### **Supporting Information**

# Oxygenation of RZn(N,O)-type complexes as an efficient route to zinc alkoxides not accessible via classical alcoholysis path

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- 1. General experimental procedures: All operations were carried out under dry nitrogen using standard Schlenk techniques.  ${}^{Bu_2Zn^1}$  was synthesized according to the literature method under a nitrogen atmosphere using standard Schlenk techniques. Synthesis of complexes of general formula [RZn(L)], (where R = Et or 'Bu and L = pyrrole-2carboxylate) were described elsewhere.<sup>2</sup> All other reagents were purchased from Sigma-Aldrich Co and use as received. Solvents were purchased from POCH (Poland) were purified prior to use using MBraun solvent purification system MB SPS-800. <sup>1</sup>H NMR spectra were acquired on Varian Mercury 400 MHz spectrometer at 298 K. Chemical shifts are expressed in  $\delta$  (ppm). The infrared spectra were recorded on an FT-IR Bruker TENSOR II spectrometer.
- 2. Synthesis of [EtOZn(L)]<sub>4</sub> (1<sub>4</sub>). A solution of 1H-pyrrole-2-carboxaldehyde (0.1 g, 0,81 mmol) in toluene (5 ml) was cooled to -78°C, and Et<sub>2</sub>Zn (0,405 ml of a 2 M solution in hexene, 0,81 mmol) was added drop wise. The reaction mixture was warmed to the room temperature and stirred for 4 h. After that the solution was cooled to -20°C and exposed to an excess of dry oxygen for approximately 2 h. Then, the excess of O<sub>2</sub> was removed and the system was purged with nitrogen by using a vacuum-nitrogen line. The resulting complex 1<sub>4</sub> was obtained from toluene solution at -20°C after 24 hours as a colorless cubic-like crystals (isolated yield 84 %, 159.2 mg). H<sup>1</sup> NMR (400MHz, C<sub>6</sub>D<sub>6</sub>): δ, ppm, 1,24 (t, 3H, ZnOCH<sub>2</sub>CH<sub>3</sub>), 2,25 (q, 2H, ZnOCH<sub>2</sub>CH<sub>3</sub>), 3,62 (s, 3H, CH<sub>3</sub>), 6,74 (s, 1H, CH<sub>pyrrol</sub>), 7,14 (d, 1H, CH<sub>pyrrol</sub>), 7,45 (s, 1H, CH<sub>pyrrol</sub>); IR (ATR) cm<sup>-1</sup>: 3458 (vw), 3101 (vw), 2959 (w), 2860 (vw), 2356 (vw), 2111 (vw), 1607 (s), 1506 (s), 1435 (s), 1379 (vs), 1355 (vs), 1302 (w), 1261 (vw), 1213 (m), 1186 (vs), 1170 (vs), 1084 (s), 1038 (vs), 995 (s), 941 (w), 881 (s), 798 (w), 743 (vs), 644 (w), 609 (w), 512 (s), 423 (s). Elemental analysis: calcd. for C<sub>32</sub>H<sub>44</sub>N<sub>4</sub>O<sub>12</sub>Zn<sub>4</sub>: % C 41; % H 4,81; found % C 40,17 , % H 4,67
- 3. Synthesis of ['BuOZn(L)]<sub>3</sub> (2<sub>3</sub>). A solution of 1H-pyrrole-2-carboxaldehyde (0.1 g, 0,81 mmol) in hexane (2,5 ml) and toluene (2,5 ml) was cooled to -78°C, and 'Bu<sub>2</sub>Zn (0,81 ml of a 1 M solution in toluene, 0,81 mmol) was added drop wise. The reaction mixture was warmed to the room temperature and stirred for 4 h. After that the solution was cooled to -20°C and exposed to an excess of dry oxygen for approximately 2 h. Then, the excess of O2 was removed and the system was purged with nitrogen by using a vacuum-nitrogen line. The resulting complex 2<sub>3</sub> was obtained from toluene/hexane solution at -20°C after 24 hours as a colorless cubic-like crystals (isolated yield 69 %, 230.1 mg). H<sup>1</sup> NMR (400MHz, C<sub>6</sub>D<sub>6</sub>): δ, ppm, 1,5 (s, 9H, ZnOC(CH<sub>3</sub>)<sub>3</sub>), 3,52 (s, 3H, CH<sub>3</sub>), 6,70 (s, 1H, CH<sub>pyrrol</sub>), 7,35 (s, 1H, CH<sub>pyrrol</sub>), 7,45 (s, 1H, CH<sub>pyrrol</sub>); IR (ATR) cm<sup>-1</sup>: 3393 (vw), 3102 (vw), 2967 (w), 2298 (vw), 2113 (vw), 1592 (m), 1507 (m), 1470 (w), 1436 (s), 1380 (s), 1357 (vs), 1306 (w), 1242 (w), 1213 (m), 1186 (vs), 1169 (vs), 1082 (m), 1039 (s), 995 (m), 938 (m), 896 (m), 795 (w), 744 (vs), 644 (w), 586 (m), 534 (m), 496 (m), 424 (m). Elemental analysis: calcd. for C<sub>30</sub>H<sub>45</sub>N<sub>3</sub>O<sub>9</sub>Zn<sub>3</sub>: % C 45,7, % H 5,71; found % C 45,48, % H 5,44

- 4. Synthesis of  $[({}^{t}Bu)_{2}Zn_{4}(\mu_{4}-O)L_{4})]$  (3). A solution of 1H-pyrrole-2-carboxaldehyde (HL) (0.1 g, 0.81 mmol) in THF (5 ml) was cooled to -78°C, and 'Bu<sub>2</sub>Zn (0.81 ml of a 1 M solution in toluene, 0,81 mmol) was added dropwise. The reaction mixture was warmed to the room temperature and stirred for 4 h. Then, volatiles was removed under vacuum and solid residues were dissolved in toluene. Complex 3 was obtained as colorless needles like crystals after 24h from a toluene solution at -20°C (isolated yield 13 %, 32.5 mg). H<sup>1</sup> NMR (400MHz, toluene -  $d_6$ ):  $\delta$ , ppm, 1,36 (s, 9H, ZnC(CH<sub>3</sub>)<sub>3</sub>), 3,66 (s, CH<sub>3</sub>), 6,72 (m, 1H, CH<sub>pyrrol</sub>), 7,19 (m, 1H, CH<sub>pyrrol</sub>), 7,31 (m, 1H, CH<sub>pyrrol</sub>), IR (ATR) cm<sup>-1</sup>: 3572 (vw), 3514 (vw), 3289 (w), 3139 (vw), 3122 (vw), 2952 (vw), 2324 (vw), 2167 (vw), 2083 (vw), 2051 (vw), 1985 (vw), 1720 (vw), 1673 (m), 1650 (m), 1613 (s), 1556 (w), 1505 (m), 1438 (s), 1404 (m), 1380 (s), 1354 (m), 1321 (s), 1265 (w), 1187 (s), 1165 (vs), 1128 (s), 1084 (s), 1040 (m), 1031 (m), 995 (m), 980 (m), 940 (w), 925 (m), 893 (m), 876 (m), 849 (m), 770 (s), 739 (vs), 645 (m), 638 (m), 606 (m), 580 (m), 533 (m), 510 (s), 491 (s), 474 (m), 458 (m), 449 (m), 436 (s), 424 (s), 414 (s). Elemental analysis: calcd. for C<sub>32</sub>H<sub>42</sub>N<sub>4</sub>O<sub>9</sub>Zn<sub>4</sub>: % C 43,23 , % H 4,73; found % C 43,12 , % H 4,63
- 5. Equimolar reaction between [EtZn(L)] and EtOH (4). A pre-formed toluene solution of [EtZn(L)] (L =N,O pyrrole-based ligand) was cooled to -78°C, and equimolar amount of EtOH was added dropwise. The reaction mixture was warmed to the room temperature and stirred for 24 h.



**Figure S1.** The H1 NMR spectra of a)  $[EtOZn(L)]_3$  (1<sub>4</sub>) b) the equimolar reaction between  $[EtZn(L)]_n$  and EtOH (4) (\*C<sub>6</sub>D<sub>6</sub>, 400 MHz, RT)

6. Equimolar reaction between of [EtZn(L)] and 'BuOH (5). A pre-formed toluene solution of [EtZn(L)] (L =N,O pyrrole-based ligand) was cooled to -78°C, and equimolar amount of 'BuOH was added dropwise. The reaction mixture was warmed to the room temperature and stirred for 24 h.



**Figure S2.** The H1 NMR spectra of a)  $[{}^{r}BuOZn(L)]_{3}$  (2<sub>3</sub>) b) the equimolar reaction between of  $[EtZn(L)]_{n}$  and  ${}^{t}BuOH$  (5) (\*C<sub>6</sub>D<sub>6</sub>, 400 MHz, RT)

### Variable-temperature 1H NMR spectra of 14 in toluene-d8



#### **Diffusivity measurement**

Application of Diffusion Ordered Spectroscopy (DOSY), which has happened to become a very routine NMR technique lately, provided us with a reliable evidence of approximate size of the species existing in the solution. As already discussed in antecedent works<sup>3,4</sup> molecular weight can be straightforwardly obtained by combining Stokes-Einstein equation (D =  $(kT)/(6\pi\eta r_H)$ ) and the relationship between molecular weight M and molar radius, which reads M =  $(4\pi r_M^3 \rho NA)/3$ , where  $r_H$ and  $r_M$  are hydrodynamic and molar radii respectively,  $\eta$  is viscosity and  $\rho$  is density of the liquid. It has also been shown that these quantities are much alike for small molecules, which is the case in our system, although it has to be noted that such estimation can lead to errors in the range of 10-20%. This is accurate enough for the purposes of assessing the aggregation state of the complex that we deal with. DOSY measurement was performed in dry and degassed toluene-d8 as we exploited the fact that the physical properties of the diluted solution, namely density and viscosity, deviate only slightly from properties of the pure solvent. Pulsed field gradient double stimulated echo convection-compensated (PFGSTE) sequence with total of 15 diffusion encoding gradients (ranging from 3 to 45 G/cm, sine shaped, equal steps in gradient squared) was used and the total width of the gradient pulse was optimised to achieve attenuation of about 90% of the initial intensity of the signals. Overall, the key acquisition parameters were as follows: total length of gradient encoding pulses gradient -2 ms, diffusion delay -50 ms, gradient recovery delay -1 ms, relaxation delay -2 s. Steady-state scans in number of 16 were performed prior to acquisition of the data. The sample was allowed to equilibrate in the set temperature (303 K) controlled by VT module. Spinner was turned off. Raw data was processed with MestReNova 6.0.2-5475.

 $\eta = 5.113$ E-04 Pa·s

 $\rho = 0.943 \text{ kg/m}^3$ 



D [10 <sup>10</sup> ·m <sup>2</sup> ·s <sup>-1</sup> ]	Rh[Å]	MW <sub>calc</sub> [g·mol <sup>-1</sup> ]	MW <sub>exp</sub> [g·mol <sup>-1</sup> ]	n	
5.82	7.46	220.52	986.45	4.47	



DOSY NMR spectra of **2** in toluene-*d8* at 30 °C.

D [ $10^{10} \cdot m^2 \cdot s^{-1}$ ]	Rh[Å]	MW <sub>calc</sub> [g·mol <sup>-1</sup> ]	MW <sub>exp</sub> [g·mol <sup>-1</sup> ]	n
7.23	6.00	262.61	514.55	1.96
8.99	4.83	262.61	267.65	1.02

#### General comments on crystallographic data:

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 complex **1** were collected at 100(2)K on a SuperNova Agilent diffractometer using Mo*K* $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were processed with *CrysAlisPro*.<sup>5</sup> The X-ray data for complexes **2** and **3** were collected at 100(2)K on a Nonius Kappa CCD diffractometer.<sup>6</sup> Using graphite monochromated Mo*K* $\alpha$  radiation ( $\lambda = 0.71073$  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).<sup>7</sup> The structures were solved by direct methods using the SHELXS-97 program and was refined by full matrix least–squares on F<sup>2</sup> using the program SHELXL-97.<sup>8</sup> 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@ccd.cam.ac.uk)

Crystal data for **1** • 2 C<sub>7</sub>H<sub>8</sub>; C<sub>46</sub>H<sub>60</sub>N<sub>4</sub>O<sub>12</sub>Zn<sub>4</sub>: M = 1122.46, crystal dimensions  $0.30 \times 0.14 \times 0.10 \text{ mm}^3$ , moclinic, space group P 21/n (no. 14), a = 16.1075(8) Å, b = 33.2173(19) Å, c = 18.7222(8) Å,  $\beta = 97.309(4)$  °, U = 9935.9(9) Å<sup>3</sup>, Z = 8, F(000) = 4640,  $D_c = 1.501$  g cm<sup>-3</sup>, K,  $\mu$ (Mo-K $\alpha$ ) = 1.971 mm<sup>-1</sup>,  $\theta_{max} = 29.146$  °, 22926 unique reflections, R1 = 0.1295, wR2 = 0.1127 for all data and 1209 parameters and 0 restraints, R1 = 0.0626, wR2 = 0.0941 for 13069 reflections with  $I_o > 2\sigma(I_o)$ . The goodness-of-fit on F<sup>2</sup> was equal 0.929. 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 = + 0.75 / -0.95 eÅ<sup>-3</sup>. CCDC-1555507



**Figure S2.** Molecular structure of **1** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Zn1 – O1	2.017(3)
Zn1 – O2	2.157(3)
Zn1 – N1	1.921(4)
Zn1 – O5	2.373(3)
Zn2 - O1	2.028(3)
Zn2 - O2	2.023(3)
Zn2 - N2	1.942(4)
Zn2 - O7	2.278(3)
Zn3 - O3	2.022(3)
Zn3 – O4	2.006(3)
Zn3 – N3	1.938(4)
Zn3 – O9	2.301(3)
Zn4 - O3	2.155(3)
Zn4 - O4	1.934(4)
Zn4 - N4	1.934(4)
Zn4 – O11	2.319(3)
O1 – C1	1.439(5)
O2 - C3	1.436(5)
O3 – C5	1.443(5)
O4 – C7	1.435(5)
C13 – O5	1.224(6)
C13 – O6	1.346(5)
C13 – C12	1.436(7)
C19 – O7	1.228(6)
C19 – O8	1.333(6)
C19 – C18	1.441(6)
C25 – O9	1.236(5)
C25 – O10	1.327(6)
C25 - C24	1.454(7)
C31 – O11	1.239(6)
C31 – O12	1.335(5)
C31 – C30	1.440(7)
O1 –Zn1 – O2	83.65(11)
O1 - Zn2 - O2	86.91(12)
O3 - Zn3 - O4	87.24(12)
O3 - Zn4 - O4	87.24(12)
O5 - C13 - O6	123.0(4)
O7 – C19 – O8	123.0(5)
O9 - C25 - O10	123.8(5)
O11 – C31 – O12	122.3(5)

Table	<b>S1</b> .	Selected	Bond	Lengths	(Å)	) and	Angles	(deg)	for	Com	bound	1.
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Crystal data for **2**;  $C_{30}H_{45}N_3O_9Zn_3$ : M = 787.80, crystal dimensions  $0.34 \times 0.22 \times 0.12 \text{ mm}^3$ , triclinic, space group P -1/n (no. 2), a = 9.5290(2) Å, b = 11.4430(3) Å, c = 16.9590(5) Å, a = 95.4520(10) °,  $\beta = 92.720(2)$  °,  $\gamma = 101.483(2)$  °, U = 1799.82(8) Å<sup>3</sup>, Z = 2, F(000) = 816,  $D_c = 1.454$  g cm<sup>-3</sup>, K,  $\mu$ (Mo-K $\alpha$ ) = 2.034 mm<sup>-1</sup>,  $\theta_{max} = 27.503$  °, 8178 unique reflections, R1 = 0.0549, wR2 = 0.0822 for all data and 418 parameters and 0 restraints, R1 = 0.0420, wR2 = 0.0777 for 6932 reflections with  $I_o > 2\sigma(I_o)$ . The goodness-of-fit on F<sup>2</sup> was equal 1.089. 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 = +0.74/-0.58 eÅ<sup>-3</sup>. CCDC - 1555508



**Figure S3.** Molecular structure of **2** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Zn1 – O1	1.928(2)
Zn1 – O3	1.916 (2)
Zn1 – O4	2.109(2)
Zn1 – N1	1.961(3)
Zn2 – O1	1.945(2)
Zn2 - O2	1.921(2)
Zn2 – O6	2.111(2)
Zn2 - N2	1.961(2)
Zn3 – O2	1.936(2)
Zn3 – O3	1.934(2)
Zn3 – O8	2.104(2)
Zn3 – N3	1.978(2)
O1 – C1	1.447(3)
O2 – C5	1.443(3)
O3 – C9	1.449(3)
C17 – O4	1.237(4)
C17 – O5	1.335(4)
C16 – C17	1.435(4)
C23 – O6	1.244(3)
C23 – O7	1.329(3)
C22 - C23	1.430(4)
C29 – O8	1.249(4)
C29 – O9	1.323(3)
C28 – C29	1.430(4)
O1 –Zn1 – O3	96.20(8)
O1 - Zn2 - O2	97.99(8)
O2 - Zn3 - O3	107.37(8)
O4 –C17 – O5	121.0(3)
O6 - C23 - O7	122.0(3)
O8 - C29 - O9	122.1(3)
N1 - Zn1 - O4	82.92(10)
N2 - Zn2 - O6	83.04(9)
N3 - Zn3 - O8	83.01(9)

Table S2. Selected Bond Lengths	s (Å) and	Angles (deg)	for Compound 2.
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Crystal data for **3**;  $C_{32}H_{42}N_4O_9Zn_4$ : M = 888.17, crystal dimensions  $0.28 \times 0.16 \times 0.08 \text{ mm}^3$ , monoclinic, space group C 2/c/n (no. 15), a = 18.0060(4) Å, b = 11.4160(2) Å, c = 18.1170(4)Å,  $\beta = 92.1610(10)$  °, U = 3721.42(13) Å<sup>3</sup>, Z = 4, F(000) = 1816,  $D_c = 1.585$  g cm<sup>-3</sup>, K,  $\mu$ (Mo-K $\alpha$ ) = 2.602 mm<sup>-1</sup>,  $\theta_{max} = 27.482$  °, 4264 unique reflections, R1 = 0.0491, wR2 = 0.0755 for all data and 227 parameters and 0 restraints, R1 = 0.0372, wR2 = 0.0715 for 3632 reflections with  $I_o > 2\sigma(I_o)$ . The goodness-of-fit on F<sup>2</sup> was equal 1.066. 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 = + 0.44 / -0.38 eÅ<sup>-3</sup>. CCDC - 1555509



**Figure S4.** Molecular structure of **3** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: (-x+1,y,-z+1/2).

Zn1 – O1	1.9349(11)
Zn1 – O2	2.2007(19
Zn1 – O4'	2.268(2)
Zn1 – C1	1.976(3)
Zn2 – O1	1.973(1)
Zn2 - O2	2.3360(19)
Zn2 - O4	2.399(2)
Zn2 – N1	1.936(2)
Zn2 - N2	1.948(2)
C9 – O2	1.255(3)
C9 – O3	1.331(3)
C9 – C8	1.416(4)
C15-O4	1.260(3)
C15 – O5	1.333(3)
C15 - C14	1.418(4)
Zn1 - O1 - Zn2	100.844(17)
Zn1 - O1 - Zn1	100.627(17)
Zn1 - O1 - Zn2	100.847(17)
Zn2 - O1 - Zn2'	121.58(14)
O2 - C9 - O3	121.6(3)
O4 - C15 - O5	121.7(3)

Table S3. Selected Bond Lengths (Å) and Angles (deg) for Compound 3.

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<sup>&</sup>lt;sup>4</sup> Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D.; *Chem. Soc. Rev.* **2008**, *37*, 479–489.

<sup>&</sup>lt;sup>5</sup> Agilent Technologies, *CrysAlisPro*, Version 1.171.35.21b

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<sup>&</sup>lt;sup>8</sup>G. M. Sheldrick, Acta Cryst. **2008**, 64A, 112-122.]