Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Alkylzinc diorganophosphates: synthesis, structural diversity and unique ability to incorporate zincoxane units

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Table of contents:

1. Experimental data

1.1. General remarks:

All manipulations connected with the synthesis of organozinc compounds were conducted under dry, oxygen-free nitrogen atmosphere in carefully dried glassware using standard Schlenk techniques. Zn*t*Bu$_2$ was synthesized according to the literature procedure.[1] All other reagents were purchased from commercial vendors and used as received. Tetrahydrofuran and toluene were dried and distilled from sodium−potassium alloy and benzophenone prior to use.

Methods: Liquid-state NMR spectra were acquired on Varian Mercury 400 MHz spectrometers spectrometer at 298 K. Chemical shifts are expressed in δ (ppm). The following abbreviations are used for NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, br = broad and m = multiplet. FT-IR spectra were measured with a Bruker Vertex 80V spectrometer. EI mass spectra were recorded on a Waters GCT Premier Mass Spectrometer.

1.2. Synthesis and characterization:

[*t*BuZn(*dpphe*)]$_4$ (1$_4$): An appropriate amount of diphenyl phosphate (0.250 g, 1 mmol) was dissolved in toluene (5 mL) and cooled to −78 °C under N$_2$ atmosphere. Then Zn*t*Bu$_2$ (1.15 mL of a 0.875 M solution in toluene, 1 mmol) was added dropwise under vigorous stirring. The reaction after few minutes was gradually warmed up to room temperature and stirred for 6 h. Then, the mother solution was concentrated to c. 2 ml. Complex **1$_4$** was obtained as colorless crystals after crystallization at -25°C. (isolated yield 0.334 g, 90%).^{1}H NMR (toluen-d8, 400 MHz, 298 K): δ = 1.35 (s, 9H, $(CH_3)_3$C-Zn); 6.7-7.2 (m, 10H, -CH_{Ar}-) ppm. ^{31}P NMR (toluen-d$_8$, 400 MHz, 298 K): δ = -16.79 ppm. IR (ATR): 3074(vw), 3045(vw), 2939(vw), 2919(vw), 2905(vw), 2862(vw), 2814(w), 2757(vw), 2696(vw), 1590(w), 1489(m), 1464(vw), 1456(vw), 1274(m), 1214(m), 1191(s), 1166(w), 1103(w), 1074(w), 1054(vs), 1026(s), 1008(m), 952(vs), 938(vs), 931(vs), 903(m), 818(w), 782(m), 758(m), 749(vs), 730(w), 687(s), 620(w), 604(vw), 567(vw), 547(vs), 517(s), 499(s), 478(m) cm^{-1}. Elemental analysis: calcd. for $C_{64}H_{76}O_{16}P_4Zn_4$: %C 51.70, %H 5.15; found: %C 51.95, %H 4.99.

[*t*BuZn(*dmphe*)]$_4$ (2$_4$): A similar procedure as for **1$_4$**, using 0.8 mmol of Zn*t*Bu$_2$ (0.91 mL of a 0.875 M solution in toluene) and 0.8 mmol (0.100 g) of dimethyl phosphate. Complex **2$_4$** was obtained as colorless crystals after crystallization at -25°C. (isolated yield 0.164 g, 83%). ^{1}H NMR (toluen-d$_8$, 400 MHz, 298 K): δ = 1,45 (s, 9H, $(CH_3)_3$C-Zn); 3,41 (d, 6H, CH_3O-, $^3J_{H,P}$ = 11.25 Hz) ppm. ^{31}P NMR (toluen-d$_8$, 400 MHz, 298 K): δ = -1,35 ppm. IR (ATR): 2953(vw), 2939(vw), 2920(vw), 2909(vw), 2860(vw), 2853(vw), 2815(vw), 2728(vw), 2696(vw), 1462(vw), 1238(w), 1221(w), 1183(m), 1101(w), 1063(m), 1032(vs), 1021(vs), 845(s), 817(m), 772(vw), 736(w), 698(vw), 564(vw), 522(m), 498(s), 466(w), 414(m) cm^{-1}. Elemental analysis: calcd. for $C_{55}H_{128}O_{32}P_8Zn_8$: %C 31.87, %H 6.22; found: %C 32.30, %H 5.98.

[{MeZn(*dpphe*)}$_3$(Me$_2$Zn$_2$O)(THF)$_2$] (3): An appropriate amount of diphenyl phosphate (0.250 g, 1 mmol) was dissolved in toluene (4 mL) and cooled to −78 °C in a N$_2$ atmosphere. Then, ZnMe$_2$ (0.73 mL of a 1.37 M solution in toluene, 1 mmol) was added dropwise under vigorous stirring. The reaction was gradually warmed up to room temperature. After 4 h, insoluble product was obtained, volatiles were removed in vacuum, and then the final product was crystallized from a THF solution at

4 °C (isolated yield 0.105 g, 40 %). ^{1}H NMR (THF-d8, 400 MHz, 298 K): δ = -1,02 (s, 15H, CH_3-Zn); 1.77 (m, 8H, -CH_{2THF}-), 3.63 (br,m, 8H, -OCH_{2THF} -), 6.7-7.4 (m, 30H, -CH_{Ar}-) ppm. ^{31}P NMR (THF-d8, 400 MHz, 298 K): δ = -9.67; -16,42 ppm. IR (ATR): 3066(vw), 3044(vw), 2963(vw), 1590(m), 1487(s), 1455(w), 1260(m), 1208(s), 1192(vs), 1161(m), 1097(vs), 1070(vs), 1023(s), 1008(s), 949(vs), 935(vs), 906(s), 870(w), 797(s), 768(vs), 755(m), 738(m), 688(vs), 660(w), 621(m), 581(m), 534(vs), 519(s), 504(s), 465(m) cm^{-1}. EI-MS of the post-reaction mixture: (m/z) = 94.1 (100%, $[PhOH]^+$), 249.9 (5,5%, $[(PhO)_2P(O)OH]^+$), 325.9 (58,53%, $[(PhO)_3POH]^+$), 481.9 (0,5%, $[(PhO)_2P(O)OP(O)(PhO)_2]^+$); triphenyl phosphate could by formed as a result of the simultaneous decomposition of pyrophosphates and later diphenyl phosphate esterification. Elemental analysis: calcd. for $C_{49}H_{61}O_{15}P_3Zn_5$: %C 44.93, %H 4.69; found: %C 45.15, %H 4.40.

[{MeZn(*dmphe*)}$_6$(Me$_2$Zn$_3$O$_2$)] (4): A solution of dimethyl phosphate (0.123 g, 0.97 mmol) in toluene (5 ml) was cooled to -78°C, and Me_2Zn (0,71 ml of a 1.37 M solution in toluene, 0.97 mmol) was added dropwise. The reaction mixture was warmed to the room temperature and stirred for 4 h. Then, complex **4** was obtained as colorless needles like crystals after 24 h (isolated yield 0.099 g, 60%).^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = -0.17 (m,br, 4H, CH_3-Zn); 3.53 (d, 6H, CH_3O-, $^{3}J_{H,P}$ = 11.11 Hz) ppm. ^{31}P NMR (C_6D_6, 400 MHz, 298 K): δ = 1.37; 5.91 ppm. IR (ATR): 2998(vw), 2958(vw), 2855(vw), 1590(vw), 1487(vw), 1455(vw), 1259(w), 1188(s), 1099(s), 1067(s), 1025(vs), 958(m), 938(m), 906(w), 834(s), 775(s), 688(w), 664(w), 582(w), 519(s), 501(s), 469(s) cm^{-1}. Elemental analysis: calcd. for $C_{20}H_{60}O_{26}P_6Zn_9$: % C 16.11, % H 4.06; found: %C 16.64, %H 3.57

2. ^{1}H NMR and ^{31}P NMR spectra

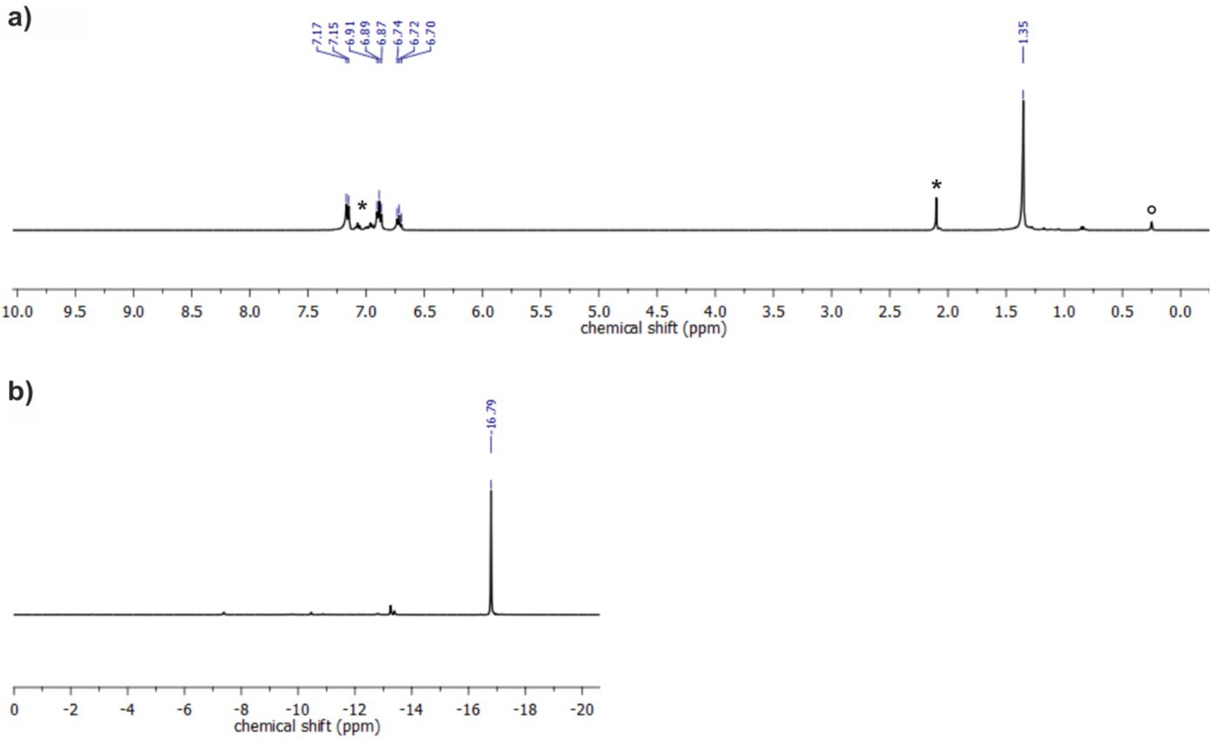

Fig. S1. a) ^{1}H NMR and b) ^{31}P NMR spectra of **1$_4$**; * toluene-d8 and ◦ silicone grease.

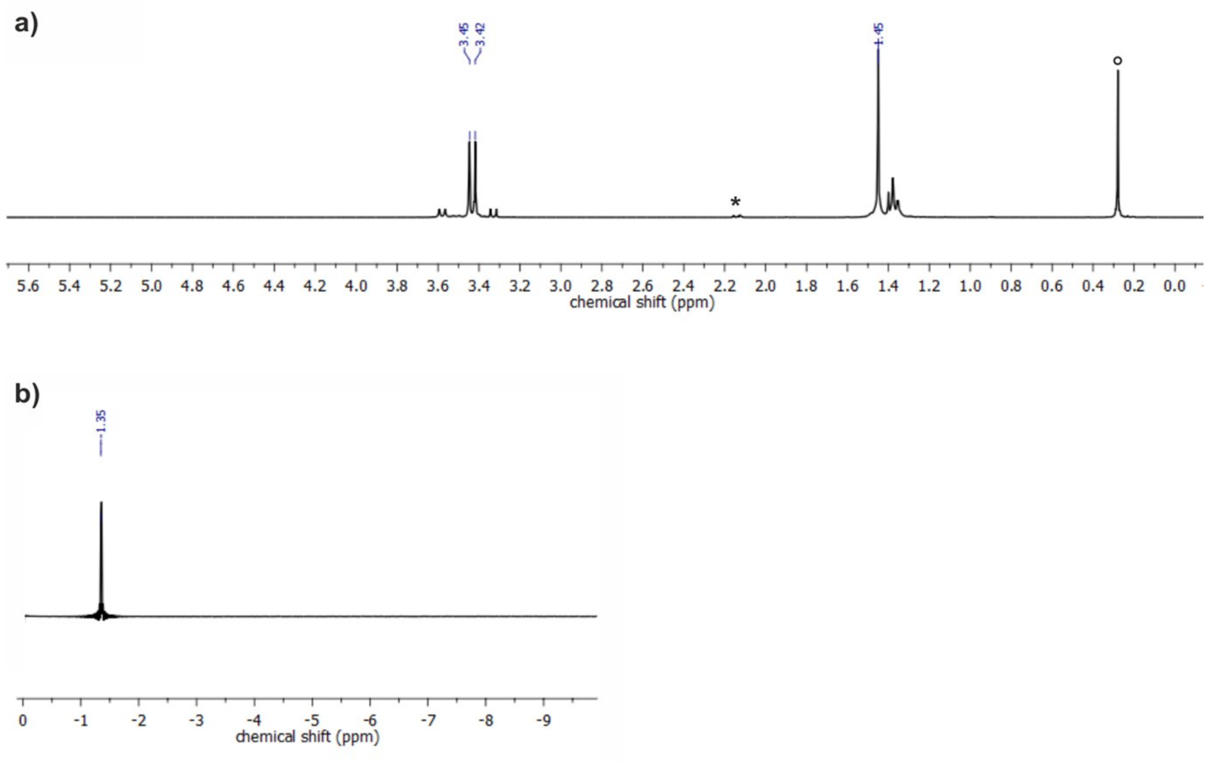

Fig. S2. a) ^{1}H NMR and b) ^{31}P NMR spectra of **2$_4$**; * toluene-d8 and ◦ silicone grease.

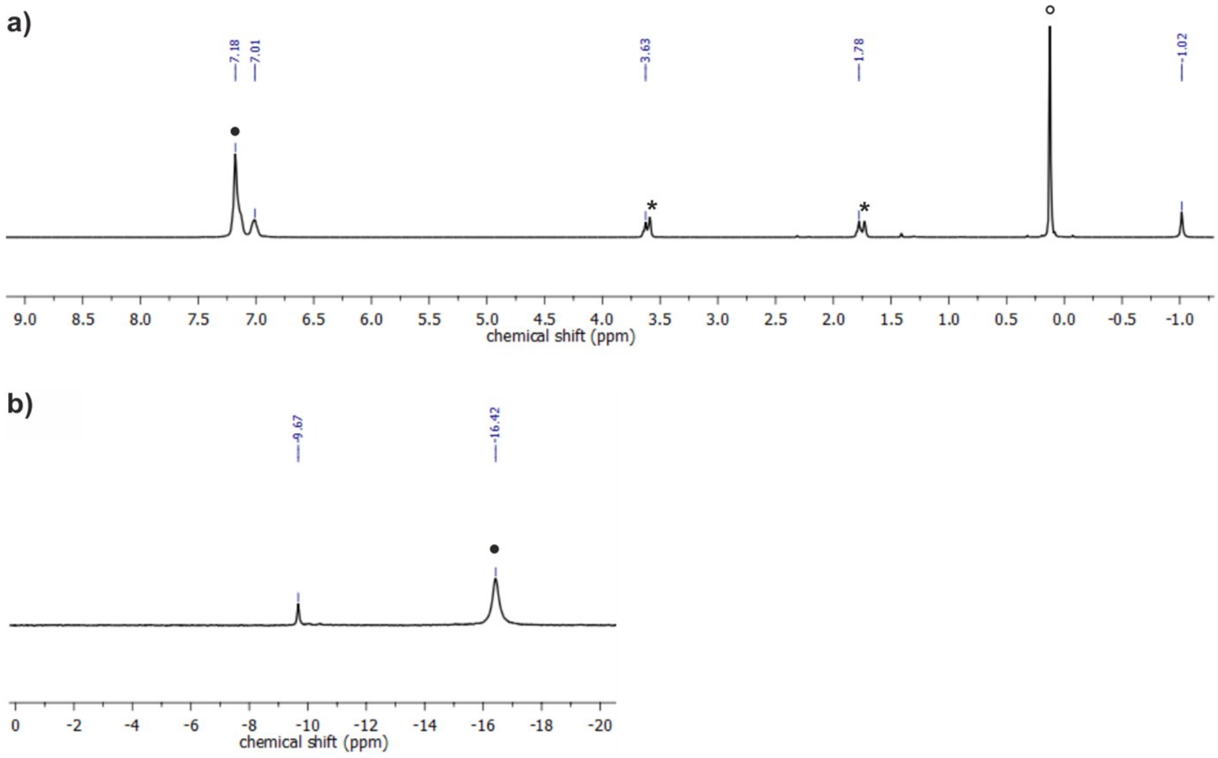

Fig. S3. a) ^{1}H NMR and b) ^{31}P NMR spectra of crude **3**; * THF-d8 and ◦ silicone grease; ● Note that due to a very low solubility of **3** in organic solvents, the NMR spectrum is contaminated by organophosphate side products; the presence of additional signals at 7.18 ppm (^{1}H NMR) and -16.42 ppm (^{31}P NMR) may be connected with the formation of well-soluble organopyrophosphate (see also the EI-MS data for of the post-reaction mixture).

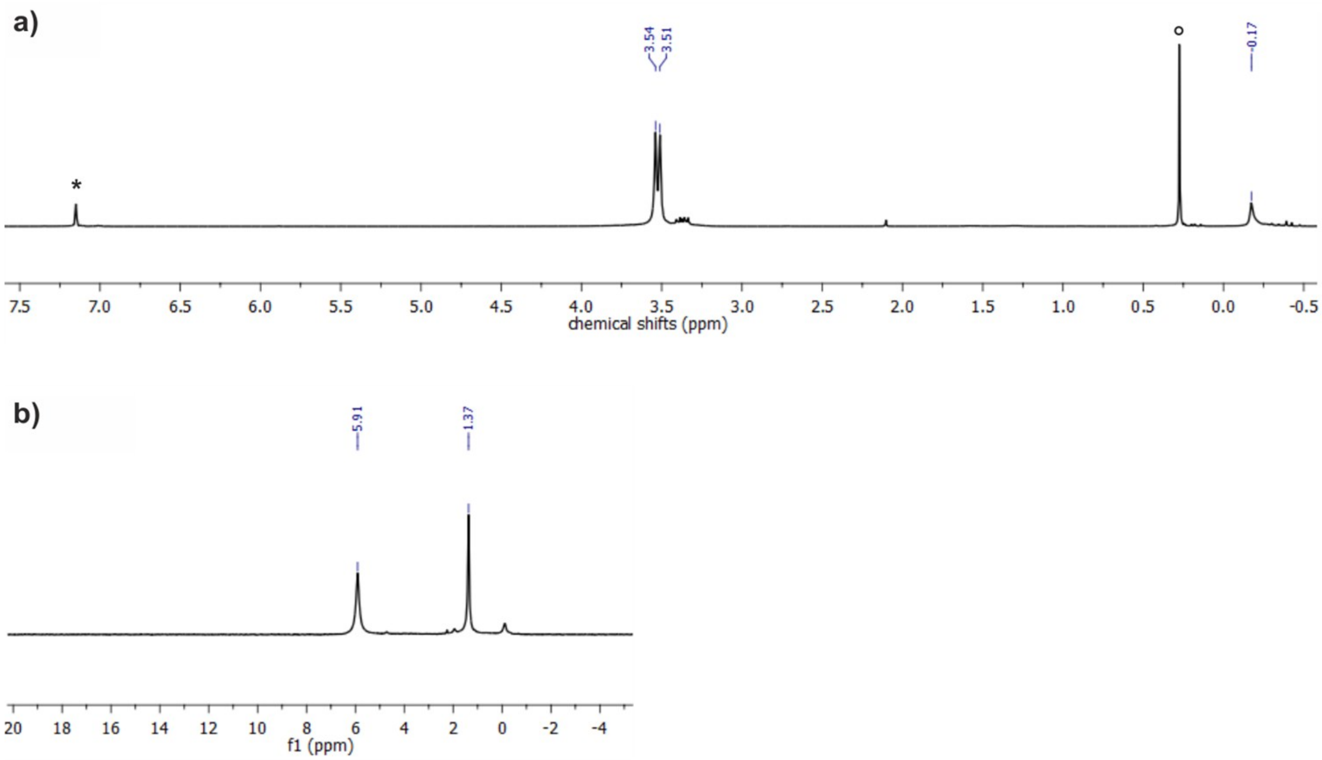

Fig. S4. a) ^{1}H NMR and b) ^{31}P NMR spectra of **4**; * C_6D_6 and ◦ silicone grease.

3. X-ray structure determination

The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data for complexes **2$_4$** and **3** were collected at 100(2)K on a Nonius Kappa CCD diffractometer[2] using graphite monochromated Mo*Kα* radiation (λ = 0.71073 Å). The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with *DENZO* and *SCALEPACK* (*HKL2000* package).[3] The X-ray data for complexes **1$_4$** and **4** were collected at 100(2)K on a SuperNova Agilent diffractometer using Mo*Kα* radiation (λ = 0.71073 Å). The data were processed with *CrysAlisPro.*[4] The structure was solved by direct methods using the SHELXS-97 program and was refined by full matrix least–squares on F^2 using the program SHELXL-97.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for 1$_4$; $C_{64}H_{76}O_{16}P_4Zn_4$: M = 1486.60, crystal dimensions 0.32 × 0.24 × 0.12 mm^3, triclinic, space group P -1 (no. 2), a = 13.3893(4) Å, b = 13.6598(4) Å, c = 20.3328(5) Å, α = 88.293(2) °, β = 87.214(2) °, γ = 66.693(2) °, U = 3411.05(17) Å^3, Z = 2, F(000) = 1536, D_c = 1.447 g cm^{-3}, T = 100(2) K, μ(Mo-Kα) = 1.547 mm^{-1}, SuperNova Agilent diffractometer, θ_{max} = 29.214 °, $R1$ = 0.0378, $wR2$ = 0.0656 for all data, $R1$ = 0.0293, $wR2$ =

0.0629 for 13723 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F^2 was equal 1.031. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.38/-0.34 eÅ^{-3}. CCDC – 1499962.

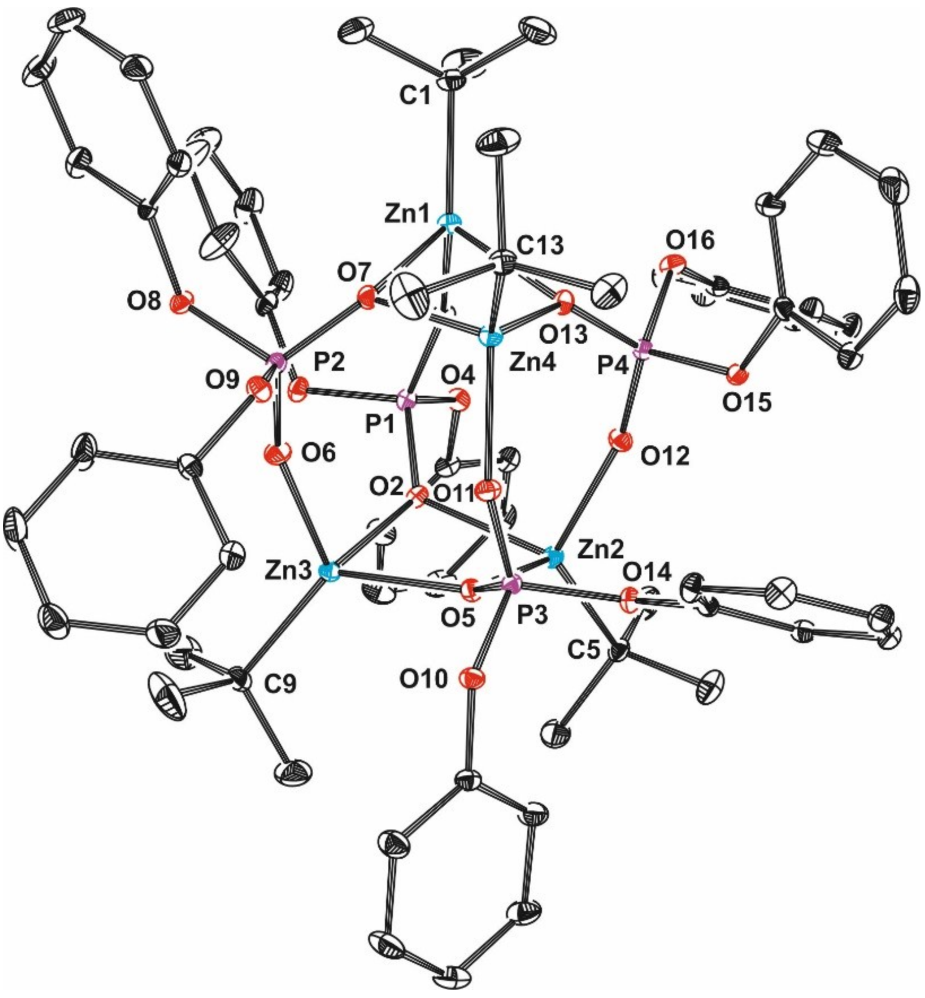

Fig. S5. Molecular structure of $\mathbf{1_4}$ with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity.

Crystal data for $\mathbf{2_4 \cdot 0.5\ PhCH_3}$; '$C_{55}H_{128}O_{32}P_8Zn_8$': M = 2072.29, crystal dimensions 0.28 × 0.18 × 0.08 mm^3, triclinic, space group P -1 (no. 2), a = 11.54200(10) Å, b = 15.7980(2) Å, c = 25.6050(4) Å, α = 78.4190(10) °, β = 83.3870(10) °, γ = 89.9080(10) °, U = 4542.24(10) Å^3, Z = 2, F(000) = 2148, D_c = 1.515 g cm^{-3}, T = 100(2) K, μ(Mo-Kα) = 2.286 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 27.435 °, $R1$ = 0.0457, $wR2$ = 0.0978 for all data, $R1$ = 0.0399, $wR2$ = 0.0948 for 17951 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F^2 was equal 1.077. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.67/-0.83 eÅ^{-3}. CCDC – 1499963.

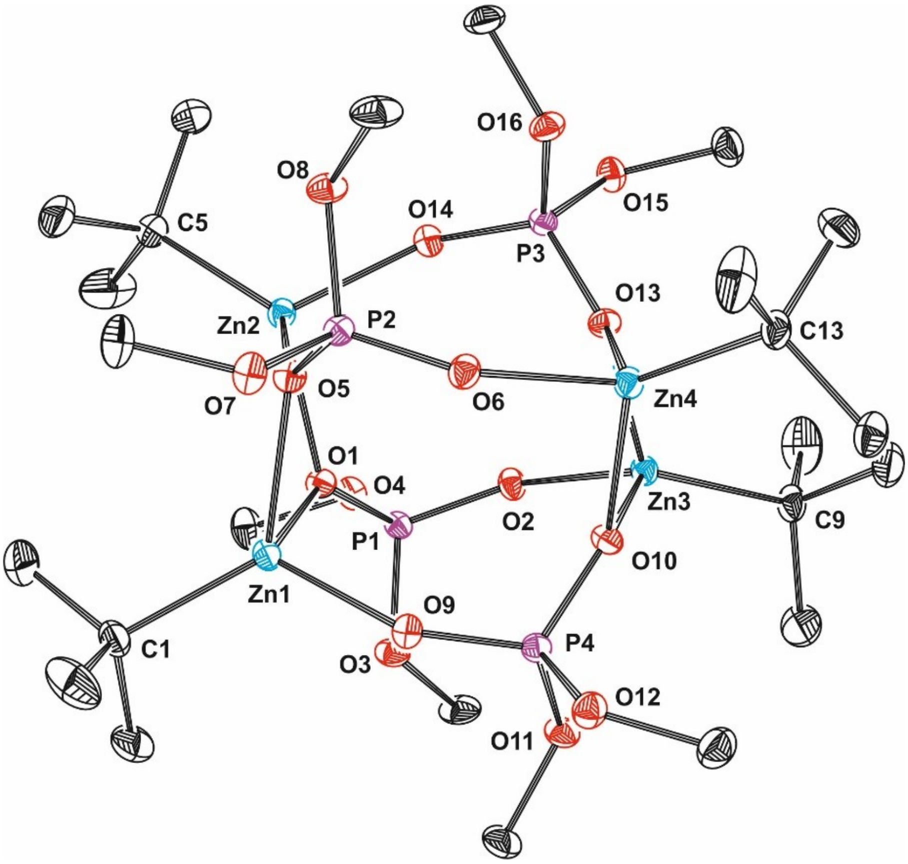

Fig. S6. Molecular structure of $\mathbf{2_4}$ with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity.

Crystal data for 3; $C_{49}H_{61}O_{15}P_3Zn_5$: M = 1309.73, crystal dimensions 0.32 × 0.18 × 0.08 mm^3, triclinic, space group P -1 (no. 2), a = 12.443(2) Å, b = 12.963(2) Å, c = 20.208(3) Å, α = 71.335(10) °, β = 76.664(9) °, γ = 65.261(8) °,U = 2786.9(8) Å^3, Z = 2, $F(000)$ = 1340, D_c = 1.561 g cm^{-3}, T = 100(2) K, μ(Mo-Kα) = 2.269 mm^{-1}, Nonius Kappa-CCD diffractometer, $\theta_{\max}$ = 24.277 °, $R1$ = 0.1642, $wR2$ = 0.2614 for all data, $R1$ = 0.1309, $wR2$ = 0.2484 for 5174 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F^2 was equal 1.248. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2\ )/3$ was used in the final stage of refinement. The residual electron density = +0.82/-0.71 eÅ^{-3}. CCDC – 1499964. Due to a poor quality of crystals of **3** for single-crystal X-ray diffraction, it was not possible to get a fully satisfactory refinement of the molecular structure, and this precludes also a detailed discussion of the geometrical parameters.

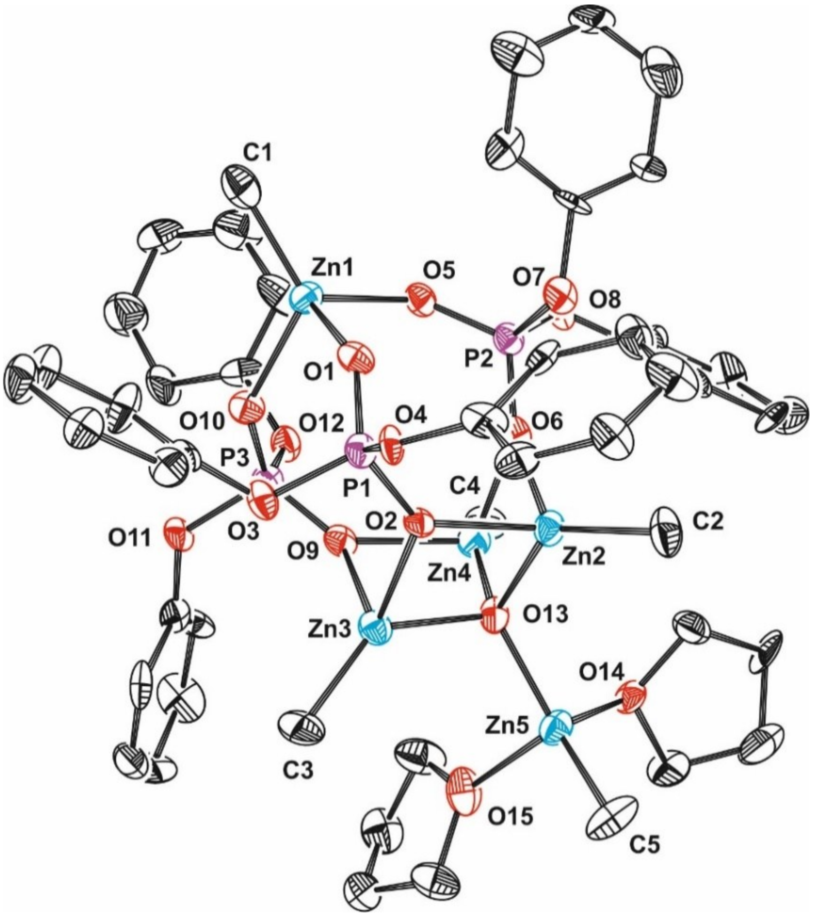

Fig. S7. Molecular structure of **3** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Crystal data for 4; $C_{20}H_{60}O_{26}P_6Zn_9$: M = 1490.83, crystal dimensions 0.29 × 0.22 × 0.11 mm^3, monoclinic, space group P 21/n (no. 14), a = 12.8404(2) Å, b = 12.5132(2) Å, c = 16.2848(3) Å, β = 100.804(2) °, U = 2570.17(8) Å^3, Z = 2, F(000) = 1496, D_c = 1.926 g cm^{-3}, T = 100(2) K, μ(Mo-Kα) = 4.382 mm^{-1}, SuperNova Agilent diffractometer, θ_{max} = 29.177 °, $R1$ = 0.0314, $wR2$ = 0.0549 for all data, $R1$ = 0.0240, $wR2$ = 0.0528 for 5119 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F^2 was equal 1.034. A weighting scheme $w = [\sigma^2(F_o{}^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ was used in the final stage of refinement. The residual electron density = +0.54/-0.48 eÅ^{-3}. CCDC – 1499965.

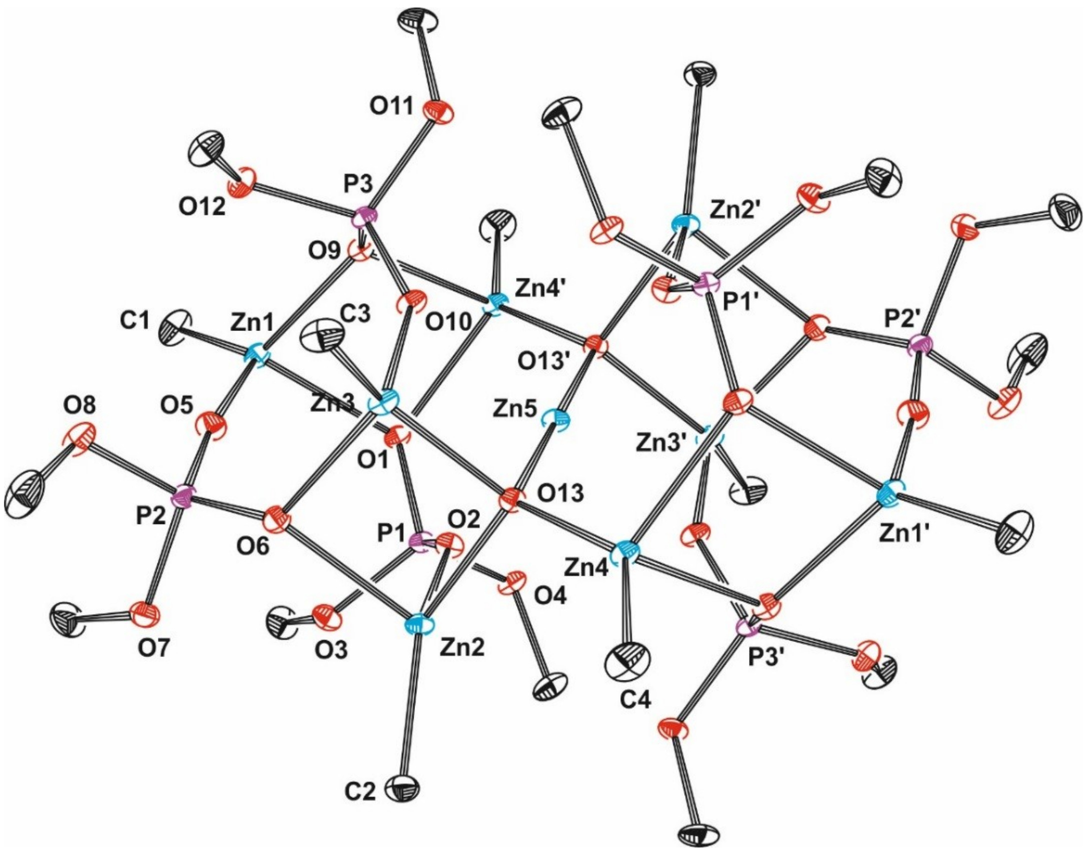

Fig. S8. Molecular structure of **4** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Symmetry codes: *(-x, -y, -z*).

4. References:

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1 J. Lewiński, M. Dranka, W. Bury, W. Śliwiński, I. Justyniak and J. Lipkowski, *J. Am. Chem. Soc.*, 2007,**129**, 3096.
2 *KappaCCD Software*; Nonius B.V.: Delft, The Netherlands, **1998**.
3 Z. Otwinowski and W. Minor, *Methods Enzymol*. 1997, **276**, 307.
4 Agilent Technologies, *CrysAlisPro*, Version 1.171.35.21b.
5 G. M. Sheldrick, *Acta Cryst*. 2008, **64A**, 112.