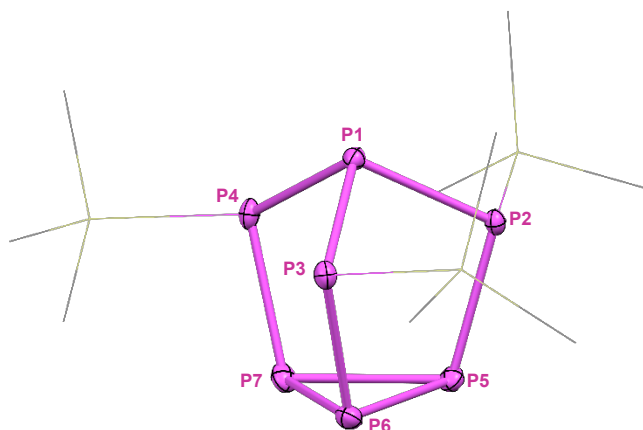


Figure S 13 Molecular structure of the novel polymorph of $(\text{tms})_3\text{P}_7$ (**1**). Heavier atoms incorporated into the core structure of the cage are shown as 30% shaped ellipsoids. Hydrogens are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$] for **1**: P1-P2 2.1856(5), P1-P3 2.1820(5), P1-P4 2.1790(5), P2-P5 2.1906(5), P3-P6 2.1958(5), P4-P7 2.1955(5), P5-P6 2.2178(7), P5-P7 2.2207(7), P6-P7 2.2202(5), P1-P2-P5 102.61(2), P2-P1-P3 97.92(2), P2-P5-P7 106.36(2), P5-P6-P7 60.05(2).

Table S 1 Crystal data and structure refinement of compounds **1** and **2**.

Compound	(tms)₃P₇ (1)	(tms)₃P₁₁ (2)
CCDC number	2353797	2353798
Empirical formula	C ₉ H ₂₇ P ₇ Si ₃	C ₉ H ₂₇ Si ₃ P ₁₁
Formula weight [g mol⁻¹]	436.36	560.24
Temperature [K]	99.98	100.01
Crystal system	orthorhombic	monoclinic
Space group	Pna2 ₁	P2 ₁ /c
a [Å]	12.6286(4)	18.9303(10)
b [Å]	10.7340(3)	11.2620(6)
c [Å]	16.7766(5)	12.0969(6)
a [°]	90	90
β [°]	90	90.707(2)
γ [°]	90	90
Volume [Å³]	2274.16(12)	2578.8(2)
Z	4	4
ρ_{calc} [g cm⁻³]	1.274	1.443
μ [mm⁻¹]	0.690	0.862
F(000)	912.0	1152.0
Crystal size [mm³]	0.22 × 0.16 × 0.16	0.14 × 0.11 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection [°]	4.98 to 60	2.152 to 53.99
Index ranges	-17 ≤ h ≤ 17, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23	-24 ≤ h ≤ 24, -13 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	107059	70032
Independent reflections	6623 [R _{int} = 0.0323, R _{sigma} = 0.0142]	5603 [R _{int} = 0.1022, R _{sigma} = 0.0574]
Data/restraints/parameters	6623/1/182	5603/0/217
Goodness-of-fit on F²	1.046	1.165
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0160, wR ₂ = 0.0397	R ₁ = 0.0520, wR ₂ = 0.1228
Final R indexes [all data]	R ₁ = 0.0168, wR ₂ = 0.0401	R ₁ = 0.0744, wR ₂ = 0.1309
Largest diff. peak/hole [e Å⁻³]	0.32 / -0.15	0.68 / -0.51

Table S 2 Crystal data and structure refinement of compounds **4** and **5**.

Compound	[(hyp)₂P₇Au]₂ (4)	[(hyp)₂P₇Ag]₄ (5)
CCDC number	2353799	2353800
Empirical formula	C ₁₈ H ₅₄ Si ₈ P ₇ Au	C ₁₈ H ₅₄ Si ₈ P ₇ Ag
Formula weight [g mol⁻¹]	909.09	819.99
Temperature [K]	100.01	100.00
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a [Å]	9.5865(3)	14.1641(6)
b [Å]	13.4060(3)	18.5778(8)
c [Å]	16.3875(5)	18.6070(8)
α [°]	77.0430(10)	60.743(2)
β [°]	86.037(2)	87.702(2)
γ [°]	89.4460(10)	75.316(2)
Volume [Å³]	2047.50(10)	4111.7(3)
Z	2	4
ρ_{calc} [g cm⁻³]	1.475	1.325
μ [mm⁻¹]	4.111	1.007
F(000)	916.0	1704.0
Crystal size [mm³]	0.1 × 0.09 × 0.06	0.08 × 0.06 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection [°]	4.452 to 57.406	3.398 to 53.998
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -22 ≤ l ≤ 22	-18 ≤ h ≤ 18, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23
Reflections collected	34431	151367
Independent reflections	10457 [R _{int} = 0.0635, R _{sigma} = 0.0866]	17886 [R _{int} = 0.1457, R _{sigma} = 0.0905]
Data/restraints/parameters	10457/0/325	17886/0/649
Goodness-of-fit on F²	0.911	1.002
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0373, wR ₂ = 0.0658	R ₁ = 0.0462, wR ₂ = 0.1098
Final R indexes [all data]	R ₁ = 0.0623, wR ₂ = 0.0741	R ₁ = 0.0911, wR ₂ = 0.1280
Largest diff. peak/hole [e Å⁻³]	1.22 / -1.25	3.01 / -1.26

Table S 3 Crystal data and structure refinement of compounds **6** and **7**.

Compound	[(hyp)₂P₇Cu]₄ (6)	[{(hyp)₂P₇}₂Zn*Et₂O] (7)
CCDC number	2353801	2353802
Empirical formula	C ₁₈ H ₅₄ Si ₈ P ₇ Cu	C ₄₀ H ₁₁₈ Si ₁₆ P ₁₄ ZnO
Formula weight [g mol⁻¹]	775.66	1563.73
Temperature [K]	99.98	100.01
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a [Å]	15.841(5)	33.8870(9)
b [Å]	16.139(5)	9.6025(3)
c [Å]	18.362(5)	27.9371(8)
α [°]	89.441(8)	90
β [°]	65.691(10)	108.6570(10)
γ [°]	74.835(9)	90
Volume [Å³]	4103(2)	8613.0(4)
Z	4	4
ρ_{calc} [g cm⁻³]	1.256	1.206
μ [mm⁻¹]	1.050	0.795
F(000)	1632.0	3320.0
Crystal size [mm³]	0.05 × 0.08 × 0.05	0.51 × 0.42 × 0.37
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection [°]	3.346 to 52	2.536 to 58
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22	-46 ≤ h ≤ 43, -13 ≤ k ≤ 13, -38 ≤ l ≤ 38
Reflections collected	63270	97323
Independent reflections	16087 [R _{int} = 0.0720, R _{sigma} = 0.0686]	11424 [R _{int} = 0.0465, R _{sigma} = 0.0294]
Data/restraints/parameters	16087/0/649	11424/28/360
Goodness-of-fit on F²	0.996	1.059
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0728, wR ₂ = 0.1968	R ₁ = 0.0465, wR ₂ = 0.1160
Final R indexes [all data]	R ₁ = 0.1071, wR ₂ = 0.2295	R ₁ = 0.0641, wR ₂ = 0.1309
Largest diff. peak/hole [e Å⁻³]	3.40 / -0.68	1.99 / -1.79