Supporting Information for

Proton storage in the periphery of zirconium(IV) porphyrinogen

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Index *Page*

Experimental Procedures

Materials and Methods. The compounds were handled, reactions were performed, and analytical samples were prepared in the inert atmosphere provided by standard Schlenk, dry-box and vacuum-line techniques. Solvents were purchased from VWR Scientific Products and purified using a Braun solvent purification system or using standard solvent purification techniques.[1] Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, dried and distilled. Reagents were purchased from Strem and used as received. Elemental analyses were conducted at H. Kolbe Mikroanalytisches Laboratorium (Mühlheim a. d. Ruhr, Germany). ^{1}H-NMR spectra were recorded at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Varian Inova-500 spectrometer. ^{1}H NMR chemical shifts are quoted in ppm relative to tetramethylsilane and spectra have been internally calibrated to the monoprotio impurity of the deuterated solvent.

Synthesis of $LZr^{IV}(NHMe_2)(THF)$. Samples of $Zr(NMe_2)_4$ (0.99 g, 3.7 mmol) and LH_4 (1.59 g, 3.7 mmol) were dissolved in 15 mL of THF and refluxed for 3 hr, then the volatiles were removed *in vacuo*. The canary yellow crude solid was redissolved in a minimum of THF and layered with pentane to yield (after drying) 0.61 g of yellow-orange crystals overnight. A second, 0.75-g crop, analytically identical to the first, was obtained from the supernatant to reach a combined yield of 58%. Characterization data for $LZr^{IV}(NHMe_2)(THF)$ is as follows. ^{1}H NMR (500 MHz, C_6D_6): δ/ppm = 6.29 (s, 8H, pyrrole), 3.54 (br s, 4H, α-THF), 3.45 (br s, $NHMe_2$), 1.77 (s, 12H, $-CH_3$), 1.74 (s, 12H, $-CH_3$), 1.39 (br s, 4H, β-THF). Anal. Calcd for $C_{34}H_{47}N_5OZr$: C, 64.51; H, 7.48; N, 11.06. Found: C, 64.68; H, 7.55; N, 10.96.

Synthesis of $[HLZr^{IV}]_2O$. $LZr^{IV}(NHMe_2)(THF)$ (100 mg, 0.158 mmol) was dissolved in 1 mL of dry THF; H_2O (1.42 μL, 0.5 eq) was added to the solution via a microsyringe. The solution was allowed to react for 3 h at room temperature. Solvent was removed *in vacuo* to give the yellow-orange product in variable yields, ranging from 55-80%. LH_4 was a byproduct in the reaction. Characterization data for $[HLZr^{IV}]_2O$ is as follows. ^{1}H NMR (500 MHz, C_6D_6): δ/ppm = 7.18 (d, 2H, J = 5 Hz, α-H-pyrrole), 6.32 (dd, 2H, J = 5 Hz, 1 Hz, α-H-pyrrole), 6.27 (d, 2H, J = 3 Hz, pyrrole), 6.23 (d, 2H, J = 3 Hz, pyrrole), 6.18 (d, 2H, J = 3 Hz, pyrrole), 6.02 (d, 2H, J = 3 Hz, pyrrole), 5.63 (d, 2H, J = 3 Hz, pyrrole), 5.58 (d, 2H, J = 3 Hz, pyrrole), 4.10 (s, 2H, α-H-pyrrole), 1.94 (s, 6H, $-CH_3$), 1.86 (s, 6H $-CH_3$), 1.80 (s, 6H, $-CH_3$), 1.62 (s, 6H, $-CH_3$), 1.54 (s, 6H, $-CH_3$), 1.53 (s, 6H, $-CH_3$), 1.28 (s, 6H, $-CH_3$), 0.48 (s, 6H, $-CH_3$).

X-ray crystal structure determinations. X-ray quality crystals were coated with Paratone N oil and mounted on a glass fiber. Diffraction data were collected on a Siemens diffractometer equipped with a CCD detector, using the Mo Kα radiation, selected by a graphite monochromator. The data were integrated to *hkℓ*-intensity and the final unit cell calculated using the program SAINT from Siemens. Solution and refinement were performed with the SHELXTL

[1] Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinmann: Oxford, 1996

suite of programs developed by G. M. Sheldrick and Siemens Industrial Automation, 1995. Least-squares refinements were applied to F^2, with hydrogen atoms placed at calculated positions using a standard riding model and refined isotropically. No absorption correction was performed. Yellow crystals of [$LZr^{IV}(NHMe_2)(THF)$] were grown from a concentrated solution in THF/toluene/pentane. The structure was solved by Patterson's method. Yellow-orange crystals of $[HLZr^{IV}]_2O$ were grown by diffusion of hexane vapor into a solution of [$LZr^{IV}(NHMe_2)(THF)$] in wet THF. The structure was solved by direct methods. The refinement of both structures proceeded and converged normally.

Table S1. Crystal data, structure solution and refinement for $LZr(NHMe_2)(THF)$.

empirical formula	$C_{34}H_{47}N_5OZr$
formula weight	632.99
T (K)	100(2)
λ (Å)	0.71073
crystal system	Monoclinic
space group	$C2/c$
a (Å)	19.8193(11)
b (Å)	17.7496(10)
c (Å)	18.6897(11)
α (deg)	90
β (deg)	109.9060(10)
γ (deg)	90
V (Å^3)	6181.9(6)
Z	8
ρ_{calcd} (g cm^{-3})	1.360
crystal size (mm^3)	0.08 × 0.05 × 0.05
abs coeff (mm^{-1})	0.391
F(000)	2672
θ range for data collection	1.58 to 23.27°
limiting indices	$-21 \le h \le 22$, $-17 \le k \le 19$, $-20 \le \ell \le 20$
no. of reflns collcd	14952
no. of ind reflns (R_{int})	4449 (0.0584)
completeness to θ = 23.27°	99.9 %
absorption corr	none
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	4449 / 0 / 558
$R1$,[a] $wR2$[b] [$I > 2\sigma$]	0.0319, 0.0743
$R1$,[a] $wR2$[b] (all data)	0.0411, 0.0791
GOF[c] on F^2	1.041
largest diff. peak and hole	0.525 and –0.254 eÅ^{-3}

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{1/2}$. [c] $GOF = (\Sigma\, w(F_o^2 - F_c^2)^2/(n-p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

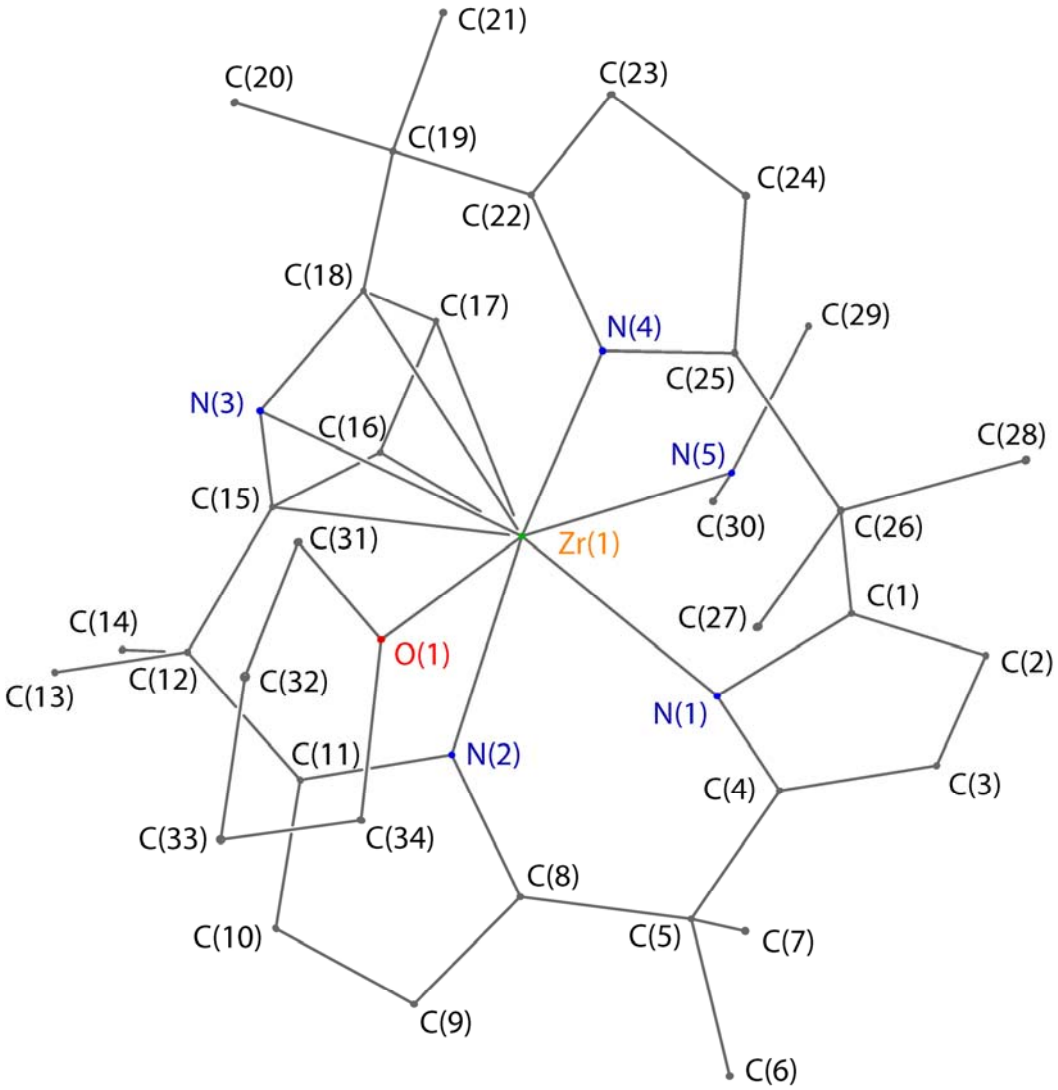

Figure S2. Atom numbering scheme for $LZr(NHMe_2)(THF)$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $LZr(NHMe_2)(THF)$.

Atom	x	y	z	U_{eq} [a]
Zr(1)	2220(1)	135(1)	5995(1)	16(1)
N(1)	2364(1)	–1029(1)	6495(1)	19(1)
N(2)	1379(1)	162(1)	6534(1)	19(1)
N(3)	2421(1)	1518(1)	5997(1)	25(1)
N(4)	3250(1)	–27(1)	5801(1)	20(1)
N(5)	1644(1)	–636(2)	4907(1)	25(1)
O(1)	2970(1)	437(1)	7204(1)	22(1)
C(1)	2794(2)	–1498(2)	6226(2)	22(1)
C(2)	2421(2)	–2138(2)	5922(2)	27(1)
C(3)	1747(2)	–2097(2)	6014(2)	24(1)
C(4)	1726(1)	–1432(2)	6377(2)	20(1)
C(5)	1187(1)	–1228(2)	6758(2)	21(1)
C(6)	1377(2)	–1677(2)	7501(2)	30(1)
C(7)	427(2)	–1467(2)	6237(2)	32(1)
C(8)	1165(1)	–399(2)	6934(2)	21(1)
C(9)	864(2)	–75(2)	7419(2)	26(1)
C(10)	880(2)	713(2)	7326(2)	27(1)
C(11)	1190(1)	846(2)	6789(2)	22(1)
C(12)	1377(2)	1595(2)	6513(2)	23(1)
C(13)	1912(2)	2029(2)	7177(2)	27(1)
C(14)	695(2)	2073(2)	6171(2)	28(1)
C(15)	1704(1)	1428(2)	5911(2)	19(1)
C(16)	1348(2)	1110(2)	5199(2)	22(1)
C(17)	1851(2)	1018(2)	4839(2)	22(1)
C(18)	2503(2)	1278(2)	5325(2)	21(1)
C(19)	3214(2)	1262(2)	5197(2)	21(1)
C(20)	3693(2)	1917(2)	5625(2)	31(1)
C(21)	3083(2)	1349(2)	4343(2)	30(1)
C(22)	3570(1)	507(2)	5471(2)	20(1)
C(23)	4203(2)	239(2)	5441(2)	26(1)
C(24)	4295(2)	–495(2)	5759(2)	26(1)
C(25)	3713(2)	–644(2)	5973(2)	22(1)
C(26)	3583(2)	–1328(2)	6393(2)	27(1)
C(27)	3931(2)	–1196(2)	7258(2)	33(1)
C(28)	3944(2)	–2013(2)	6180(2)	38(1)
C(29)	2028(2)	–757(2)	4361(2)	32(1)
C(30)	866(2)	–530(2)	4491(2)	33(1)
C(31)	3664(2)	823(2)	7404(2)	30(1)
C(32)	4005(2)	726(2)	8251(2)	39(1)
C(33)	3379(2)	665(2)	8530(2)	35(1)
C(34)	2842(2)	219(2)	7908(2)	26(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Bond lengths (in Å) for $LZr(NHMe_2)(THF)$.

Bond	Distance	Bond	Distance
Zr(1)—N(4)	2.211(2)	C(5)—C(8)	1.511(4)
Zr(1)—N(2)	2.223(2)	C(5)—C(6)	1.533(4)
Zr(1)—N(1)	2.247(2)	C(5)—C(7)	1.550(4)
Zr(1)—O(1)	2.3059(18)	C(8)—C(9)	1.370(4)
Zr(1)—N(5)	2.394(2)	C(9)—C(10)	1.411(4)
Zr(1)—N(3)	2.485(2)	C(10)—C(11)	1.365(4)
Zr(1)—C(15)	2.495(3)	C(11)—C(12)	1.517(4)
Zr(1)—C(16)	2.538(3)	C(12)—C(15)	1.506(4)
Zr(1)—C(18)	2.543(3)	C(12)—C(13)	1.537(4)
Zr(1)—C(17)	2.566(3)	C(12)—C(14)	1.539(4)
N(1)—C(1)	1.401(3)	C(15)—C(16)	1.396(4)
N(1)—C(4)	1.401(3)	C(16)—C(17)	1.389(4)
N(2)—C(8)	1.394(4)	C(17)—C(18)	1.381(4)
N(2)—C(11)	1.400(4)	C(18)—C(19)	1.507(4)
N(3)—C(15)	1.384(4)	C(19)—C(22)	1.519(4)
N(3)—C(18)	1.387(4)	C(19)—C(21)	1.537(4)
N(4)—C(25)	1.394(4)	C(19)—C(20)	1.541(4)
N(4)—C(22)	1.394(4)	C(22)—C(23)	1.363(4)
N(5)—C(29)	1.482(4)	C(23)—C(24)	1.419(4)
N(5)—C(30)	1.484(4)	C(24)—C(25)	1.371(4)
O(1)—C(31)	1.467(4)	C(25)—C(26)	1.513(4)
O(1)—C(34)	1.472(3)	C(26)—C(28)	1.530(4)
C(1)—C(2)	1.369(4)	C(26)—C(27)	1.544(5)
C(1)—C(26)	1.518(4)	C(31)—C(32)	1.505(5)
C(2)—C(3)	1.407(4)	C(32)—C(33)	1.505(5)
C(3)—C(4)	1.369(4)	C(33)—C(34)	1.505(4)
C(4)—C(5)	1.515(4)		

Table S4. Bond angles (in deg) for $LZr(NHMe_2)(THF)$.

Bond Angle	Angle	Bond Angle	Angle
N(4)–Zr(1)–N(2)	162.57(8)	C(4)–C(3)–C(2)	107.2(3)
N(4)–Zr(1)–N(1)	87.45(8)	C(3)–C(4)–N(1)	109.9(2)
N(2)–Zr(1)–N(1)	80.69(8)	C(3)–C(4)–C(5)	125.7(3)
N(4)–Zr(1)–O(1)	82.44(8)	N(1)–C(4)–C(5)	123.1(2)
N(2)–Zr(1)–O(1)	83.26(7)	C(8)–C(5)–C(4)	114.3(2)
N(1)–Zr(1)–O(1)	81.80(7)	C(8)–C(5)–C(6)	108.9(2)
N(4)–Zr(1)–N(5)	89.22(9)	C(4)–C(5)–C(6)	107.9(2)
N(2)–Zr(1)–N(5)	100.52(8)	C(8)–C(5)–C(7)	108.1(2)
N(1)–Zr(1)–N(5)	77.48(9)	C(4)–C(5)–C(7)	109.3(2)
O(1)–Zr(1)–N(5)	157.98(8)	C(6)–C(5)–C(7)	108.2(3)
N(4)–Zr(1)–N(3)	88.42(8)	C(9)–C(8)–N(2)	109.6(3)
N(2)–Zr(1)–N(3)	97.08(8)	C(9)–C(8)–C(5)	127.2(3)
N(1)–Zr(1)–N(3)	155.52(8)	N(2)–C(8)–C(5)	122.7(2)
O(1)–Zr(1)–N(3)	73.73(7)	C(8)–C(9)–C(10)	107.6(3)
N(5)–Zr(1)–N(3)	126.59(8)	C(11)–C(10)–C(9)	107.2(3)
N(4)–Zr(1)–C(15)	119.42(9)	C(10)–C(11)–N(2)	109.9(3)
N(2)–Zr(1)–C(15)	69.80(8)	C(10)–C(11)–C(12)	128.6(3)
N(1)–Zr(1)–C(15)	149.67(8)	N(2)–C(11)–C(12)	121.3(2)
O(1)–Zr(1)–C(15)	87.78(8)	C(15)–C(12)–C(11)	107.4(2)
N(5)–Zr(1)–C(15)	113.97(9)	C(15)–C(12)–C(13)	110.3(2)
N(3)–Zr(1)–C(15)	32.26(8)	C(11)–C(12)–C(13)	110.3(2)
N(4)–Zr(1)–C(16)	118.38(9)	C(15)–C(12)–C(14)	109.8(2)
N(2)–Zr(1)–C(16)	77.61(9)	C(11)–C(12)–C(14)	110.1(2)
N(1)–Zr(1)–C(16)	146.68(9)	C(13)–C(12)–C(14)	108.9(2)
O(1)–Zr(1)–C(16)	119.93(8)	N(3)–C(15)–C(16)	108.8(2)
N(5)–Zr(1)–C(16)	81.95(9)	N(3)–C(15)–C(12)	125.2(2)
N(3)–Zr(1)–C(16)	53.47(9)	C(16)–C(15)–C(12)	125.8(3)
C(15)–Zr(1)–C(16)	32.18(9)	N(3)–C(15)–Zr(1)	73.47(14)
N(4)–Zr(1)–C(18)	69.67(9)	C(16)–C(15)–Zr(1)	75.60(16)
N(2)–Zr(1)–C(18)	122.11(8)	C(12)–C(15)–Zr(1)	113.88(18)
N(1)–Zr(1)–C(18)	157.00(8)	C(17)–C(16)–C(15)	107.2(3)
O(1)–Zr(1)–C(18)	96.96(8)	C(17)–C(16)–Zr(1)	75.30(17)
N(5)–Zr(1)–C(18)	99.18(9)	C(15)–C(16)–Zr(1)	72.22(15)
N(3)–Zr(1)–C(18)	31.99(8)	C(18)–C(17)–C(16)	107.9(3)
C(15)–Zr(1)–C(18)	52.44(9)	C(18)–C(17)–Zr(1)	73.43(16)
C(16)–Zr(1)–C(18)	52.29(9)	C(16)–C(17)–Zr(1)	73.12(17)
N(4)–Zr(1)–C(17)	87.48(9)	C(17)–C(18)–N(3)	109.0(3)
N(2)–Zr(1)–C(17)	109.05(9)	C(17)–C(18)–C(19)	127.3(3)
N(1)–Zr(1)–C(17)	150.70(9)	N(3)–C(18)–C(19)	123.6(2)
O(1)–Zr(1)–C(17)	125.98(8)	C(17)–C(18)–Zr(1)	75.21(17)
N(5)–Zr(1)–C(17)	73.62(10)	N(3)–C(18)–Zr(1)	71.70(15)

Bond Angle	Angle	Bond Angle	Angle
N(3)–Zr(1)–C(17)	52.97(9)	C(19)–C(18)–Zr(1)	115.97(17)
C(15)–Zr(1)–C(17)	52.57(9)	C(18)–C(19)–C(22)	108.3(2)
C(16)–Zr(1)–C(17)	31.58(9)	C(18)–C(19)–C(21)	109.1(2)
C(18)–Zr(1)–C(17)	31.36(9)	C(22)–C(19)–C(21)	109.5(2)
C(1)–N(1)–C(4)	105.5(2)	C(18)–C(19)–C(20)	110.4(2)
C(1)–N(1)–Zr(1)	113.74(17)	C(22)–C(19)–C(20)	110.9(2)
C(4)–N(1)–Zr(1)	115.05(16)	C(21)–C(19)–C(20)	108.7(3)
C(8)–N(2)–C(11)	105.7(2)	C(23)–C(22)–N(4)	110.2(2)
C(8)–N(2)–Zr(1)	129.79(18)	C(23)–C(22)–C(19)	128.5(3)
C(11)–N(2)–Zr(1)	120.04(17)	N(4)–C(22)–C(19)	121.4(2)
C(15)–N(3)–C(18)	107.0(2)	C(22)–C(23)–C(24)	107.0(3)
C(15)–N(3)–Zr(1)	74.27(15)	C(25)–C(24)–C(23)	107.4(3)
C(18)–N(3)–Zr(1)	76.31(15)	C(24)–C(25)–N(4)	109.5(3)
C(25)–N(4)–C(22)	106.0(2)	C(24)–C(25)–C(26)	127.9(3)
C(25)–N(4)–Zr(1)	129.47(18)	N(4)–C(25)–C(26)	122.4(2)
C(22)–N(4)–Zr(1)	124.55(18)	C(25)–C(26)–C(1)	113.5(2)
C(29)–N(5)–C(30)	110.0(3)	C(25)–C(26)–C(28)	109.0(3)
C(29)–N(5)–Zr(1)	117.3(2)	C(1)–C(26)–C(28)	109.2(3)
C(30)–N(5)–Zr(1)	118.8(2)	C(25)–C(26)–C(27)	109.1(3)
C(31)–O(1)–C(34)	109.1(2)	C(1)–C(26)–C(27)	107.8(2)
C(31)–O(1)–Zr(1)	126.36(17)	C(28)–C(26)–C(27)	108.1(3)
C(34)–O(1)–Zr(1)	124.44(16)	O(1)–C(31)–C(32)	105.1(3)
C(2)–C(1)–N(1)	109.5(3)	C(31)–C(32)–C(33)	104.2(3)
C(2)–C(1)–C(26)	128.5(3)	C(32)–C(33)–C(34)	102.6(3)
N(1)–C(1)–C(26)	121.3(2)	O(1)–C(34)–C(33)	105.2(2)
C(1)–C(2)–C(3)	107.8(3)		

Table S5. Anisotropic thermal displacement parameters ($Å^2 \times 10^3$) for $LZr(NHMe_2)(THF)$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	19(1)	16(1)	14(1)	0(1)	6(1)	1(1)
N(1)	19(1)	19(1)	18(1)	4(1)	6(1)	3(1)
N(2)	20(1)	20(1)	17(1)	0(1)	6(1)	1(1)
N(3)	28(1)	24(1)	22(1)	3(1)	9(1)	4(1)
N(4)	23(1)	19(1)	21(1)	1(1)	11(1)	2(1)
N(5)	37(2)	20(2)	20(1)	1(1)	12(1)	–2(1)
O(1)	24(1)	25(1)	16(1)	1(1)	5(1)	–6(1)
C(1)	27(2)	18(2)	24(2)	8(1)	12(1)	7(1)
C(2)	39(2)	17(2)	29(2)	–1(1)	17(2)	4(1)
C(3)	29(2)	19(2)	22(2)	–1(1)	9(1)	–4(1)
C(4)	21(2)	20(2)	18(2)	5(1)	5(1)	1(1)
C(5)	21(2)	23(2)	20(2)	1(1)	8(1)	–2(1)
C(6)	40(2)	27(2)	24(2)	4(1)	14(2)	1(2)
C(7)	24(2)	36(2)	38(2)	–5(2)	11(2)	–6(2)
C(8)	18(1)	25(2)	19(2)	1(1)	5(1)	–1(1)
C(9)	28(2)	30(2)	24(2)	1(1)	14(1)	–3(1)
C(10)	28(2)	27(2)	29(2)	–7(1)	16(1)	2(1)
C(11)	20(2)	24(2)	22(2)	–4(1)	8(1)	2(1)
C(12)	24(2)	22(2)	24(2)	–1(1)	8(1)	1(1)
C(13)	37(2)	22(2)	26(2)	–3(1)	14(2)	–1(2)
C(14)	26(2)	24(2)	37(2)	0(2)	12(2)	2(1)
C(15)	22(2)	14(2)	20(2)	3(1)	7(1)	5(1)
C(16)	25(2)	16(2)	23(2)	3(1)	6(1)	1(1)
C(17)	33(2)	15(2)	17(2)	1(1)	8(1)	1(1)
C(18)	34(2)	12(2)	19(2)	5(1)	11(1)	6(1)
C(19)	28(2)	18(2)	19(2)	2(1)	10(1)	–1(1)
C(20)	37(2)	25(2)	32(2)	0(2)	13(2)	–8(2)
C(21)	36(2)	27(2)	28(2)	7(2)	14(2)	5(2)
C(22)	24(2)	20(2)	17(2)	–1(1)	7(1)	–4(1)
C(23)	25(2)	29(2)	26(2)	6(1)	12(1)	–4(1)
C(24)	21(2)	28(2)	32(2)	3(1)	12(1)	7(1)
C(25)	24(2)	21(2)	23(2)	–1(1)	10(1)	3(1)
C(26)	29(2)	20(2)	35(2)	5(1)	15(1)	6(1)
C(27)	24(2)	35(2)	37(2)	13(2)	9(2)	6(2)
C(28)	33(2)	27(2)	62(3)	7(2)	28(2)	7(2)
C(29)	55(2)	22(2)	22(2)	–5(2)	17(2)	–4(2)
C(30)	36(2)	36(2)	21(2)	–4(2)	3(2)	–10(2)
C(31)	28(2)	33(2)	27(2)	2(2)	7(1)	–8(2)
C(32)	34(2)	45(2)	31(2)	–4(2)	0(2)	–11(2)
C(33)	40(2)	39(2)	19(2)	2(2)	1(2)	–3(2)
C(34)	26(2)	36(2)	16(2)	1(1)	7(1)	–1(2)

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $LZr(NHMe_2)(THF)$.

Atom	x	y	z	U_{eq}
H(1)	2587(16)	–2512(18)	5716(17)	30(9)
H(2)	1405(15)	–2463(16)	5865(15)	19(8)
H(3)	1857(17)	–1544(16)	7860(17)	27(8)
H(4)	1345(17)	–2170(20)	7380(18)	35(9)
H(5)	1006(18)	–1609(18)	7757(18)	40(9)
H(6)	270(18)	–1190(20)	5760(20)	47(10)
H(7)	414(17)	–2020(20)	6135(18)	35(9)
H(8)	120(17)	–1397(17)	6483(17)	27(9)
H(9)	678(15)	–326(16)	7739(16)	20(8)
H(10)	722(17)	1064(19)	7572(19)	39(10)
H(11)	2022(16)	2507(19)	7024(17)	31(9)
H(12)	2362(16)	1742(17)	7388(16)	22(8)
H(13)	1711(17)	2096(17)	7546(19)	32(9)
H(14)	803(15)	2552(18)	5992(16)	23(8)
H(15)	341(17)	1810(18)	5762(18)	32(9)
H(16)	444(16)	2157(17)	6520(18)	31(9)
H(17)	883(17)	986(18)	5022(18)	34(9)
H(18)	1762(15)	856(16)	4405(18)	20(8)
H(19)	3520(17)	1337(17)	4271(17)	28(9)
H(20)	2787(17)	960(20)	4045(18)	37(9)
H(21)	2873(16)	1790(20)	4185(17)	30(9)
H(22)	4149(16)	1908(16)	5543(15)	21(8)
H(23)	3809(17)	1860(18)	6170(20)	39(9)
H(24)	3453(15)	2394(19)	5459(17)	28(8)
H(25)	4509(15)	467(17)	5260(16)	21(8)
H(26)	4642(16)	–822(16)	5792(16)	22(8)
H(27)	4430(18)	–1083(18)	7383(18)	38(9)
H(28)	3886(16)	–1640(20)	7545(18)	38(9)
H(29)	3729(18)	–780(20)	7414(19)	41(10)
H(30)	4455(17)	–1917(17)	6295(16)	29(8)
H(31)	3734(15)	–2100(15)	5634(18)	18(8)
H(32)	3886(16)	–2460(20)	6462(18)	38(9)
H(33)	1679(15)	–1032(17)	5115(16)	14(8)
H(34)	2023(18)	–310(20)	4088(19)	39(10)
H(35)	2534(19)	–883(19)	4611(19)	42(10)
H(36)	1801(19)	–1120(20)	4030(20)	48(11)
H(37)	797(17)	–75(18)	4150(19)	35(9)
H(38)	670(17)	–956(19)	4178(19)	37(9)
H(39)	631(14)	–430(16)	4859(16)	18(7)
H(40)	3564(15)	1342(19)	7272(16)	26(8)

Atom	x	y	z	U_{eq}
H(41)	3923(15)	607(16)	7105(16)	21(8)
H(42)	4300(18)	1120(20)	8450(20)	43(10)
H(43)	4284(19)	280(20)	8340(20)	46(11)
H(44)	3181(17)	1190(20)	8556(18)	42(10)
H(45)	3510(17)	423(19)	9020(20)	39(9)
H(46)	2377(17)	309(15)	7841(15)	18(8)
H(47)	2947(15)	–356(18)	7956(16)	26(8)

Table S7. Crystal data, structure solution and refinement for $[HLZr]_2O$.

Empirical formula	$C_{56}H_{66}N_8OZr_2$
Formula weight	1049.61
T (K)	100(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	42.064(2)
b (Å)	12.5032(6)
c (Å)	19.0221(9)
α (°)	90
β (°)	101.0830(10)
γ (°)	90
V / Å^3	9817.9(8)
Z	8
ρ_{calcd} (g/cm^3)	1.420
Absorption coefficient (mm^{-1})	0.474
F(000)	4368
Crystal size (mm^3)	0.12 × 0.09 × 0.04
θ range for data collection	0.99 to 23.27°
Index ranges	$-41 \le h \le 46$, $-11 \le k \le 13$, $-21 \le \ell \le 19$
No. of coll. reflns	23488
No. of ind. reflns (R_{int})	7051 (0.0629)
Completeness to θ = 23.27°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7-51 / 0 / 620
GOF[a] on F^2	1.051
$R1$,[b] w$R2$[c] ($I > 2\sigma$)	0.0310, 0.0735
$R1$,[b] w$R2$[c] (all data)	0.0377, 0.0774
Largest diff. peak and hole (e.Å^{-3})	0.472 and –0.339

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{1/2}$. [c] GOF = $(\Sigma\, w(F_o^2 - F_c^2)^2/(n-p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

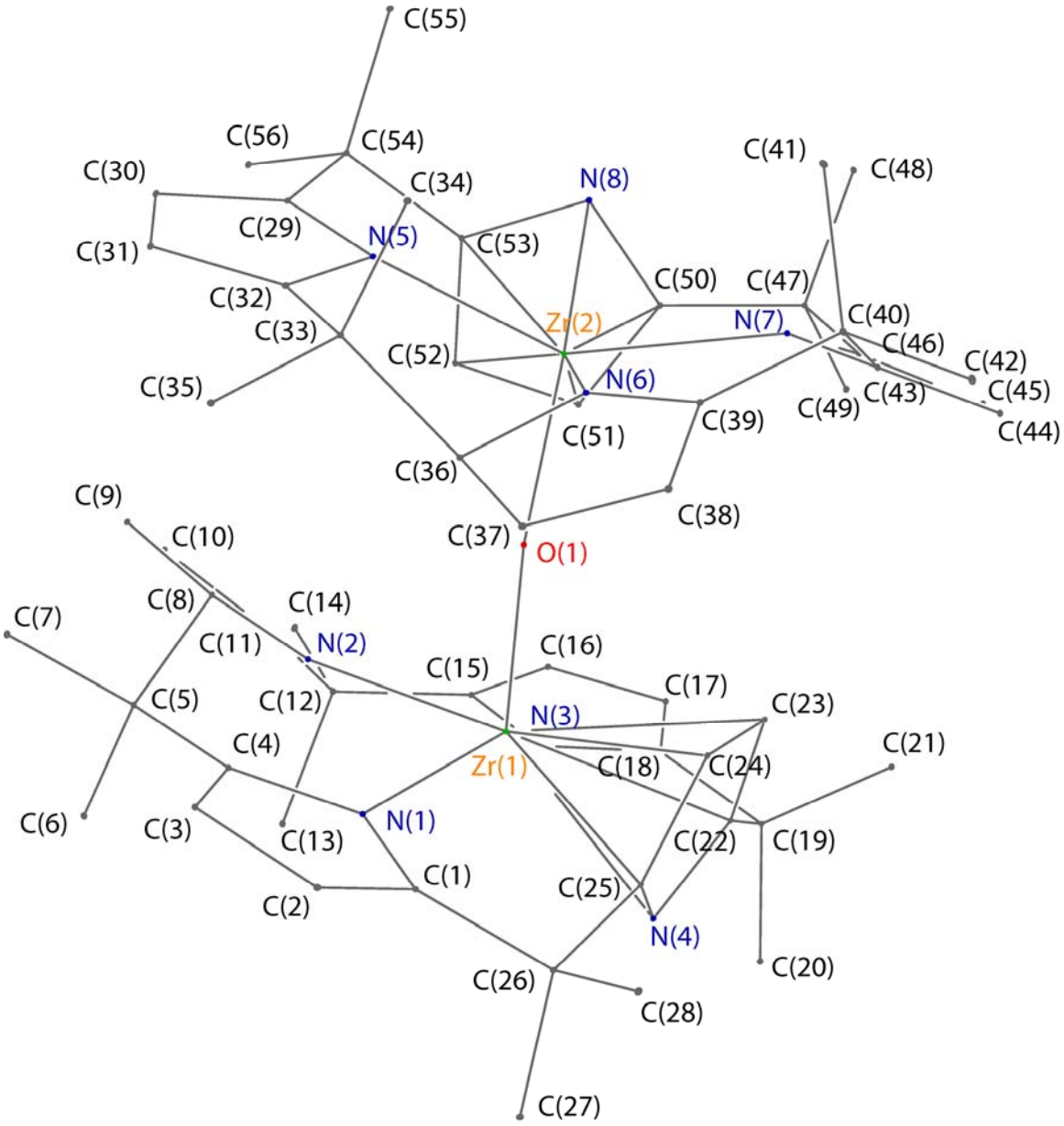

Figure S1. Atom numbering scheme for $[HLZr]_2O$.

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[HLZr]_2O$.

Atom	x	y	z	U_{eq}
Zr(1)	784(1)	2817(1)	1601(1)	15(1)
Zr(2)	1710(1)	3208(1)	2039(1)	15(1)
O(1)	1252(1)	2877(1)	1789(1)	18(1)
N(1)	679(1)	1179(2)	1155(1)	20(1)
N(2)	880(1)	1815(2)	2644(1)	19(1)
N(3)	613(1)	3933(2)	2359(1)	19(1)
N(4)	381(1)	3597(2)	696(1)	20(1)
N(5)	1943(1)	1654(2)	2395(1)	19(1)
N(6)	1715(1)	2374(2)	961(1)	19(1)
N(7)	1796(1)	4603(2)	1380(1)	19(1)
N(8)	2026(1)	4189(2)	3017(1)	22(1)
C(1)	600(1)	1043(2)	412(2)	21(1)
C(2)	670(1)	27(2)	228(2)	26(1)
C(3)	794(1)	–523(2)	874(2)	26(1)
C(4)	795(1)	182(2)	1429(2)	22(1)
C(5)	864(1)	–68(2)	2218(2)	25(1)
C(6)	542(1)	–185(3)	2475(2)	34(1)
C(7)	1056(1)	–1114(2)	2363(2)	34(1)
C(8)	1077(1)	842(2)	2642(2)	22(1)
C(9)	1195(1)	601(2)	3411(2)	25(1)
C(10)	1065(1)	1289(2)	3805(2)	26(1)
C(11)	867(1)	2035(2)	3309(2)	22(1)
C(12)	655(1)	2894(2)	3526(2)	26(1)
C(13)	307(1)	2425(3)	3352(2)	34(1)
C(14)	742(1)	3120(3)	4328(2)	40(1)
C(15)	667(1)	3919(2)	3109(2)	21(1)
C(16)	688(1)	4940(2)	3368(2)	25(1)
C(17)	639(1)	5640(2)	2774(2)	25(1)
C(18)	587(1)	5014(2)	2173(2)	20(1)
C(19)	474(1)	5330(2)	1398(2)	19(1)
C(20)	102(1)	5418(2)	1243(2)	26(1)
C(21)	620(1)	6397(2)	1238(2)	26(1)
C(22)	577(1)	4458(2)	938(1)	18(1)
C(23)	878(1)	4355(2)	729(1)	19(1)
C(24)	864(1)	3404(2)	331(1)	20(1)
C(25)	553(1)	2971(2)	303(1)	19(1)
C(26)	428(1)	1931(2)	–42(2)	23(1)
C(27)	61(1)	1824(3)	–76(2)	29(1)
C(28)	497(1)	1884(3)	–806(2)	33(1)
C(29)	2034(1)	1452(2)	3131(2)	22(1)
C(30)	2050(1)	379(2)	3256(2)	30(1)

Atom	x	y	z	U_{eq}
C(31)	1970(1)	–129(2)	2583(2)	30(1)
C(32)	1905(1)	644(2)	2066(2)	23(1)
C(33)	1850(1)	473(2)	1263(2)	23(1)
C(34)	2171(1)	629(3)	1001(2)	30(1)
C(35)	1726(1)	–663(2)	1074(2)	29(1)
C(36)	1587(1)	1276(2)	871(2)	21(1)
C(37)	1507(1)	1127(3)	84(2)	27(1)
C(38)	1605(1)	1978(3)	–233(2)	29(1)
C(39)	1740(1)	2737(2)	334(2)	23(1)
C(40)	1899(1)	3791(3)	233(2)	29(1)
C(41)	2267(1)	3662(3)	530(2)	39(1)
C(42)	1849(1)	4083(3)	–558(2)	44(1)
C(43)	1770(1)	4671(2)	643(2)	24(1)
C(44)	1663(1)	5665(2)	406(2)	28(1)
C(45)	1626(1)	6263(2)	1015(2)	28(1)
C(46)	1715(1)	5614(2)	1598(2)	22(1)
C(47)	1779(1)	5879(2)	2384(2)	20(1)
C(48)	2119(1)	6371(2)	2600(2)	28(1)
C(49)	1528(1)	6685(2)	2543(2)	29(1)
C(50)	1760(1)	4846(2)	2789(1)	19(1)
C(51)	1484(1)	4376(2)	2965(2)	21(1)
C(52)	1581(1)	3410(2)	3305(1)	19(1)
C(53)	1913(1)	3319(2)	3342(1)	20(1)
C(54)	2120(1)	2372(2)	3647(2)	23(1)
C(55)	2480(1)	2658(3)	3725(2)	30(1)
C(56)	2048(1)	2079(3)	4384(2)	31(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S9. Bond lengths (in Å) for $[HLZr]_2O$.

Bond	Distance	Bond	Distance
Zr(1)—O(1)	1.9362(18)	C(11)—C(12)	1.502(4)
Zr(1)—N(3)	2.221(2)	C(12)—C(15)	1.512(4)
Zr(1)—N(1)	2.228(2)	C(12)—C(14)	1.527(4)
Zr(1)—N(2)	2.315(2)	C(12)—C(13)	1.552(4)
Zr(1)—N(4)	2.382(2)	C(15)—C(16)	1.365(4)
Zr(1)—C(22)	2.477(3)	C(16)—C(17)	1.413(4)
Zr(1)—C(25)	2.481(3)	C(17)—C(18)	1.369(4)
Zr(1)—C(24)	2.609(3)	C(18)—C(19)	1.512(4)
Zr(1)—C(23)	2.621(3)	C(19)—C(22)	1.513(4)
Zr(2)—O(1)	1.9363(18)	C(19)—C(21)	1.524(4)
Zr(2)—N(7)	2.218(2)	C(19)—C(20)	1.541(4)
Zr(2)—N(5)	2.222(2)	C(22)—C(23)	1.405(4)
Zr(2)—N(6)	2.304(2)	C(23)—C(24)	1.404(4)
Zr(2)—N(8)	2.405(2)	C(24)—C(25)	1.407(4)
Zr(2)—C(53)	2.466(3)	C(25)—C(26)	1.506(4)
Zr(2)—C(50)	2.481(3)	C(26)—C(27)	1.536(4)
Zr(2)—C(52)	2.581(3)	C(26)—C(28)	1.538(4)
Zr(2)—C(51)	2.604(3)	C(29)—C(30)	1.362(4)
N(1)—C(1)	1.399(4)	C(29)—C(54)	1.510(4)
N(1)—C(4)	1.402(4)	C(30)—C(31)	1.410(4)
N(2)—C(11)	1.305(4)	C(31)—C(32)	1.368(4)
N(2)—C(8)	1.472(4)	C(32)—C(33)	1.515(4)
N(3)—C(18)	1.397(4)	C(33)—C(35)	1.532(4)
N(3)—C(15)	1.402(4)	C(33)—C(34)	1.540(4)
N(4)—C(25)	1.380(4)	C(33)—C(36)	1.573(4)
N(4)—C(22)	1.382(4)	C(36)—C(37)	1.482(4)
N(5)—C(29)	1.402(4)	C(37)—C(38)	1.326(4)
N(5)—C(32)	1.406(4)	C(38)—C(39)	1.467(4)
N(6)—C(39)	1.299(4)	C(39)—C(40)	1.506(4)
N(6)—C(36)	1.473(4)	C(40)—C(43)	1.507(4)
N(7)—C(43)	1.387(4)	C(40)—C(42)	1.524(4)
N(7)—C(46)	1.395(4)	C(40)—C(41)	1.553(4)
N(8)—C(53)	1.382(4)	C(43)—C(44)	1.370(4)
N(8)—C(50)	1.391(4)	C(44)—C(45)	1.412(4)
C(1)—C(2)	1.365(4)	C(45)—C(46)	1.368(4)
C(1)—C(26)	1.505(4)	C(46)—C(47)	1.503(4)
C(2)—C(3)	1.416(4)	C(47)—C(50)	1.515(4)
C(3)—C(4)	1.375(4)	C(47)—C(49)	1.532(4)
C(4)—C(5)	1.507(4)	C(47)—C(48)	1.537(4)
C(5)—C(6)	1.534(4)	C(50)—C(51)	1.397(4)
C(5)—C(7)	1.535(4)	C(51)—C(52)	1.394(4)
C(5)—C(8)	1.572(4)	C(52)—C(53)	1.388(4)
C(8)—C(9)	1.482(4)	C(53)—C(54)	1.517(4)
C(9)—C(10)	1.325(4)	C(54)—C(56)	1.534(4)
C(10)—C(11)	1.468(4)	C(54)—C(55)	1.536(4)

Table S10. Bond angles (in deg) for $[HLZr]_2O$.

Bond Angle	Angle	Bond Angle	Angle
O(1)–Zr(1)–N(3)	107.50(8)	C(9)–C(10)–C(11)	107.0(3)
O(1)–Zr(1)–N(1)	103.01(8)	N(2)–C(11)–C(10)	111.4(3)
N(3)–Zr(1)–N(1)	139.44(8)	N(2)–C(11)–C(12)	123.7(3)
O(1)–Zr(1)–N(2)	81.90(8)	C(10)–C(11)–C(12)	124.8(3)
N(3)–Zr(1)–N(2)	79.02(8)	C(11)–C(12)–C(15)	112.4(2)
N(1)–Zr(1)–N(2)	79.53(8)	C(11)–C(12)–C(14)	111.5(3)
O(1)–Zr(1)–N(4)	132.48(8)	C(15)–C(12)–C(14)	109.9(3)
N(3)–Zr(1)–N(4)	86.45(8)	C(11)–C(12)–C(13)	104.8(2)
N(1)–Zr(1)–N(4)	92.29(8)	C(15)–C(12)–C(13)	109.4(2)
N(2)–Zr(1)–N(4)	145.54(8)	C(14)–C(12)–C(13)	108.5(3)
O(1)–Zr(1)–C(22)	107.84(8)	C(16)–C(15)–N(3)	110.0(2)
N(3)–Zr(1)–C(22)	71.63(9)	C(16)–C(15)–C(12)	127.6(3)
N(1)–Zr(1)–C(22)	122.89(9)	N(3)–C(15)–C(12)	121.9(2)
N(2)–Zr(1)–C(22)	150.62(9)	C(15)–C(16)–C(17)	107.5(3)
N(4)–Zr(1)–C(22)	32.97(8)	C(18)–C(17)–C(16)	106.8(3)
O(1)–Zr(1)–C(25)	111.66(8)	C(17)–C(18)–N(3)	110.5(2)
N(3)–Zr(1)–C(25)	118.91(9)	C(17)–C(18)–C(19)	129.5(3)
N(1)–Zr(1)–C(25)	71.44(9)	N(3)–C(18)–C(19)	119.6(2)
N(2)–Zr(1)–C(25)	149.96(9)	C(18)–C(19)–C(22)	107.7(2)
N(4)–Zr(1)–C(25)	32.90(8)	C(18)–C(19)–C(21)	111.1(2)
C(22)–Zr(1)–C(25)	52.89(9)	C(22)–C(19)–C(21)	110.1(2)
O(1)–Zr(1)–C(24)	81.40(8)	C(18)–C(19)–C(20)	108.8(2)
N(3)–Zr(1)–C(24)	122.64(9)	C(22)–C(19)–C(20)	109.5(2)
N(1)–Zr(1)–C(24)	87.55(9)	C(21)–C(19)–C(20)	109.5(2)
N(2)–Zr(1)–C(24)	155.97(8)	N(4)–C(22)–C(23)	110.4(2)
N(4)–Zr(1)–C(24)	54.27(8)	N(4)–C(22)–C(19)	122.3(2)
C(22)–Zr(1)–C(24)	52.43(9)	C(23)–C(22)–C(19)	127.2(3)
C(25)–Zr(1)–C(24)	31.97(9)	N(4)–C(22)–Zr(1)	69.70(14)
O(1)–Zr(1)–C(23)	79.32(8)	C(23)–C(22)–Zr(1)	79.71(16)
N(3)–Zr(1)–C(23)	93.27(8)	C(19)–C(22)–Zr(1)	114.44(17)
N(1)–Zr(1)–C(23)	118.44(9)	C(24)–C(23)–C(22)	106.4(2)
N(2)–Zr(1)–C(23)	156.49(8)	C(24)–C(23)–Zr(1)	73.94(16)
N(4)–Zr(1)–C(23)	54.19(8)	C(22)–C(23)–Zr(1)	68.45(15)
C(22)–Zr(1)–C(23)	31.83(9)	C(23)–C(24)–C(25)	106.8(2)
C(25)–Zr(1)–C(23)	52.42(9)	C(23)–C(24)–Zr(1)	74.91(16)
C(24)–Zr(1)–C(23)	31.15(9)	C(25)–C(24)–Zr(1)	69.03(15)
O(1)–Zr(2)–N(7)	107.00(8)	N(4)–C(25)–C(24)	110.1(2)
O(1)–Zr(2)–N(5)	104.29(8)	N(4)–C(25)–C(26)	123.2(2)
N(7)–Zr(2)–N(5)	138.51(8)	C(24)–C(25)–C(26)	126.5(3)
O(1)–Zr(2)–N(6)	82.16(7)	N(4)–C(25)–Zr(1)	69.57(14)
N(7)–Zr(2)–N(6)	79.75(8)	C(24)–C(25)–Zr(1)	79.00(16)

Bond Angle	Angle	Bond Angle	Angle
N(5)–Zr(2)–N(6)	78.25(8)	C(26)–C(25)–Zr(1)	113.81(18)
O(1)–Zr(2)–N(8)	132.49(8)	C(1)–C(26)–C(25)	107.3(2)
N(7)–Zr(2)–N(8)	84.84(8)	C(1)–C(26)–C(27)	109.2(2)
N(5)–Zr(2)–N(8)	93.67(8)	C(25)–C(26)–C(27)	111.0(2)
N(6)–Zr(2)–N(8)	145.12(8)	C(1)–C(26)–C(28)	110.9(2)
O(1)–Zr(2)–C(53)	113.25(8)	C(25)–C(26)–C(28)	109.3(2)
N(7)–Zr(2)–C(53)	117.50(9)	C(27)–C(26)–C(28)	109.1(2)
N(5)–Zr(2)–C(53)	72.27(9)	C(30)–C(29)–N(5)	110.3(3)
N(6)–Zr(2)–C(53)	149.24(9)	C(30)–C(29)–C(54)	129.8(3)
N(8)–Zr(2)–C(53)	32.93(9)	N(5)–C(29)–C(54)	119.8(2)
O(1)–Zr(2)–C(50)	106.73(8)	C(29)–C(30)–C(31)	106.9(3)
N(7)–Zr(2)–C(50)	70.82(9)	C(32)–C(31)–C(30)	108.3(3)
N(5)–Zr(2)–C(50)	124.25(9)	C(31)–C(32)–N(5)	109.0(3)
N(6)–Zr(2)–C(50)	150.56(9)	C(31)–C(32)–C(33)	126.5(3)
N(8)–Zr(2)–C(50)	33.03(8)	N(5)–C(32)–C(33)	123.9(3)
C(53)–Zr(2)–C(50)	53.21(9)	C(32)–C(33)–C(35)	110.3(2)
O(1)–Zr(2)–C(52)	82.72(8)	C(32)–C(33)–C(34)	109.6(2)
N(7)–Zr(2)–C(52)	122.51(9)	C(35)–C(33)–C(34)	108.7(2)
N(5)–Zr(2)–C(52)	87.72(9)	C(32)–C(33)–C(36)	110.2(2)
N(6)–Zr(2)–C(52)	156.12(8)	C(35)–C(33)–C(36)	107.7(2)
N(8)–Zr(2)–C(52)	54.03(8)	C(34)–C(33)–C(36)	110.3(2)
C(53)–Zr(2)–C(52)	31.83(9)	N(6)–C(36)–C(37)	104.0(2)
C(50)–Zr(2)–C(52)	52.58(9)	N(6)–C(36)–C(33)	109.3(2)
O(1)–Zr(2)–C(51)	79.13(8)	C(37)–C(36)–C(33)	113.7(2)
N(7)–Zr(2)–C(51)	93.58(9)	C(38)–C(37)–C(36)	109.1(3)
N(5)–Zr(2)–C(51)	118.74(9)	C(37)–C(38)–C(39)	107.2(3)
N(6)–Zr(2)–C(51)	157.34(8)	N(6)–C(39)–C(38)	111.2(3)
N(8)–Zr(2)–C(51)	53.90(8)	N(6)–C(39)–C(40)	122.6(3)
C(53)–Zr(2)–C(51)	52.37(9)	C(38)–C(39)–C(40)	126.2(3)
C(50)–Zr(2)–C(51)	31.77(9)	C(39)–C(40)–C(43)	111.2(2)
C(52)–Zr(2)–C(51)	31.19(9)	C(39)–C(40)–C(42)	110.8(3)
Zr(1)–O(1)–Zr(2)	169.17(11)	C(43)–C(40)–C(42)	109.9(3)
C(1)–N(1)–C(4)	105.4(2)	C(39)–C(40)–C(41)	107.4(3)
C(1)–N(1)–Zr(1)	119.19(18)	C(43)–C(40)–C(41)	108.7(3)
C(4)–N(1)–Zr(1)	130.34(18)	C(42)–C(40)–C(41)	108.8(3)
C(11)–N(2)–C(8)	107.8(2)	C(44)–C(43)–N(7)	110.2(3)
C(11)–N(2)–Zr(1)	133.07(19)	C(44)–C(43)–C(40)	128.4(3)
C(8)–N(2)–Zr(1)	116.79(17)	N(7)–C(43)–C(40)	120.7(3)
C(18)–N(3)–C(15)	105.0(2)	C(43)–C(44)–C(45)	106.9(3)
C(18)–N(3)–Zr(1)	117.61(17)	C(46)–C(45)–C(44)	107.2(3)
C(15)–N(3)–Zr(1)	130.06(18)	C(45)–C(46)–N(7)	109.9(3)
C(25)–N(4)–C(22)	106.2(2)	C(45)–C(46)–C(47)	130.2(3)

Bond Angle	Angle	Bond Angle	Angle
C(25)–N(4)–Zr(1)	77.53(15)	N(7)–C(46)–C(47)	119.2(2)
C(22)–N(4)–Zr(1)	77.33(14)	C(46)–C(47)–C(50)	107.5(2)
C(29)–N(5)–C(32)	105.6(2)	C(46)–C(47)–C(49)	110.0(2)
C(29)–N(5)–Zr(2)	118.87(18)	C(50)–C(47)–C(49)	110.7(2)
C(32)–N(5)–Zr(2)	130.17(18)	C(46)–C(47)–C(48)	109.6(2)
C(39)–N(6)–C(36)	108.1(2)	C(50)–C(47)–C(48)	110.1(2)
C(39)–N(6)–Zr(2)	132.5(2)	C(49)–C(47)–C(48)	109.0(2)
C(36)–N(6)–Zr(2)	117.35(17)	N(8)–C(50)–C(51)	109.5(2)
C(43)–N(7)–C(46)	105.6(2)	N(8)–C(50)–C(47)	122.9(2)
C(43)–N(7)–Zr(2)	129.05(19)	C(51)–C(50)–C(47)	127.5(3)
C(46)–N(7)–Zr(2)	117.85(18)	N(8)–C(50)–Zr(2)	70.50(14)
C(53)–N(8)–C(50)	106.1(2)	C(51)–C(50)–Zr(2)	78.97(16)
C(53)–N(8)–Zr(2)	75.94(15)	C(47)–C(50)–Zr(2)	114.73(18)
C(50)–N(8)–Zr(2)	76.47(15)	C(52)–C(51)–C(50)	107.0(3)
C(2)–C(1)–N(1)	110.5(3)	C(52)–C(51)–Zr(2)	73.49(16)
C(2)–C(1)–C(26)	130.1(3)	C(50)–C(51)–Zr(2)	69.26(16)
N(1)–C(1)–C(26)	119.1(2)	C(53)–C(52)–C(51)	107.3(2)
C(1)–C(2)–C(3)	107.0(3)	C(53)–C(52)–Zr(2)	69.51(15)
C(4)–C(3)–C(2)	107.5(3)	C(51)–C(52)–Zr(2)	75.32(16)
C(3)–C(4)–N(1)	109.6(3)	N(8)–C(53)–C(52)	110.1(2)
C(3)–C(4)–C(5)	127.2(3)	N(8)–C(53)–C(54)	124.2(2)
N(1)–C(4)–C(5)	122.7(3)	C(52)–C(53)–C(54)	125.5(3)
C(4)–C(5)–C(6)	108.9(2)	N(8)–C(53)–Zr(2)	71.14(14)
C(4)–C(5)–C(7)	110.4(3)	C(52)–C(53)–Zr(2)	78.66(16)
C(6)–C(5)–C(7)	109.3(3)	C(54)–C(53)–Zr(2)	113.75(18)
C(4)–C(5)–C(8)	110.0(2)	C(29)–C(54)–C(53)	107.4(2)
C(6)–C(5)–C(8)	111.0(3)	C(29)–C(54)–C(56)	110.4(2)
C(7)–C(5)–C(8)	107.2(2)	C(53)–C(54)–C(56)	109.7(2)
N(2)–C(8)–C(9)	104.2(2)	C(29)–C(54)–C(55)	110.3(2)
N(2)–C(8)–C(5)	109.5(2)	C(53)–C(54)–C(55)	109.8(2)
C(9)–C(8)–C(5)	114.1(2)	C(56)–C(54)–C(55)	109.3(2)
C(10)–C(9)–C(8)	109.3(3)		

Table S11. Anisotropic thermal displacement parameters ($Å^2 \times 10^3$) for $[HLZr]_2O$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	15(1)	17(1)	14(1)	1(1)	3(1)	1(1)
Zr(2)	15(1)	17(1)	13(1)	0(1)	2(1)	1(1)
O(1)	19(1)	18(1)	16(1)	0(1)	4(1)	1(1)
N(1)	18(1)	20(1)	21(1)	1(1)	4(1)	0(1)
N(2)	20(1)	20(1)	19(1)	2(1)	6(1)	1(1)
N(3)	20(1)	21(1)	16(1)	1(1)	6(1)	3(1)
N(4)	19(1)	22(1)	17(1)	3(1)	2(1)	3(1)
N(5)	17(1)	20(1)	18(1)	0(1)	2(1)	2(1)
N(6)	16(1)	22(1)	18(1)	–1(1)	3(1)	1(1)
N(7)	20(1)	21(1)	16(1)	2(1)	3(1)	–1(1)
N(8)	25(1)	24(1)	17(1)	–3(1)	0(1)	–1(1)
C(1)	19(2)	24(2)	20(2)	–3(1)	2(1)	–3(1)
C(2)	27(2)	26(2)	25(2)	–9(1)	4(1)	1(1)
C(3)	25(2)	15(2)	36(2)	–2(1)	3(1)	1(1)
C(4)	19(2)	19(2)	28(2)	2(1)	4(1)	–1(1)
C(5)	28(2)	19(2)	27(2)	3(1)	4(1)	0(1)
C(6)	34(2)	34(2)	34(2)	9(2)	7(2)	–8(2)
C(7)	43(2)	21(2)	37(2)	2(1)	3(2)	3(2)
C(8)	25(2)	19(2)	22(2)	5(1)	6(1)	4(1)
C(9)	25(2)	27(2)	23(2)	9(1)	0(1)	4(1)
C(10)	29(2)	32(2)	19(2)	5(1)	6(1)	2(1)
C(11)	23(2)	26(2)	18(2)	5(1)	5(1)	–2(1)
C(12)	31(2)	30(2)	19(2)	4(1)	10(1)	4(1)
C(13)	34(2)	30(2)	44(2)	8(2)	19(2)	6(2)
C(14)	60(2)	39(2)	22(2)	5(2)	15(2)	16(2)
C(15)	22(2)	26(2)	17(2)	0(1)	7(1)	5(1)
C(16)	26(2)	32(2)	17(2)	–2(1)	7(1)	4(1)
C(17)	25(2)	22(2)	29(2)	–1(1)	10(1)	3(1)
C(18)	18(2)	21(2)	22(2)	1(1)	6(1)	5(1)
C(19)	19(2)	18(2)	20(2)	4(1)	3(1)	4(1)
C(20)	24(2)	23(2)	30(2)	0(1)	4(1)	5(1)
C(21)	29(2)	24(2)	25(2)	1(1)	4(1)	2(1)
C(22)	20(2)	19(2)	14(2)	5(1)	1(1)	4(1)
C(23)	17(2)	22(2)	17(2)	6(1)	4(1)	1(1)
C(24)	21(2)	26(2)	14(2)	5(1)	6(1)	4(1)
C(25)	21(2)	24(2)	11(2)	2(1)	0(1)	5(1)
C(26)	22(2)	29(2)	17(2)	–4(1)	2(1)	3(1)
C(27)	24(2)	31(2)	29(2)	–6(1)	–2(1)	2(1)
C(28)	43(2)	34(2)	21(2)	–4(1)	6(2)	6(2)

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(29)	19(2)	25(2)	20(2)	2(1)	1(1)	4(1)
C(30)	35(2)	27(2)	23(2)	8(1)	–7(1)	3(1)
C(31)	35(2)	17(2)	33(2)	–1(1)	–5(1)	3(1)
C(32)	18(2)	23(2)	25(2)	–3(1)	0(1)	3(1)
C(33)	22(2)	20(2)	26(2)	–4(1)	2(1)	3(1)
C(34)	25(2)	31(2)	33(2)	–6(1)	6(1)	4(1)
C(35)	29(2)	25(2)	31(2)	–7(1)	3(1)	2(1)
C(36)	21(2)	23(2)	18(2)	–5(1)	1(1)	–1(1)
C(37)	26(2)	30(2)	24(2)	–10(1)	3(1)	2(1)
C(38)	34(2)	37(2)	17(2)	–3(1)	5(1)	2(2)
C(39)	24(2)	29(2)	17(2)	0(1)	6(1)	5(1)
C(40)	37(2)	31(2)	24(2)	–1(1)	13(1)	–5(2)
C(41)	34(2)	43(2)	48(2)	–7(2)	22(2)	–5(2)
C(42)	72(3)	41(2)	25(2)	–1(2)	21(2)	–9(2)
C(43)	26(2)	29(2)	17(2)	2(1)	4(1)	–6(1)
C(44)	35(2)	31(2)	19(2)	8(1)	3(1)	–6(2)
C(45)	34(2)	19(2)	29(2)	6(1)	3(1)	–3(1)
C(46)	20(2)	19(2)	27(2)	3(1)	3(1)	–2(1)
C(47)	20(2)	18(2)	22(2)	–1(1)	2(1)	1(1)
C(48)	31(2)	26(2)	26(2)	0(1)	6(1)	–6(1)
C(49)	33(2)	23(2)	32(2)	3(1)	7(1)	6(1)
C(50)	24(2)	17(2)	16(2)	–5(1)	2(1)	2(1)
C(51)	23(2)	24(2)	17(2)	–5(1)	2(1)	–1(1)
C(52)	22(2)	23(2)	12(2)	0(1)	0(1)	–7(1)
C(53)	28(2)	21(2)	9(1)	–3(1)	2(1)	–4(1)
C(54)	23(2)	27(2)	16(2)	1(1)	–1(1)	3(1)
C(55)	24(2)	36(2)	27(2)	–3(1)	–2(1)	4(1)
C(56)	41(2)	33(2)	18(2)	6(1)	3(1)	3(2)

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $[HLZr]_2O$.

Atom	x	y	z	U_{eq}
H(2)	641	–257	–243	31
H(3)	864	–1247	915	31
H(6A)	407	447	2332	51
H(6B)	583	–254	2997	51
H(6C)	428	–825	2258	51
H(7A)	947	–1678	2048	51
H(7B)	1070	–1325	2864	51
H(7C)	1275	–1008	2269	51
H(8)	1266	997	2409	26
H(9)	1340	41	3593	30
H(10)	1095	1297	4313	32
H(13A)	240	2340	2832	52
H(13B)	158	2913	3528	52
H(13C)	304	1728	3585	52
H(14A)	724	2459	4595	59
H(14B)	594	3658	4456	59
H(14C)	965	3387	4450	59
H(16)	729	5143	3859	30
H(17)	642	6400	2789	29
H(20A)	8	4745	1370	38
H(20B)	25	5564	732	38
H(20C)	36	6002	1527	38
H(21A)	550	6957	1535	39
H(21B)	547	6575	731	39
H(21C)	857	6345	1346	39
H(23)	1059	4888	808	23
H(24)	1033	3132	71	24
H(27A)	–15	1149	–311	43
H(27B)	–51	2423	–350	43
H(27C)	16	1832	411	43
H(28A)	731	1925	–786	49
H(28B)	390	2486	–1086	49
H(28C)	414	1210	–1033	49
H(30)	2104	37	3709	36
H(31)	1962	–880	2502	36
H(34A)	2254	1352	1122	44
H(34B)	2134	531	480	44
H(34C)	2330	103	1233	44
H(35A)	1875	–1181	1351	43

Atom	x	y	z	U_{eq}
H(35B)	1714	–790	561	43
H(35C)	1510	–746	1189	43
H(36)	1386	1219	1076	25
H(37)	1402	519	–156	33
H(38)	1590	2077	–733	35
H(41A)	2379	4326	453	59
H(41B)	2352	3074	279	59
H(41C)	2303	3504	1043	59
H(42A)	1616	4140	–755	67
H(42B)	1944	3527	–817	67
H(42C)	1954	4769	–612	67
H(44)	1621	5907	–77	34
H(45)	1552	6981	1018	33
H(48A)	2168	6490	3118	41
H(48B)	2126	7055	2351	41
H(48C)	2279	5882	2467	41
H(49A)	1311	6366	2426	44
H(49B)	1535	7329	2253	44
H(49C)	1577	6875	3052	44
H(51)	1263	4701	2898	25
H(52)	1443	2920	3534	23
H(55A)	2612	2023	3877	45
H(55B)	2535	3223	4084	45
H(55C)	2522	2909	3264	45
H(56A)	1818	1893	4336	46
H(56B)	2098	2690	4709	46
H(56C)	2182	1466	4579	46