Supporting information

Tipping the balance between *twist* and *chair* ligand conformers in multinuclear ethylzinc cyclophosphazenates.

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Experimental

General methods. All manipulations were performed under a dry N_2 nitrogen atmosphere. Solvents were dried over potassium (thf, hexane) and sodium (toluene). Phosphazene ligand precursors were prepared as reported previously.[S1] Diethylzinc (1.0 M in hexane) was purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker AMX 400 spectrometer (^{1}H NMR: 400.13 MHz, ^{13}C{^{1}H} NMR: 100.62 MHz, ^{31}P{^{1}H} NMR: 161.97 MHz) at room temperature in toluene-d_8 using $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards.

Synthesis of 5. To a suspension of **1** (1.00 g, 3.17 mmol) in thf (20 mL) was added Et_2Zn solution (19.35 mL, 19.35 mmol). The reaction mixture was refluxed for 15 minutes resulting in a clear solution that was filtered after left to cool under stirring for 1 h. Storing the solution at -20 °C yielded colourless crystals. Yield 2.39 g (86 %). m.p. 190 °C (dec.). ^{1}H NMR: δ 0.39 [m, 24H, ZnC*H*$_2$CH$_3$], 1.29 [m, 36H, ZnCH$_2$C*H*$_3$], 2.52 [br, 36H, NC*H*$_3$]. ^{13}C{^{1}H} NMR: δ 11.8 [m, Zn*C*H$_2$CH$_3$], 32.2 [m, ZnCH$_2$*C*H$_3$], 32.1 [br, N*C*H$_3$]. ^{31}P{^{1}H} NMR: δ 44.9 [d, 1P, ^2J 8.5 = Hz], 37.7 [dd, 1P, ^2J = 8.5 and 28.8 Hz] and 26.8 [d, 1P, ^2J = 28.8 Hz].

Synthesis of 6. To a suspension of **2** (1.00 g, 2.50 mmol) in hexane (20 mL) was added Et_2Zn solution (15.27 mL, 15.27 mmol). The reaction mixture was refluxed for 15 minutes resulting in a clear solution that was filtered after left to cool under stirring for 1 h. Storing the solution at room temperature yielded colourless crystals. Yield 1.71 g (76 %). m.p. 118 °C (dec.). ^{1}H NMR: δ 0.67 [m, 20H, ZnC*H*$_2$CH$_3$], 1.28 [m, 30H, ZnCH$_2$C*H*$_3$], 1.28 - 1.49 [m, 18H, NCH$_2$C*H*$_3$], 3.13 [m, 12H, NC*H*$_2$CH$_3$]. ^{13}C{^{1}H} NMR: δ 12.7 [m, Zn*C*H$_2$CH$_3$], 18.0 [br, NCH$_2$*C*H$_3$], 30.3 [m, ZnCH$_2$*C*H$_3$], 40.5 [br, N*C*H$_2$CH$_3$]. ^{31}P{^{1}H} NMR: δ 44.7 [1P], 39.5 [2P].

Synthesis of 7. To a suspension of **3** (1.00 g, 2.07 mmol) in hexane (20 mL) was added Et_2Zn solution (12.61 mL, 12.61 mmol). The reaction mixture was refluxed for 2 h resulting in a clear solution that was filtered after left to cool under stirring for 1 h. Storing the solution at -20 °C yielded colourless crystals. Yield 0.50 g (82 %). m.p. 142 °C (dec.). ^{1}H NMR: δ 0.65 [m, 20H, ZnC*H*$_2$CH$_3$], 0.75 [m, 36H, NCH$_2$CH$_2$C*H*$_3$], 1.10 [m, 30H, ZnCH$_2$C*H*$_3$], 1.34 [m, 24H, NCH$_2$C*H*$_2$CH$_3$], 2.90 [m, 24H, NC*H*$_2$CH$_2$CH$_3$]. ^{13}C{^{1}H} NMR: δ 11.9 [m, Zn*C*H$_2$CH$_3$], 12.0 [br, NCH$_2$CH$_2$*C*H$_3$], 30.3 [m, ZnCH$_2$*C*H$_3$), 30.5 [br, NCH$_2$*C*H$_2$CH$_3$), 42.0 [br, N*C*H$_2$CH$_2$CH$_3$). ^{31}P{^{1}H} NMR: δ 45.2 [1P], 38.9 [2P].

Synthesis of 9. To a suspension of **4** (0.30 g, 0.53 mmol) in hexane (15 mL) was added Et_2Zn solution (3.7 mL, 3.7 mmol). The reaction mixture was refluxed for 15 minutes resulting in a clear solution that was filtered after left to cool under stirring for 1 h. The filtrate was concentrated (3 ml) and stored at -20 °C. Colourless crystals formed after 2 days. Yield: 0.25 g (42%); m.p. 186 °C (dec.); ^{1}H NMR: δ 0.32 [q, 12 H, CH$_3$C*H*$_2$Zn, ^3J = 8.2 Hz], 0.88 [d, 36H, N(CH$_2$CH(C*H*$_3$)$_2$), ^3J = 6.4 Hz], 1.14 [t, 18 H, C*H*$_3$CH$_2$Zn, ^3J = 8.2 Hz], 1.52-1.58 [m, 6H, (CH$_2$C*H*(CH$_3$)$_2$)], 2.68 - 2.72 [m, 12H, N(C*H*$_2$CH(CH$_3$)$_2$)].

$^{13}C\{^1H\}$ NMR: δ 1.2 [s, CH_3CH_2Zn], 12.5 [s, CH_3], 21.3 [s, CH_3CH_2Zn], 32.5 [s, CH_2], 52.6 [s, CH]. $^{31}P\{^1H\}$ NMR: δ 42.6.

Synthesis of 10. To a suspension of **4** (0.30 g, 0.53 mmol) in hexane (15 mL) was added Et_2Zn solution (3.7 mL, 3.7 mmol). The reaction mixture was refluxed for 2 days and then filtered. The filtrate was concentrated (3 ml) and stored at -20 °C. Colourless crystals formed after 2 days. Yield: 0.41 g (77%); m.p. 208 °C (dec.); ^1H NMR: δ 0.6-0.8 [m, 16 H, CH_3CH_2Zn], 0.9-1.2 [m, 36H, $N(CH_2CH(CH_3)_2)$], 1.55 [m, 12 H, CH_3CH_2Zn], 1.76 - 1.82 [m, 4H, $N(CH_2CH(CH_3)_2)$], 1.91 - 1.97 [m, 2H, $N(CH_2CH(CH_3)_2)$], 2.93 - 3.07 [m, 8H, $N(CH_2CH(CH_3)_2)$], 3.17 - 3.25 [m, 4H, $N(CH_2CH(CH_3)_2)$]. $^{13}C\{^1H\}$ NMR: δ -0.7 - 1.3 [m, CH_3CH_2Zn], 11.4 - 12.9 [m, CH_3], 20.5 - 21.7 [m, CH_3CH_2Zn], 30.7 - 31.7 [m, CH_2], 50.8 - 53.5 [m, CH]. $^{31}P\{^1H\}$ NMR: δ 41.4 [d, 2P, ^2J = 9.9 Hz], 43.3 [t, 1P, ^2J = 9.9 Hz].

S1 J. F. Bickley, R. Bonar-Law, G. T. Lawson, P. I. Richards, F. Rivals, A. Steiner and S. Zacchini, *Dalton Trans.*, 2003, 1235.

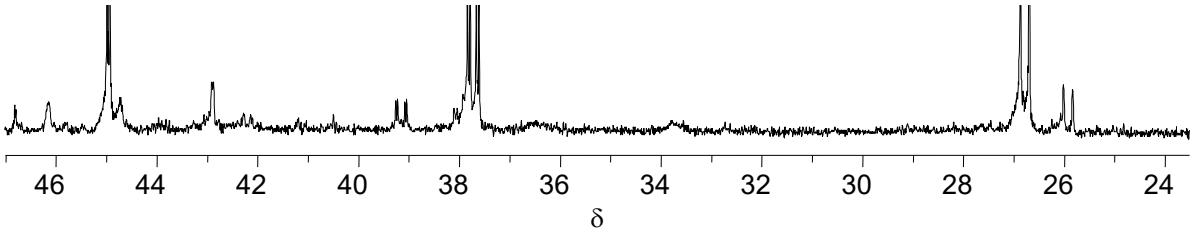
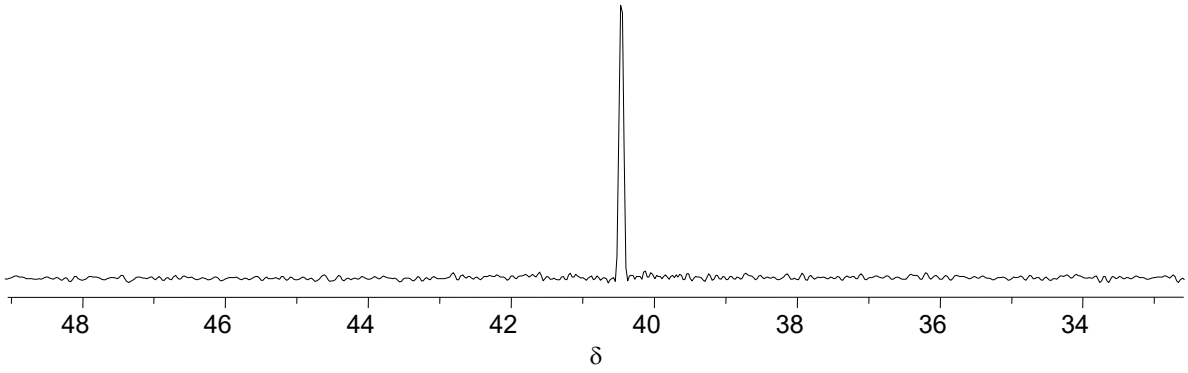
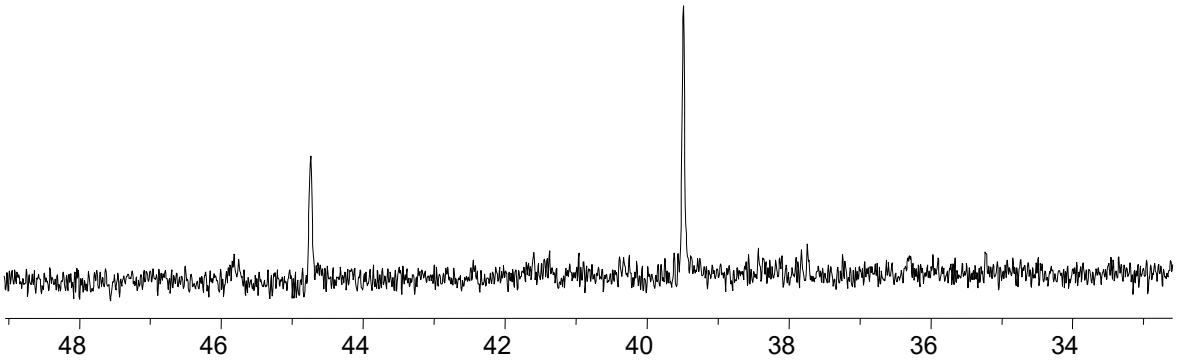


Fig. S1 $^{31}P\{^1H\}$ NMR of crystals of **5** redissolved in hexane.



(a)



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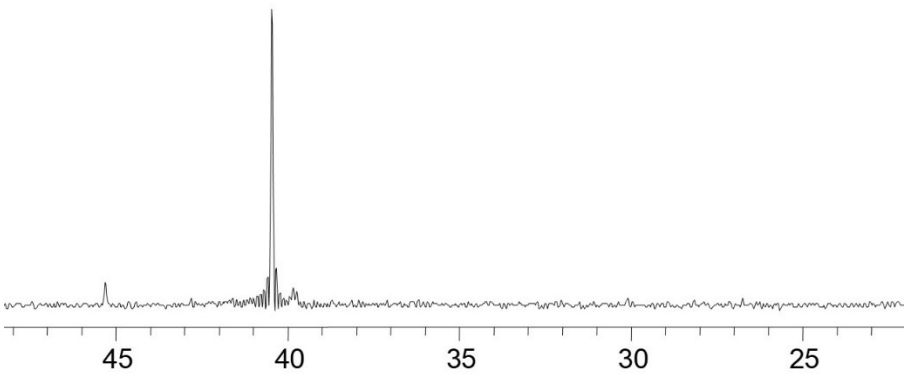

(c)

Fig. S2 $^{31}P\{^{1}H\}$ NMR spectra of (a) reaction solution of **6a** prior to crystallisation, (b) crystals of **6** redissolved in hexane, (c) crystals of **6** redissolved in hexane and treated with one equivalent Et_2Zn.

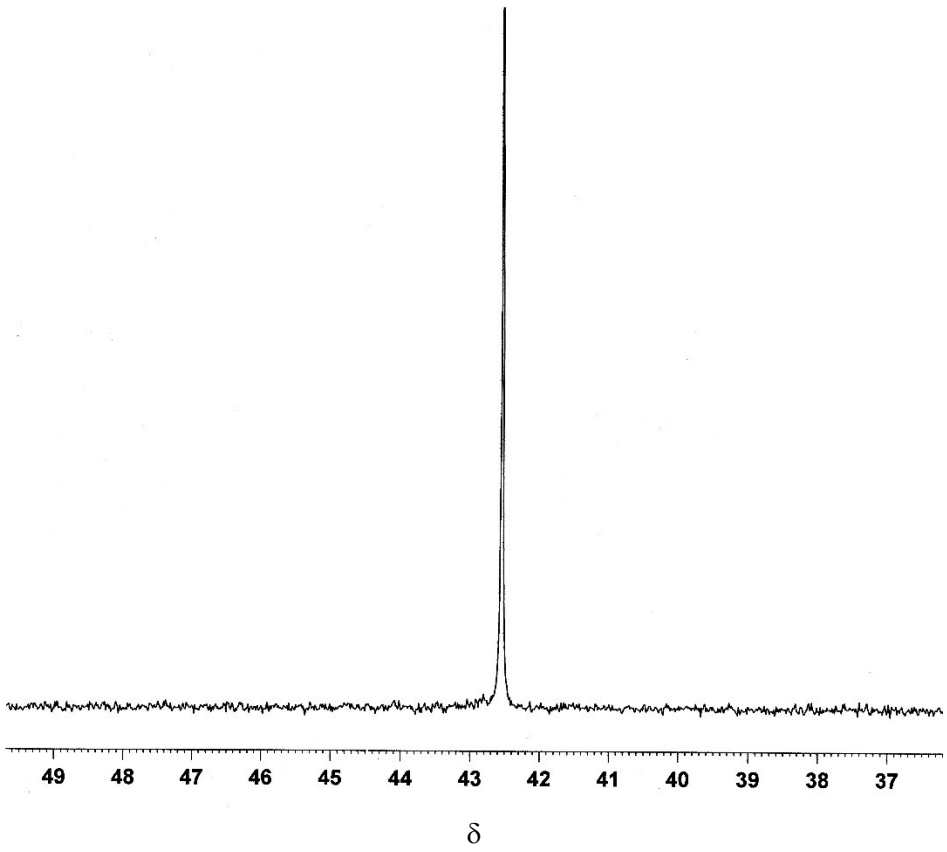

Fig. S3 $^{31}P\{^{1}H\}$ NMR of redissolved crystals of **9**.

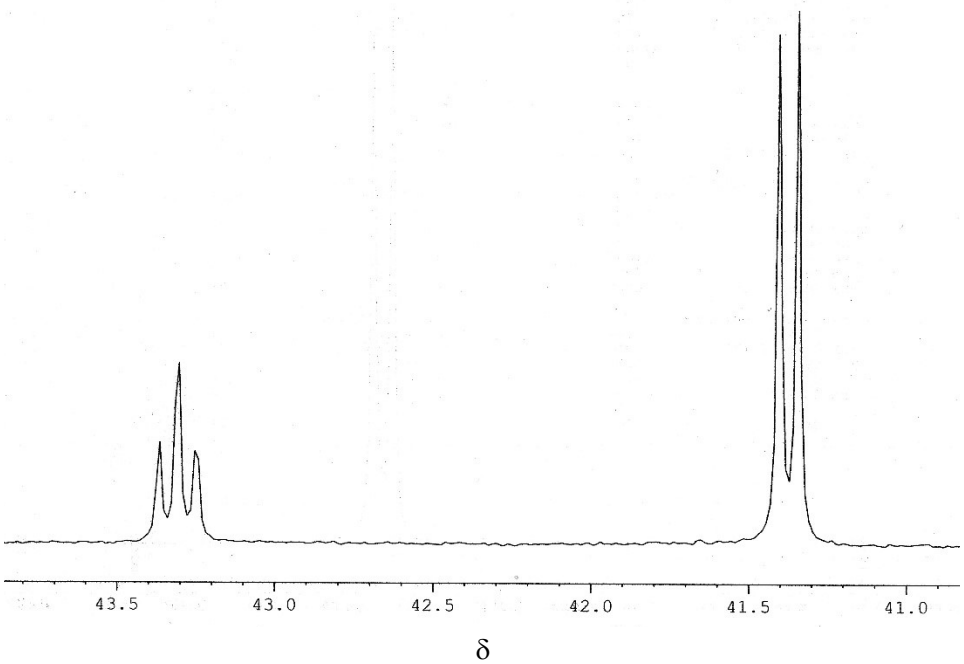

Fig. S4 $^{31}P\{^{1}H\}$ NMR of redissolved crystals of **10**.

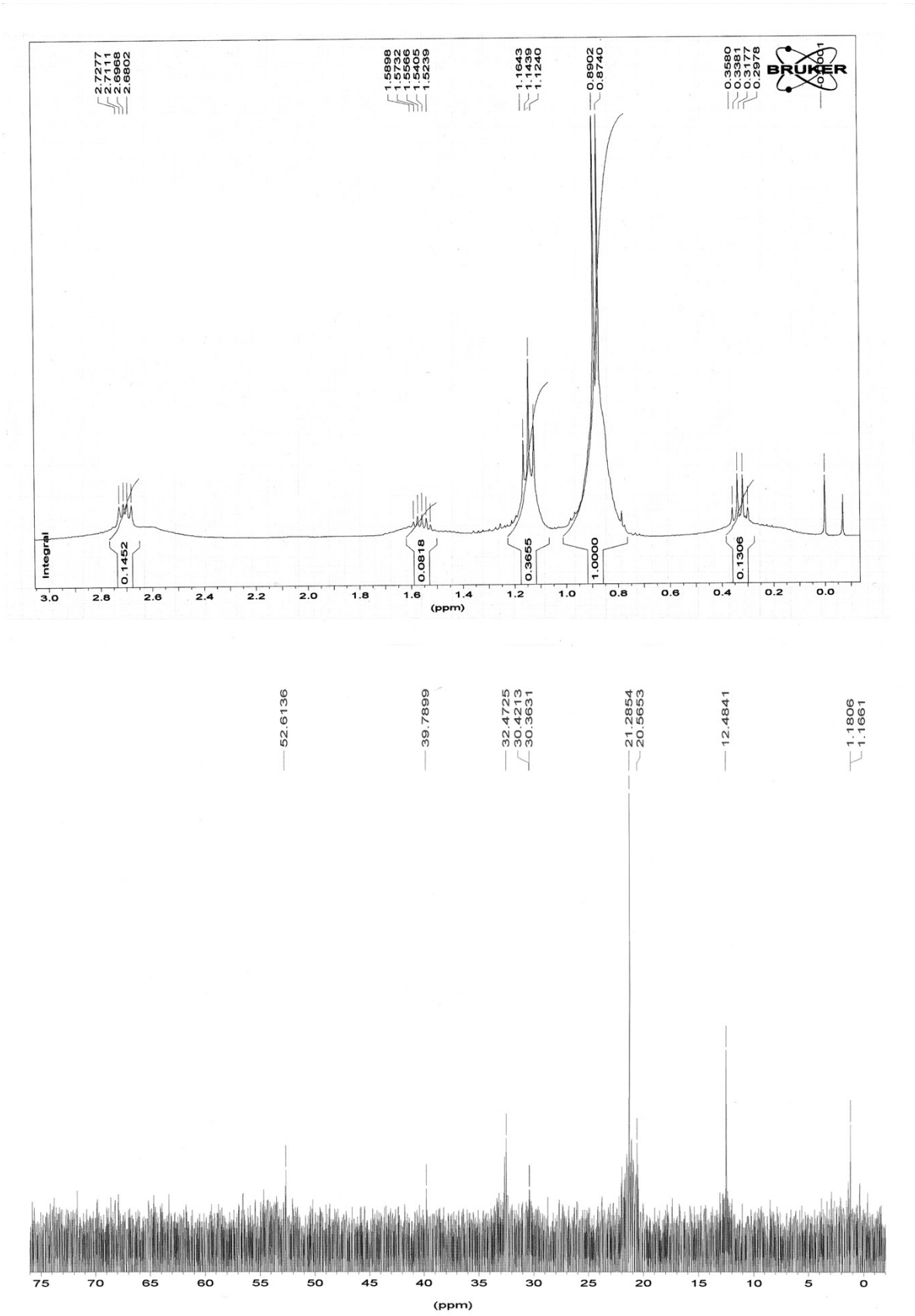

Fig. S5 ^{1}H NMR (top) and ^{13}C NMR (bottom) of redissolved crystals of **9**.

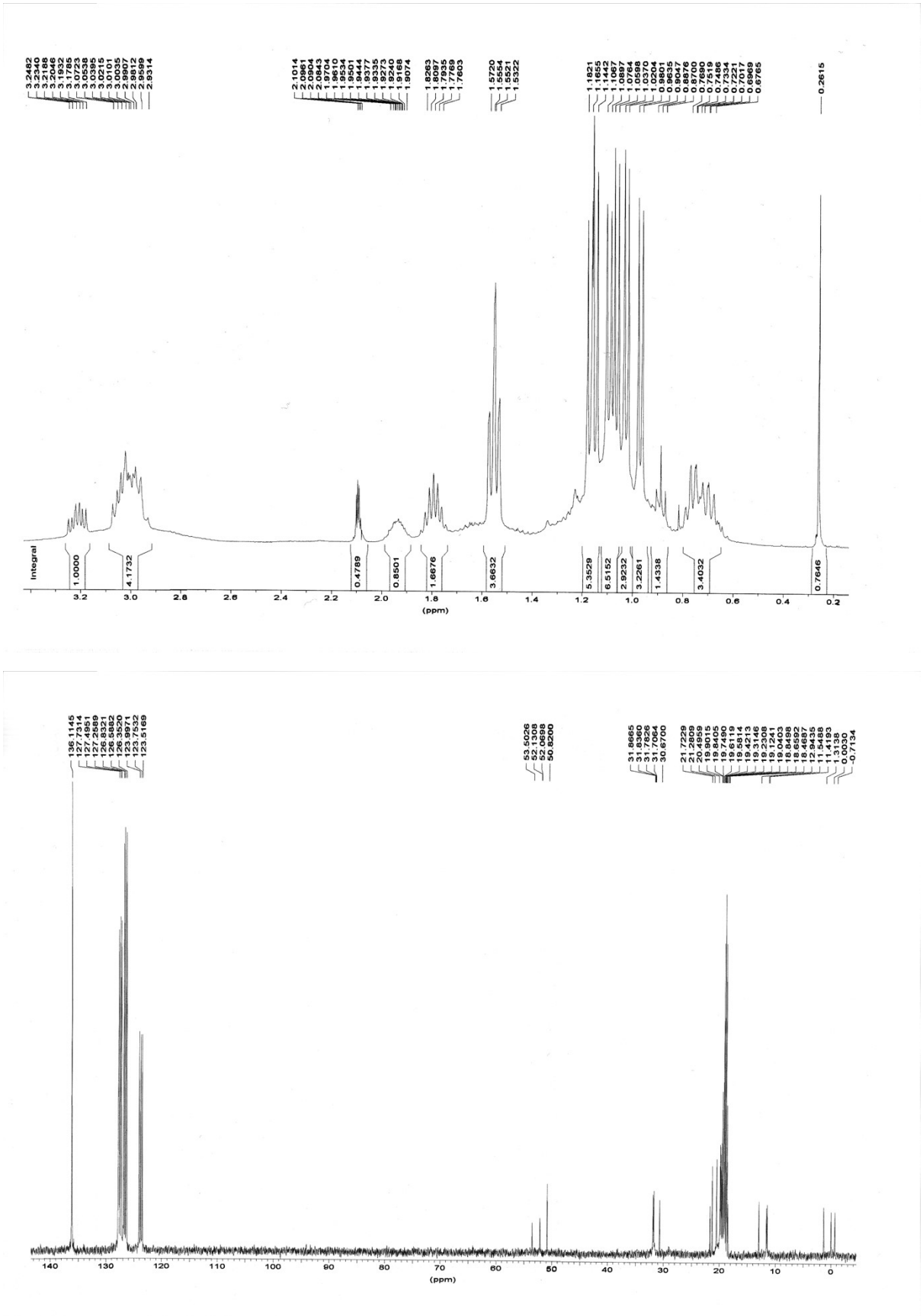

Fig. S6 ^{1}H NMR (top) and ^{13}C NMR (bottom) of redissolved crystals of **10**.

X-ray crystallography

Reflections were collected on a Bruker Smart Apex diffractometer at 150 K and a Stoe IPDS at 200 K, respectively, using monochromated MoK_α radiation (λ = 0.71073 Å). All structures were refined against F^2 with full-matrix least-squares using the SHELX programme.[S2] Crystallographic data are listed in Table S1. The crystal structures of **10** contains one molecule of hexane per formula unit. A pseudo-merohedral twin refinement was carried out for **10**. Non-hydrogen atoms were refined anisotropically. H-atoms were fixed in geometrical positions. Disorder was encountered in some alkyl groups and in the hexane molecule. Disordered atom positions were split on two positions and refined with restraints.[S1] Crystal of **8** diffracted weakly which is reflected in the high R_{sigma}. It gives nonetheless an adequate model that confirms the connectivity of atoms in the structure. The coverage for crystals is only 91.7 % ; the missing cusp of data due to rotation about one axis in conjunction with low Laue symmetry.

Crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk); deposition numbers are as follows: **5**, CCDC 2383655 ; **6**, CCDC 2383657 ; **7**, CCDC 2383658 ; **8**, CCDC 2383656 ; **9**, CCDC 2383654 ; **10**, CCDC 2383659.

S2 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3.

Table S1 Crystallographic data.

	5	**6**	**7**
formula	$C_{36}H_{96}N_{18}P_6Zn_{12}$	$C_{44}H_{110}N_{18}P_6Zn_{11}$	$C_{56}H_{134}N_{18}P_6Zn_{11}$
MW	1751.56	1796.38	1964.69
spacegroup	*P*-1	*P*-1	$P2_1/n$
a/Å	11.922(3)	12.380(3)	13.2503(18)
b/Å	12.490(3)	14.952(3)	28.806(5)
c/Å	25.336(7)	20.629(4)	22.918(3)
α/°	91.175(4)	79.43(3)	90
β/°	99.758(4)	89.22(3)	96.989(16)
γ/°	118.034(4)	79.88(3)	90
V/Å^3	3259.9(15)	3694.7(14)	8683(2)
Z	2	2	4
T/K	150(2)	200(2)	200(2)
d/g cm^{-3}	1.784	1.615	1.503
μ/mm-1	4.516	3.673	3.133
θ(max)	24.4	24.3	24.2
R_{int}	0.040	0.078	0.100
R_{sigma}	0.102	0.097	0.100
refl(unique)	10536	11004	13259
refl(>2σ(I))	5851	6921	7383
parameters	676	735	812
restraints	1200	1856	2139
*R*1(>2σ(*I*))	0.069	0.059	0.067
*wR*2(all)	0.210	0.148	0.1703

Table S1 Crystallographic data (continued).

	8	**9**	**10**
formula	$C_{60}H_{144}N_{18}P_6Zn_{12}$ · $C_{54}H_{136}N_{18}O_3P_6Zn_{13}$	$C_{36}H_{84}N_9P_3Zn_6$	$C_{64}H_{148}N_{18}P_6Zn_{10}$ · C_6H_{14}
MW	4233.63	1128.25	2095.69
spacegroup	*C*2	*P*-1	$P2_1/n$
a/Å	26.800(5)	11.703(2)	13.385(4)
b/Å	13.633(2)	12.007(3)	37.277(10)
c/Å	25.325(4)	20.205(4)	20.034(6)
α/°	90	100.408(3)	90
β/°	107.425(5)	95.061(4)	90.025(5)
γ/°	90	112.248(3)	90
V/Å^3	8828(2)	2545.8(9)	9996(5)
Z	2	2	4
T/K	150(2)	150(2)	150(2)
d/g cm^{-3}	1.593	1.472	1.393
μ/mm-1	3.483	2.909	2.494
θ (max)	24.4	25.0	28.0
R_{int}	0.115	0.053	0.060
R_{sigma}	0.297	0.030	0.083
refl(unique)	13852	8713	22777
refl(>2σ(I))	5190	7498	18673
parameter	881	491	983
restraints	2037	0	91
*R*1(>2σ(*I*))	0.082	0.047	0.050
*wR*2(all)	0.218	0.131	0.116

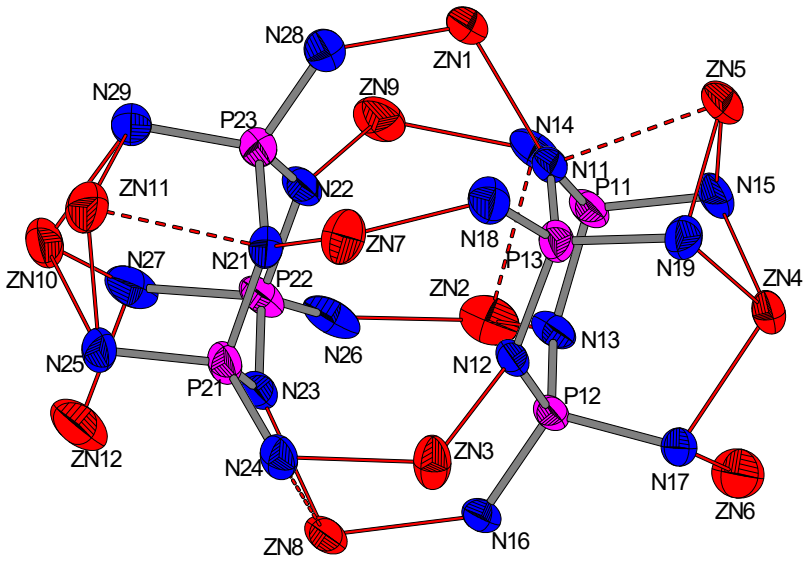

Fig. S7 Core structure of complex **5** with 30 % probability ellipsoids (methyl substituents and Zn bound ethyl groups are omitted for clarity). Selected bond lengths (Å) and angles (°):

P11	N11	1.626(8)	P22	N26	1.599(10)	Zn5	N19	2.167(10)
P11	N13	1.630(8)	P22	N27	1.723(10)	Zn6	N17	1.893(9)
P11	N14	1.622(10)	P23	N21	1.659(9)	Zn7	N18	1.949(9)
P11	N15	1.640(9)	P23	N22	1.641(9)	Zn7	N21	2.043(9)
P12	N12	1.615(8)	P23	N28	1.572(9)	Zn8	N16	2.016(8)
P12	N13	1.619(9)	P23	N29	1.651(9)	Zn8	N23	2.073(8)
P12	N16	1.602(8)	Zn1	N11	2.072(8)	Zn8	N24	2.333(9)
P12	N17	1.700(8)	Zn1	N28	1.953(8)	Zn9	N14	2.051(10)
P13	N11	1.666(9)	Zn2	N13	2.065(9)	Zn9	N22	2.014(8)
P13	N12	1.644(7)	Zn2	N14	2.400(9)	Zn10	N25	2.193(9)
P13	N18	1.592(9)	Zn2	N26	2.038(10)	Zn10	N27	2.076(13)
P13	N19	1.657(9)	Zn3	N12	2.014(7)	Zn10	N29	2.049(10)
P21	N21	1.635(9)	Zn3	N24	2.049(8)	Zn11	N21	2.466(7)
P21	N23	1.645(9)	Zn4	N15	2.190(10)	Zn11	N25	2.112(10)
P21	N24	1.629(9)	Zn4	N17	2.124(8)	Zn11	N29	2.158(10)
P21	N25	1.626(8)	Zn4	N19	2.059(9)	Zn12	N27	1.902(9)
P22	N22	1.621(8)	Zn5	N11	2.392(7)			
P22	N23	1.637(8)	Zn5	N15	2.079(10)			

P11	N11	P13	120.0(5)	N16	P12	N13	116.3(5)	N25	P21	N23	111.7(5)
P12	N12	P13	119.6(4)	N12	P12	N17	110.5(4)	N25	P21	N24	116.7(4)
P12	N13	P11	122.2(5)	N13	P12	N17	101.7(4)	N26	P22	N22	105.5(4)
P21	N21	P23	119.9(5)	N16	P12	N17	109.8(4)	N22	P22	N23	112.8(4)
P22	N22	P23	119.2(5)	N12	P13	N11	108.4(4)	N26	P22	N23	116.6(5)
P22	N23	P21	119.5(5)	N18	P13	N11	113.9(5)	N22	P22	N27	109.7(5)
N14	P11	N11	113.4(5)	N19	P13	N11	100.3(5)	N23	P22	N27	100.9(4)
N11	P11	N13	110.5(4)	N18	P13	N12	107.3(4)	N26	P22	N27	111.3(6)
N14	P11	N13	102.8(5)	N12	P13	N19	113.9(4)	N22	P23	N21	108.2(4)

			100.7(5				113.0(5				112.8(5
N11	P11	N15	)	N18	P13	N19	)	N28	P23	N21	)
			112.6(5				112.5(5				101.0(4
N13	P11	N15	)	N24	P21	N21	)	N29	P23	N21	)
			117.0(5				101.7(4				108.1(5
N14	P11	N15	)	N25	P21	N21	)	N28	P23	N22	)
			107.3(4				111.7(4				113.3(5
N16	P12	N12	)	N21	P21	N23	)	N22	P23	N29	)
			111.2(4				102.8(4				113.3(5
N12	P12	N13	)	N24	P21	N23	)	N28	P23	N29	)

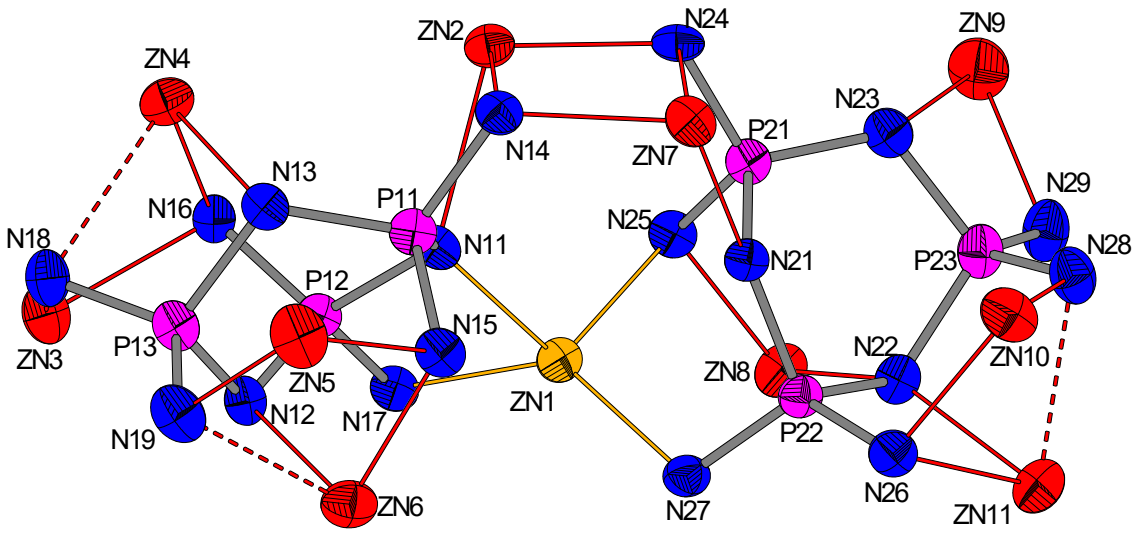

Fig. S8 Core structure of complex **6** with 30 % probability ellipsoids (ethyl substituents and Zn bound ethyl groups are omitted for clarity, Zn atoms in red are part of EtZn moieties). Selected bond lengths (Å) and angles (°):

P11	N11	1.671(5)	P22	N27	1.588(6)	Zn5	N15	2.177(6)
P11	N13	1.661(6)	P22	N21	1.639(6)	Zn5	N19	2.001(7)
P11	N14	1.637(6)	P23	N23	1.640(7)	Zn6	N12	2.123(6)
P11	N15	1.649(7)	P23	N28	1.645(7)	Zn6	N15	2.126(6)
P12	N11	1.682(6)	P23	N29	1.600(7)	Zn6	N19	2.417(7)
P12	N12	1.641(6)	P23	N22	1.671(7)	Zn7	N14	2.120(6)
P12	N16	1.647(6)	Zn1	N11	2.184(6)	Zn7	N21	2.183(6)
P12	N17	1.604(6)	Zn1	N17	1.968(6)	Zn7	N24	2.242(6)
P13	N12	1.673(6)	Zn1	N25	2.114(6)	Zn8	N22	2.059(6)
P13	N13	1.665(6)	Zn1	N27	2.002(6)	Zn8	N25	2.064(6)
P13	N18	1.604(7)	Zn2	N11	2.276(6)	Zn9	N23	2.184(6)
P13	N19	1.621(7)	Zn2	N14	2.153(6)	Zn9	N29	1.955(8)
P21	N21	1.641(6)	Zn2	N24	2.091(6)	Zn10	N26	2.082(6)
P21	N23	1.629(6)	Zn3	N16	2.139(6)	Zn10	N28	2.011(7)
P21	N24	1.632(6)	Zn3	N18	2.006(6)	Zn11	N22	2.178(6)
P21	N25	1.681(6)	Zn4	N13	2.177(6)	Zn11	N26	2.172(6)
P22	N22	1.702(6)	Zn4	N16	2.151(6)	Zn11	N28	2.345(7)
P22	N26	1.627(6)	Zn4	N18	2.412(7)			

P11	N11	P12	112.1(3)	N12	P12	N16	102.8(3)	N21	P22	N22	106.7(3)
P12	N12	P13	116.0(4	N17	P12	N16	117.8(3	N26	P22	N22	100.0(3

			)				)				)
P11	N13	P13	114.8(4)	N13	P13	N12	104.9(3)	N27	P22	N22	109.7(3)
P22	N21	P21	115.7(3)	N18	P13	N12	107.4(3)	N27	P22	N26	118.1(4)
P23	N22	P22	116.6(4)	N19	P13	N12	107.6(4)	N23	P23	N22	109.2(3)
P21	N23	P23	115.5(4)	N18	P13	N13	109.3(4)	N28	P23	N22	100.5(4)
N13	P11	N11	107.8(3)	N19	P13	N13	107.4(3)	N29	P23	N22	112.5(4)
N14	P11	N11	100.0(3)	N18	P13	N19	119.4(4)	N29	P23	N23	99.9(4)
N15	P11	N11	116.6(3)	N23	P21	N21	109.9(3)	N23	P23	N28	120.1(4)
N14	P11	N13	114.1(3)	N24	P21	N21	103.2(3)	N29	P23	N28	115.1(4)
N15	P11	N13	103.4(3)	N23	P21	N24	113.3(3)	N17	Zn1	N11	73.5(2)
N14	P11	N15	115.1(3)	N21	P21	N25	103.8(3)	N25	Zn1	N11	104.9(2)
N12	P12	N11	109.2(3)	N23	P21	N25	111.1(3)	N27	Zn1	N11	127.2(2)
N16	P12	N11	113.2(3)	N24	P21	N25	114.7(3)	N17	Zn1	N25	118.5(2)
N17	P12	N11	98.5(3)	N26	P22	N21	115.7(3)	N27	Zn1	N25	99.3(2)
N17	P12	N12	115.6(3)	N27	P22	N21	105.9(3)	N17	Zn1	N27	131.4(3)

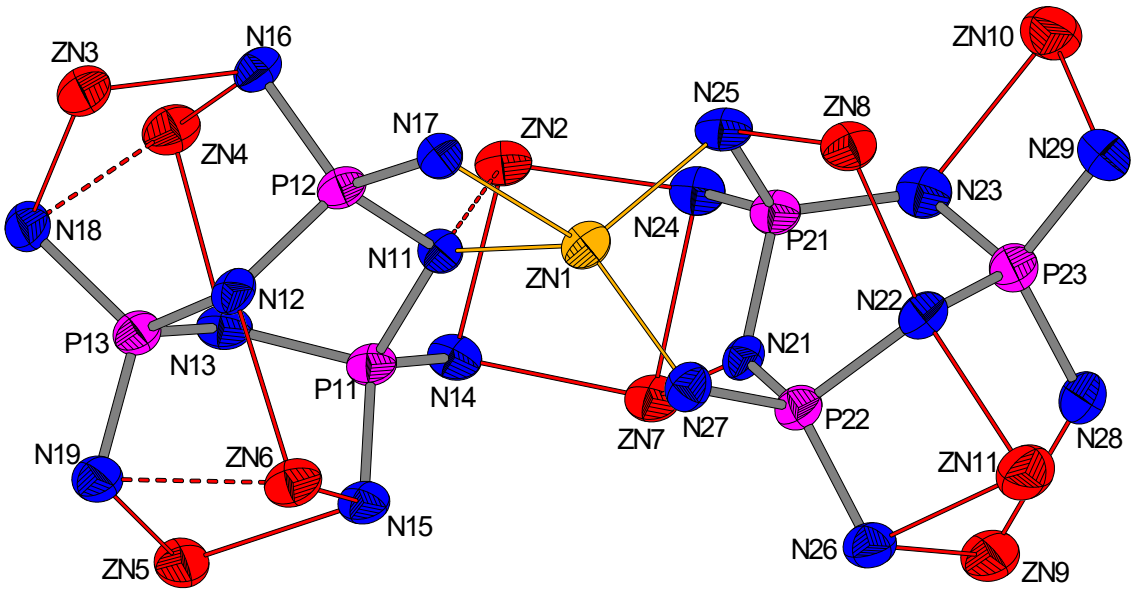

Fig. S9 Core structure of complex **6** with 30 % probability ellipsoids (propyl substituents and Zn bound ethyl groups are omitted for clarity, Zn atoms in red are part of EtZn moieties). Selected bond lengths (Å) and angles (°):

P11	N11	1.670(7)	P22	N26	1.646(7)	Zn5	N15	2.193(7)
P11	N13	1.627(8)	P22	N27	1.602(7)	Zn5	N19	2.008(7)
P11	N14	1.650(7)	P23	N22	1.677(8)	Zn6	N12	2.140(7)
P11	N15	1.614(8)	P23	N23	1.656(9)	Zn6	N15	2.130(7)
P12	N11	1.690(6)	P23	N28	1.630(8)	Zn6	N19	2.411(8)
P12	N12	1.645(7)	P23	N29	1.592(8)	Zn7	N14	2.162(7)
P12	N16	1.654(7)	Zn1	N11	2.171(7)	Zn7	N21	2.150(7)
P12	N17	1.578(7)	Zn1	N17	1.972(6)	Zn7	N24	2.257(7)
P13	N12	1.649(7)	Zn1	N25	2.107(7)	Zn8	N22	2.086(7)
P13	N13	1.687(7)	Zn1	N27	1.977(7)	Zn8	N25	2.041(7)
P13	N18	1.626(8)	Zn2	N11	2.319(7)	Zn9	N26	2.103(7)
P13	N19	1.621(8)	Zn2	N14	2.141(7)	Zn9	N28	1.966(8)
P21	N21	1.624(7)	Zn2	N24	2.092(8)	Zn10	N23	2.175(8)
P21	N23	1.610(8)	Zn3	N16	2.126(7)	Zn10	N29	1.944(9)
P21	N24	1.632(7)	Zn3	N18	2.014(7)	Zn11	N22	2.125(7)
P21	N25	1.686(6)	Zn4	N13	2.185(7)	Zn11	N26	2.132(8)
P22	N21	1.645(7)	Zn4	N16	2.135(7)			
P22	N22	1.691(8)	Zn4	N18	2.413(8)			

P11	N11	P12	111.9(4)	N12	P12	N16	102.7(4)	N26	P22	N22	98.6(4)
P12	N12	P13	115.7(4)	N17	P12	N16	117.3(4)	N27	P22	N22	111.0(4)
P11	N13	P13	115.8(5	N18	P13	N12	106.8(4	N21	P22	N26	116.8(4

			)				)				)
P21	N21	P22	115.3(4)	N19	P13	N12	108.8(4)	N27	P22	N26	117.4(4)
P23	N22	P22	117.8(4)	N12	P13	N13	104.8(4)	N23	P23	N22	108.3(4)
P21	N23	P23	115.1(5)	N18	P13	N13	109.9(4)	N28	P23	N22	102.4(4)
N13	P11	N11	107.8(3)	N19	P13	N13	106.7(4)	N29	P23	N22	112.0(4)
N14	P11	N11	100.4(3)	N19	P13	N18	119.0(4)	N28	P23	N23	119.1(4)
N15	P11	N11	117.1(4)	N23	P21	N21	111.0(4)	N29	P23	N23	99.2(4)
N15	P11	N13	102.4(4)	N21	P21	N24	102.5(4)	N29	P23	N28	116.0(4)
N13	P11	N14	114.6(4)	N23	P21	N24	112.2(4)	N17	Zn1	N11	73.5(2)
N15	P11	N14	114.9(4)	N21	P21	N25	104.6(3)	N25	Zn1	N11	103.0(3)
N12	P12	N11	109.7(3)	N23	P21	N25	110.5(4)	N27	Zn1	N11	127.4(3)
N16	P12	N11	113.2(4)	N24	P21	N25	115.4(4)	N17	Zn1	N25	115.6(3)
N17	P12	N11	98.8(3)	N27	P22	N21	106.1(3)	N27	Zn1	N25	101.6(3)
N17	P12	N12	115.4(4)	N21	P22	N22	106.2(4)	N17	Zn1	N27	132.2(3)

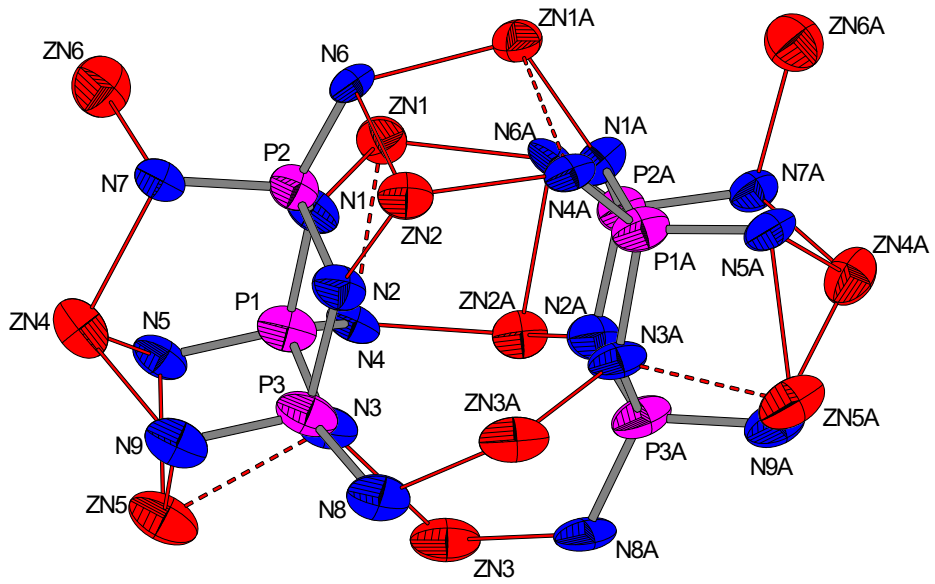

Fig. S10 Core structure of complex **8a** with 30 % probability ellipsoids (propyl substituents and Zn bound ethyl groups are omitted for clarity, Zn atoms in red are part of EtZn moieties). Selected bond lengths (Å) and angles (°):

P1	N1	1.63(2)	P3	N3	1.68(2)	Zn3	N3	2.14(3)
P1	N3	1.65(2)	P3	N8	1.60(2)	Zn3	N8a	2.00(3)
P1	N4	1.64(2)	P3	N9	1.65(2)	Zn4	N5	2.17(2)
P1	N5	1.61(2)	Zn1	N1	2.06(2)	Zn4	N7	2.17(2)
P2	N1	1.66(2)	Zn1	N4	2.31(2)	Zn4	N9	2.05(3)
P2	N2	1.61(3)	Zn1	N6a	2.11(2)	Zn5	N3	2.33(2)
P2	N6	1.62(2)	Zn2	N2	2.06(2)	Zn5	N5	2.16(2)
P2	N7	1.66(2)	Zn2	N4a	2.08(2)	Zn5	N9	2.15(2)
P3	N2	1.68(3)	Zn2	N6	2.30(2)	Zn6	N7	1.98(2)

P11	N11	P12	130.5(15)	N11	P12	N12	110.5(12)	N19	P13	N12	99.2(11)
P12	N12	P13	127.8(14)	N16	P12	N11	118.3(12)	N19	P13	N13	114.1(12)
P11	N13	P13	123.7(14)	N16	P12	N12	103.7(12)	N19	P13	N18	114.0(11)
N11	P11	N13	113.7(13)	N16	P12	N17	107.5(13)	Zn11	O1	Zn11a	112.8(12)
N11	P11	N14	102.9(12)	N17	P12	N11	104.5(13)	Zn12	O2	Zn11	111.9(8)
N11	P11	N15	112.0(12)	N17	P12	N12	112.6(14)	O1	Zn11	O2	127.3(8)
N14	P11	N13	113.2(12)	N12	P13	N13	112.9(11)	O2	Zn12	O2a	128.8(10)
N14	P11	N15	113.1(13)	N18	P13	N12	115.7(12)				
N15	P11	N13	102.4(12)	N18	P13	N13	101.7(11)				

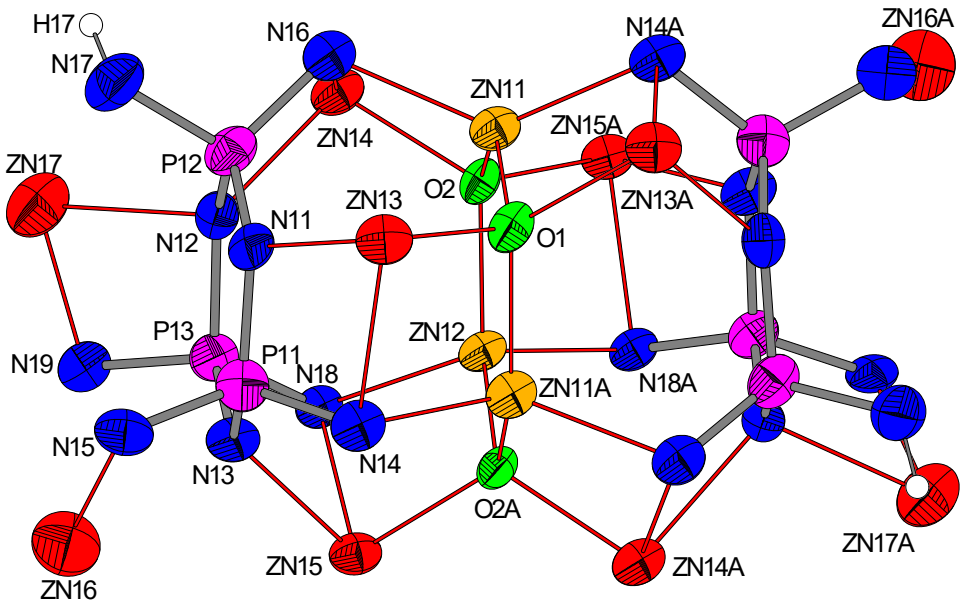

Fig. S11 Core structure of complex **8b** with 30 % probability ellipsoids (propyl substituents and Zn bound ethyl groups are omitted for clarity, Zn atoms in red are part of EtZn moieties). Selected bond lengths (Å) and angles (°):

P11	N11	1.59(2)	Zn11	N14a	2.04(2)	Zn14	N12	2.22(2)
P11	N13	1.65(2)	Zn11	N16	2.09(2)	Zn14	N16	2.24(2)
P11	N14	1.61(2)	Zn11	O1	1.968(14)	Zn14	O2	1.967(17)
P11	N15	1.62(2)	Zn11	O2	1.989(17)	Zn15	N13	2.16(2)
P12	N11	1.63(3)	Zn12	N18a	2.05(2)	Zn15	N18	2.23(2)
P12	N12	1.64(2)	Zn12	N18	2.05(2)	Zn15	O2a	1.978(18)
P12	N16	1.59(2)	Zn12	O2	1.957(18)	Zn16	N13	2.48(2)
P12	N17	1.62(2)	Zn12	O2a	1.957(18)	Zn16	N15	1.88(2)
P13	N12	1.66(2)	Zn13	N11	2.17(2)	Zn17	N12	2.28(2)
P13	N13	1.69(2)	Zn13	N14	2.30(2)	Zn17	N19	1.94(2)
P13	N18	1.66(2)	Zn13	O1	1.984(14)			
P13	N19	1.63(2)	Zn13	O1a	1.984(14)			

P11	N11	P12	130.5(15)	N11	P12	N12	110.5(12)	N19	P13	N12	99.2(11)
P12	N12	P13	127.8(14)	N16	P12	N11	118.3(12)	N19	P13	N13	114.1(12)
P11	N13	P13	123.7(14)	N16	P12	N12	103.7(12)	N19	P13	N18	114.0(11)
N11	P11	N13	113.7(13)	N16	P12	N17	107.5(13)	Zn11	O1	Zn11a	112.8(12)
N11	P11	N14	102.9(12)	N17	P12	N11	104.5(13)	Zn12	O2	Zn11	111.9(8)
N11	P11	N15	112.0(12)	N17	P12	N12	112.6(14)	O1	Zn11	O2	127.3(8)
N14	P11	N13	113.2(12)	N12	P13	N13	112.9(11)	O2	Zn12	O2a	128.8(10)
N14	P11	N15	113.1(13)	N18	P13	N12	115.7(12)				
N15	P11	N13	102.4(12	N18	P13	N13	101.7(11				

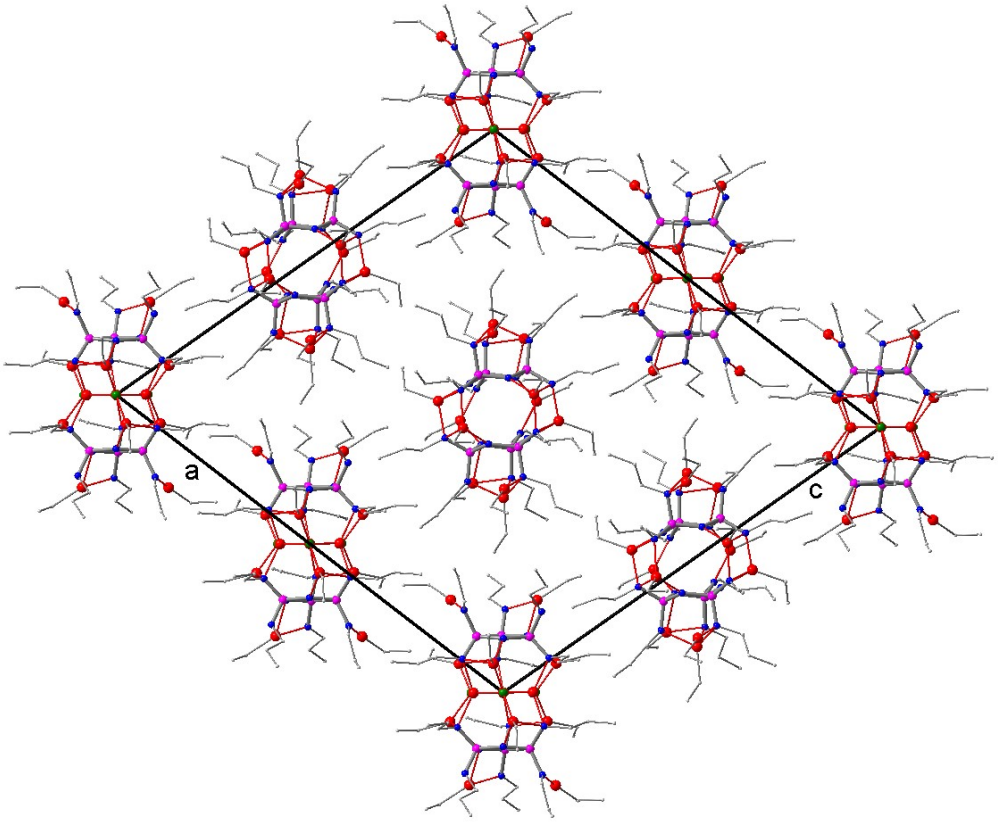

Fig. S12 Unit cell of co-crystal **8** viewed along the b-axis.

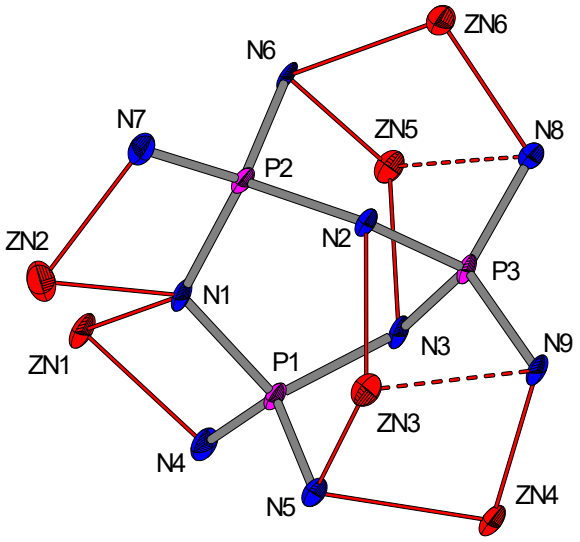

Fig. S13 Core structure of complex **6** with 30 % probability ellipsoids (isopropyl substituents and Zn bound ethyl groups are omitted for clarity). Selected bond lengths (Å) and angles (°):

P1	N1	1.671(3)	P3	N3	1.656(3)	Zn3	N9	2.306(3)
P1	N3	1.649(3)	P3	N8	1.625(3)	Zn4	N5	2.122(3)
P1	N4	1.599(3)	P3	N9	1.628(3)	Zn4	N9	2.057(3)
P1	N5	1.653(3)	Zn1	N1	2.231(3)	Zn5	N3	2.136(3)
P2	N1	1.670(3)	Zn1	N4	1.920(3)	Zn5	N6	2.235(3)
P2	N2	1.653(3)	Zn2	N1	2.248(3)	Zn5	N8	2.296(3)
P2	N6	1.655(3)	Zn2	N7	1.920(3)	Zn6	N6	2.091(3)
P2	N7	1.606(3)	Zn3	N2	2.132(3)	Zn6	N8	2.069(3)
P3	N2	1.660(3)	Zn3	N5	2.179(3)			

P2	N1	P1	114.58(17)	N7	P2	N1	98.80(16)	N7	Zn2	N1	72.80(12)
P2	N2	P3	115.58(18)	N7	P2	N2	115.22(16)	N2	Zn3	N5	98.23(11)
P1	N3	P3	115.81(19)	N2	P2	N6	101.72(15)	N2	Zn3	N9	72.03(11)
N3	P1	N1	108.78(16)	N7	P2	N6	117.35(16)	N5	Zn3	N9	83.27(11)
N4	P1	N1	99.25(16)	N3	P3	N2	107.34(15)	N9	Zn4	N5	91.00(12)
N5	P1	N1	114.81(16)	N8	P3	N2	107.85(16)	N3	Zn5	N6	97.03(11)
N4	P1	N3	114.89(16)	N9	P3	N2	105.28(15)	N3	Zn5	N8	72.31(11)
N3	P1	N5	102.24(15)	N8	P3	N3	105.87(16)	N6	Zn5	N8	81.72(11)
N4	P1	N5	117.16(16)	N9	P3	N3	107.59(15)	N8	Zn6	N6	90.90(12)
N2	P2	N1	108.49(15)	N8	P3	N9	122.17(16)				
N6	P2	N1	115.61(16)	N4	Zn1	N1	73.35(12)				

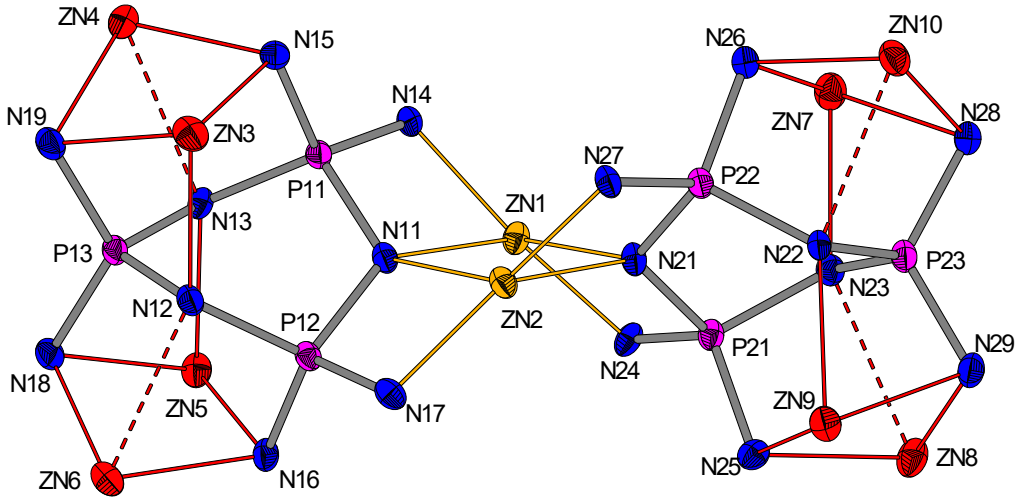

Fig. S14 Core structure of complex **10** with 30 % probability ellipsoids (isopropyl substituents and Zn bound ethyl groups are omitted for clarity, Zn atoms in red are part of EtZn moieties). Selected bond lengths (Å) and angles (°):

P11	N11	1.657(4)	P22	N27	1.605(4)	Zn5	N13	2.182(4)
P11	N13	1.647(4)	P23	N22	1.652(4)	Zn5	N16	2.181(4)
P11	N14	1.602(4)	P23	N23	1.654(4)	Zn5	N18	2.226(4)
P11	N15	1.656(4)	P23	N28	1.631(4)	Zn6	N12	2.479(4)
P12	N11	1.658(4)	P23	N29	1.618(4)	Zn6	N16	2.114(4)
P12	N12	1.650(4)	Zn1	N11	2.201(4)	Zn6	N18	2.071(4)
P12	N16	1.665(4)	Zn1	N14	1.945(4)	Zn7	N23	2.166(4)
P12	N17	1.607(4)	Zn1	N21	2.220(4)	Zn7	N26	2.201(4)
P13	N12	1.655(4)	Zn1	N24	1.933(4)	Zn7	N28	2.220(4)
P13	N13	1.666(4)	Zn2	N11	2.221(4)	Zn8	N23	2.481(4)
P13	N18	1.631(4)	Zn2	N17	1.933(4)	Zn8	N25	2.108(4)
P13	N19	1.620(4)	Zn2	N21	2.195(4)	Zn8	N29	2.077(4)
P21	N21	1.655(4)	Zn2	N27	1.933(4)	Zn9	N22	2.165(4)
P21	N23	1.662(4)	Zn3	N12	2.175(4)	Zn9	N25	2.201(4)
P21	N24	1.611(4)	Zn3	N15	2.170(4)	Zn9	N29	2.230(4)
P21	N25	1.648(4)	Zn3	N19	2.247(4)	Zn10	N22	2.453(4)
P22	N21	1.660(4)	Zn4	N13	2.463(4)	Zn10	N26	2.101(4)
P22	N22	1.663(4)	Zn4	N15	2.115(4)	Zn10	N28	2.090(4)
P22	N26	1.651(4)	Zn4	N19	2.073(4)			

P11	N11	P12	116.6(2)	N18	P13	N12	106.9(2)	N28	P23	N22	107.2(2)
P12	N12	P13	115.3(2)	N19	P13	N12	106.8(2)	N29	P23	N22	106.4(2)
P11	N13	P13	115.7(2)	N12	P13	N13	107.68(19)	N22	P23	N23	108.5(2)

P21	N21	P22	116.4(2)	N18	P13	N13	106.2(2)	N28	P23	N23	105.8(2)
P23	N22	P22	115.1(2)	N19	P13	N13	106.6(2)	N29	P23	N23	107.1(2)
P23	N23	P21	114.8(3)	N19	P13	N18	122.0(2)	N29	P23	N28	121.3(2)
N13	P11	N11	107.5(2)	N24	P21	N21	98.4(2)	N14	Zn1	N11	72.85(15)
N14	P11	N11	98.6(2)	N25	P21	N21	116.4(2)	N24	Zn1	N11	130.84(16)
N15	P11	N11	116.0(2)	N21	P21	N23	107.9(2)	N24	Zn1	N14	152.16(17)
N14	P11	N13	117.7(2)	N24	P21	N23	117.7(2)	N11	Zn1	N21	86.72(14)
N13	P11	N15	100.6(2)	N25	P21	N23	100.7(2)	N14	Zn1	N21	129.59(16)
N14	P11	N15	117.0(2)	N24	P21	N25	116.3(2)	N24	Zn1	N21	72.69(15)
N12	P12	N11	107.9(2)	N26	P22	N21	115.8(2)	N17	Zn2	N11	72.85(16)
N17	P12	N11	98.7(2)	N27	P22	N21	98.5(2)	N21	Zn2	N11	86.85(14)
N17	P12	N12	117.2(2)	N21	P22	N22	107.7(2)	N27	Zn2	N11	130.14(16)
N11	P12	N16	115.8(2)	N26	P22	N22	100.3(2)	N27	Zn2	N17	150.72(16)
N12	P12	N16	101.32(19)	N27	P22	N22	118.1(2)	N17	Zn2	N21	132.00(16)
N17	P12	N16	116.3(2)	N27	P22	N26	117.0(2)	N27	Zn2	N21	73.34(15)

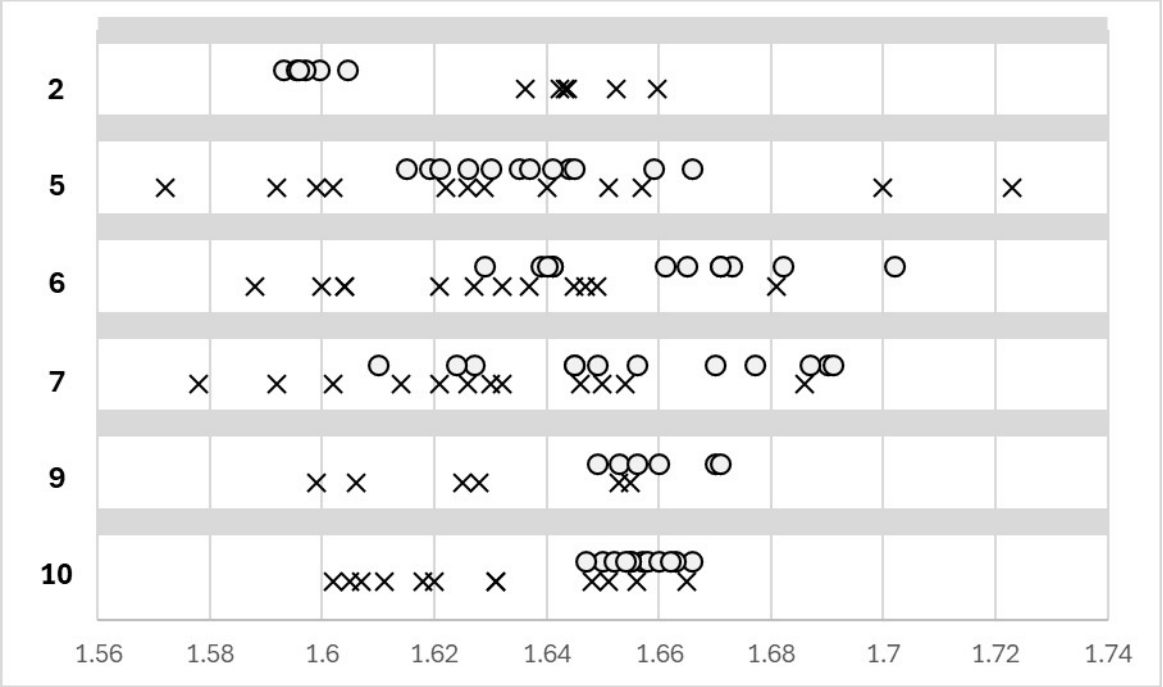

Fig. S15 Distribution of P-N bond lengths (Å) in crystal structures of **2**, **5**, **6**, **7**, **9** and **10**. Circles represent P-N(ring) bonds, crosses P-N(exo) bonds.

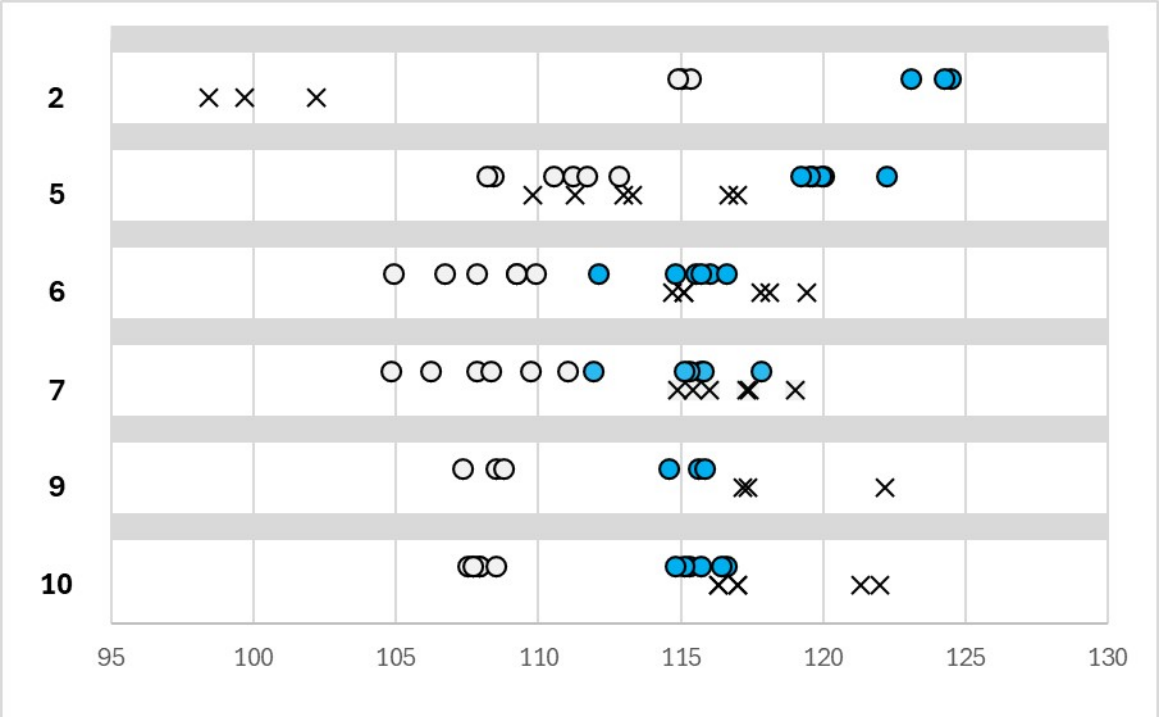

Fig. S16 Distribution of bond angles (°) in crystal structures of **2**, **5**, **6**, **7**, **9** and **10**.. Circles represent angles in the ring (N-P-N, grey; P-N-P, blue), crosses N(exo)-P-N(exo) angles.

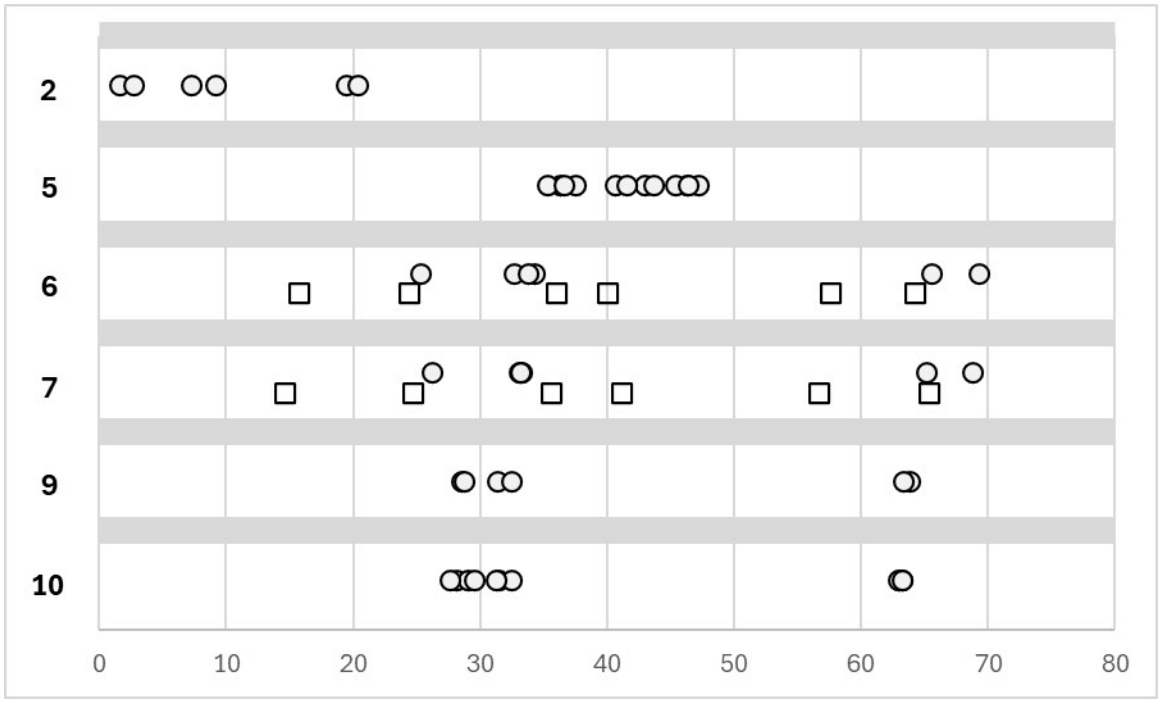

Fig. S17 Distribution of phosphazene ring torsion angles (°) in crystal structures of **2**, **5**, **6**, **7**, **9** and **10**. For **6** and **7** circles represent rings with twist, squares rings with *twist-boat* conformation.

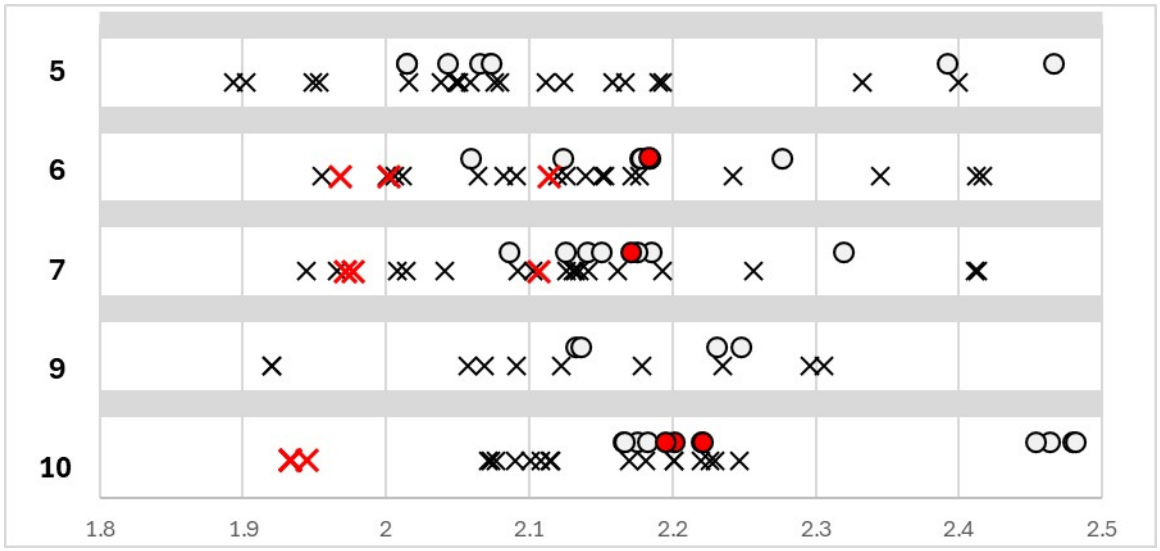

Fig. S18 Distribution of Zn-N bond lengths (Å) in crystal structures of **5**, **6**, **7**, **9** and **10**. Circles represent Zn-N(ring) bonds, crosses Zn-N(exo) bonds. Ticks marked in red denote bonds involving Zn atoms that do not bear ethyl groups.

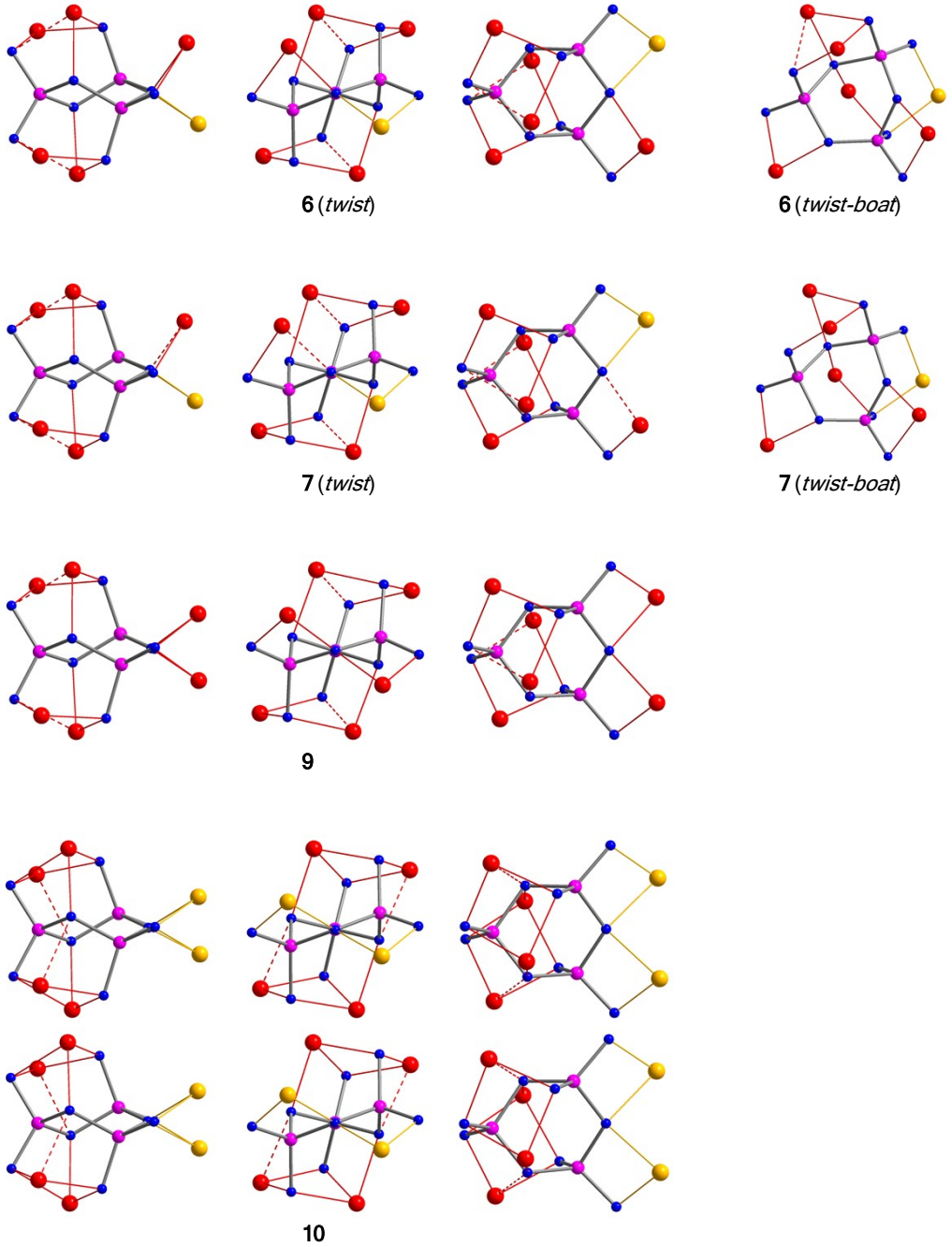

Fig. S19 The three columns on the left show different views of the coordination pattern of *twist* conformers. The fourth column shows the coordination pattern of *twist-boat* conformers found in **6** and **7**. Alkyl substituents and zinc bound ethyl groups are omitted for clarity; Zn atoms in red are part of EtZn moieties, those in yellow do not bear ethyl groups.

Ring puckering parameters

Ring puckering parameters of the phosphazene rings were calculated according to Cremer and Pople.[S3] The puckering of a six-membered ring is defined by three parameters. In polar coordinates these are Q, θ and ϕ. Q is the total puckering amplitude, while the angles θ and ϕ determine the ring conformation. At $Q = 0$, the ring is planar. On a sphere with radius Q, the angles θ and ϕ define latitude and longitude, respectively. Positions at the poles ($\theta = 0°$ and 180°) correspond to a *chair* conformation, while *boat* and *twist* conformations are found at the equator ($\theta = 90°$); the *boat* occurs at phase angles $\phi = 0$, 60, 120, 180, 240, 300° and the *twist* at $\phi = 30$, 90, 150, 210, 270, 330°. Note that at $\theta = 0°$ and 180° ϕ is not defined.

Table S7 lists puckering parameters of EtZn complexes that are based on coordinates obtained from X-ray structure analysis. Angles θ and ϕ are normalised to $0° < \theta < 90°$ and $0° < \phi < 30°$, respectively.

Table S2 Puckering parameters of and conformations phosphazene rings in EtZn complexes.

	Q	θ (°)	ϕ (°)	ring conformation
5	0.442	10.2	7.5	*chair*
	0.449	11.1	6.9	*chair*
6	0.840	88.3	27.3	*twist*
	0.776	88.3	20.1	*twist-boat*
7	0.826	88.7	28.0	*twist*
	0.767	88.0	20.5	*twist-boat*
8a	0.467	6.0	19.4	*chair*
9	0.801	89.7	29.6	*twist*
10	0.805	89.9	29.5	*twist*
	0.811	89.8	29.3	*twist*

S3 D. Cremer, J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.

Appendix

^{1}H and ^{13}C NMR spectra of **5**, **6** and **7** have been presented in the PhD thesis "Phosphazenate ligands as stable platforms for multinuclear organometallic arryas" by Philip I. Richards; $[(ZnEt)_6A]_2$ refers to **5**, $(Zn)(ZnEt)_6B_2$ to **6** and $(Zn)(ZnEt)_6E_2$ to **7**.

8.4 Zinc complexes.

$[(ZnEt)_6A]_2$.

1g (3.17×10^{-3} mol) of the hexakis(methylamino) cyclotriphosphazene, AH_6, are suspended in 20 mL of thf. To this suspension is added 19.35 mL (19.35×10^{-3} mol, 6.1eq) of $ZnEt_2$. The solution is heated to reflux for 15 mins. During which time the suspension dissolves to leave a clear solution.

Single crystals suitable for x-ray diffraction are collected from a thf/hexane solution at -20°C.

Yield 2.39g (86%)

^{1}H NMR (400.13MHz, d^8toluene, 25°C, TMS): δ = 0.39 ppm (m, 24H, $ZnCH_2CH_3$), 1.29 ppm (m, 36H, $ZnCH_2CH_3$), 2.52 ppm (br, 36H, NCH_3).

$^{13}C\{^{1}H\}$ NMR (100.62MHz, d^8toluene, 25°C, TMS): δ = 11.8 ppm (m, 12C, $ZnCH_2CH_3$), 32.15 ppm (m, 12C, $ZnCH_2CH_3$), 32.1 ppm (br, 12C, NCH_3).

^{31}P NMR (161.97MHz, Toluene, 25°C, 85% H_3PO_4): δ = 44.95 ppm (^{2}J = 8.47 Hz, second coupling not seen), 37.71 ppm (^{2}J = 8.47 Hz, ^{2}J = 28.83 Hz) and 26.75 ppm (^{2}J = 28.83 Hz, other coupling not seen).

IR (Nujol): ν(cm^{-1}) = 1165, 1056 (P-N stretch), 905, 832, 658.

Elemental analysis $P_6N_{18}C_{36}H_{96}Zn_{12}$ (1751.80): calcd. C 24.68, H 5.52, N 14.40; found C 24.72, H 5.41, N 12.41.

m.p. = +350°C, blackens at 190°C.

Chemical Formula	$C_{36}H_{96}N_{18}P_6Zn_{12}$	V/ Å^3	3270.1(14)
FW	1751.80	Z	4
Crystal system	Triclinic	ρ_{calc}/g cm^{-3}	1.779
Space group	P-1	T/K	150(2)
a/ Å	11.937(3)	$\lambda(MoK_\alpha)$/ Å	0.71073
b/ Å	12.505(3)	$\mu(MoK_\alpha)$mm^{-1}	4.502
c/ Å	25.365(7)	Data/parameters	8463 / 673
α /°	91.181(4)	$R_1(I>2\sigma(I))$	0.0665
β /°	99.781(4)	wR^2(all data)	0.2192
γ /°	118.070(4)		

(Zn)(ZnEt)$_{10}$*B*.

1g (2.50 x10^{-3} mol) of the hexakis(ethylamino) cyclotriphosphazene, ***B***H$_6$, are suspended in 20 mL of hexane. To this suspension is added 15.27 mL (15.27 x10^{-3} mol, 6.1 eq) of $ZnEt_2$. The solution is heated to reflux for 15 mins. During which time the suspension dissolves to leave a clear solution.

Single crystals suitable for x-ray diffraction are collected from a hexane solution at 25°C.

Yield 1.71g (76%)

^{1}H NMR (400.13MHz, d^{8}toluene, 25°C, TMS): δ = 0.67 ppm (m, 20H, $ZnCH_2CH_3$), 1.28 ppm (m, 30H, $ZnCH_2CH_3$), 1.28 – 1.49 ppm (m, 18H, NCH_2CH_3), 3.13 ppm (m, 12H, NCH_2CH_3).

^{13}C{^{1}H} NMR (100.62MHz, d^{8}toluene, 25°C, TMS): δ = 12.7 ppm (m, 10C, $ZnCH_2CH_3$), 18 ppm (br, 12C, NCH_2CH_3), 30.3 ppm (m, 10C, $ZnCH_2CH_3$), 40.5 ppm (br, 12C, NCH_2CH_3).

^{31}P NMR (161.97MHz, Toluene, 25°C, 85% H_3PO_4): δ = 44.74, 39.49 ppm (Coupling not observed).

IR (Nujol): $\nu(cm^{-1})$ = 1258, 1093 (P-N stretch), 1043 (P-N stretch), 874, 796.

Elemental analysis $P_6N_{18}C_{44}H_{110}Zn_{11}$ (1796.38): calcd. C 29.42, H 6.17, N 14.04; found C 29.03, H 6.03, N 12.35.

m.p. = 118°C accompanied by a blackening transition.

Chemical Formula	$C_{44}H_{110}N_{18}P_6Zn_{11}$	V/ Å^3	7396(3)
FW	1796.38	Z	8
Crystal system	Monoclinic	ρ_{calc}/g cm^{-3}	1.724
Space group	P2(1)/c	T/K	150(2)
a/ Å	20.369(4)	$\lambda(MoK_\alpha)$/ Å	0.71073
b/ Å	12.655(3)	$\mu(MoK_\alpha)$mm^{-1}	3.989
c/ Å	28.711(6)	Data/parameters	9585 / 767
α /°	90.00	$R_1(I>2\sigma(I))$	0.0392
β /°	91.98(3)	wR^2(all data)	0.1145
γ /°	90.00		

$(Zn)(ZnEt)_{10}E$.

1g (2.07 x10^{-3} mol) of the hexakis(*n*-propylamino) cyclotriphosphazene, EH_6, are dissolved in 20 mL of hexane. To this solution is added 12.61 mL (12.61 x10^{-3} mol, 6.1eq) of $ZnEt_2$. The solution is heated to reflux for 2 h.

Single crystals suitable for x-ray diffraction are collected from a hexane solution at -20°C.

Yield 1.67g (82%)

^{1}H NMR (400.13MHz, d^{8}toluene, 25°C, TMS): δ = 0.65 ppm (m, 20H, $ZnCH_2CH_3$), 0.75 ppm (m, 36H, $NCH_2CH_2CH_3$), 1.10 ppm (m, 30H, $ZnCH_2CH_3$), 1.34 ppm (m, 24H, $NCH_2CH_2CH_3$), 2.90 ppm (m, 24H, $NCH_2CH_2CH_3$).

^{13}C{^{1}H} NMR (100.62MHz, d^{8}toluene, 25°C, TMS): δ = 11.9 ppm (m, 10C, $ZnCH_2CH_3$), 12 ppm (br, 12C, $NCH_2CH_2CH_3$), 30.3 ppm (m, 10C, $ZnCH_2CH_3$), 30.5 ppm (br, 12C, $NCH_2CH_2CH_3$), 42 ppm (br, 12C, $NCH_2CH_2CH_3$).

^{31}P NMR (161.97MHz, Toluene, 25°C, 85% H_3PO_4): δ = 45.21, 38.85 ppm (Coupling not observed).

IR (Nujol): ν(cm^{-1}) = 1258, 1089 (P-N stretch), 1019 (P-N stretch), 943, 868, 801.

Elemental analysis $P_6N_{18}C_{56}H_{134}Zn_{11}$ (1964.69): calcd. C 34.23, H 6.87, N 12.84; found C 30.10, H 6.79, N 7.63.

m.p. = 142°C accompanied by a blackening transition.

Chemical Formula	$C_{56}H_{134}N_{18}P_6Zn_{11}$	V/ Å^3	8684(4)
FW	1964.69	Z	4
Crystal system	Monoclinic	ρ_{calc}/g cm^{-3}	2.241
Space group	P2(1)/n	T/K	150(2)
a/ Å	13.276(2)	λ(MoK$_\alpha$)/ Å	0.71073
b/ Å	28.803(11)	μ(MoK$_\alpha$)mm^{-1}	6.894
c/ Å	22.877(4)	Data/parameters	11036 / 880
α /°	90.00	$R_1(I>2\sigma(I))$	0.0664
β /°	96.93(2)	wR^2(all data)	0.1743
γ /°	90.00		