New nodes for MOF construction: Synthesis, Characterization and H_2 up-take

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Supporting Information

Experimental section

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services at the London Metropolitan University. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400 MHz or a Gemini at 300 MHz (^{1}H) and 282.2 MHz (^{19}F) at 298 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (nujol mulls, KBr/CsI windows) were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers. The precursor [$(C_6F_5)_2$Zn·toluene] was prepared by the method of Bochmann. [1]

Example of type **I** (R = Me, $R^{/}$ = $R^{//}$ - C_6F_5):

1,1-Me_2NNH_2 (0.14 cm^3, 1.85 mmol) and $(C_6F_5)_2$Zn.toluene (1.0 g, 2.03 mmol) were heated in toluene for 2 h. Following removal of volatiles *in-vacuo*, the residue was extracted into MeCN (30 cm^3) and cooled at 0 ^{o}C to afford colourless prisms in 60 - 70 yields. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 3.61 (s, 1H, N*H*), 3.48 (s, 1H, N*H*), 3.16 (s, 1H, N*H*), 3.09 (s, 3H. N*Me*), 2.99 (s, 3H. N*Me*), 2.96 (s, 1H, N*H*), 2.85 (s, 3H. N*Me*), 2.82 (s, 3H. N*Me*), 2.64 (s, 3H. N*Me*), 2.53 (s, 3H. N*Me*), 2.43 (s, 3H. N*Me*), 2.37 (s, 3H. N*Me*). ^{19}F NMR (CDCl$_3$, 282 MHz) δ: -114.28 (m, 2F, *o*-F), -115.29 (m, 2F, *o*-F), -115.72 (m, 2F, *o*-F), -116.28 (m, 2F, *o*-F), -154.28 (t, 1F, *p*-F), -155.15 (t, 1F, *p*-F), -

155.34 (t, 1F, *p*-F), -156.46 (t, 1F, *p*-F), -159.88 (m, 2F, *m*-F), -160.17 (m, 2F, *m*-F), -160.49 (m, 2F, *m*-F), -161.11 (m, 2F, *m*-F). IR: 3183w (NH), 1316s, 1262m, 1243w, 1154s, 1100s, 1031s, 802s, 773m, 722w, 674w, 640w. Mass Spec (EI): M^+ 1166, 707 (M^+ - $2C_6F_5$ – Zn – Me_2NNH).

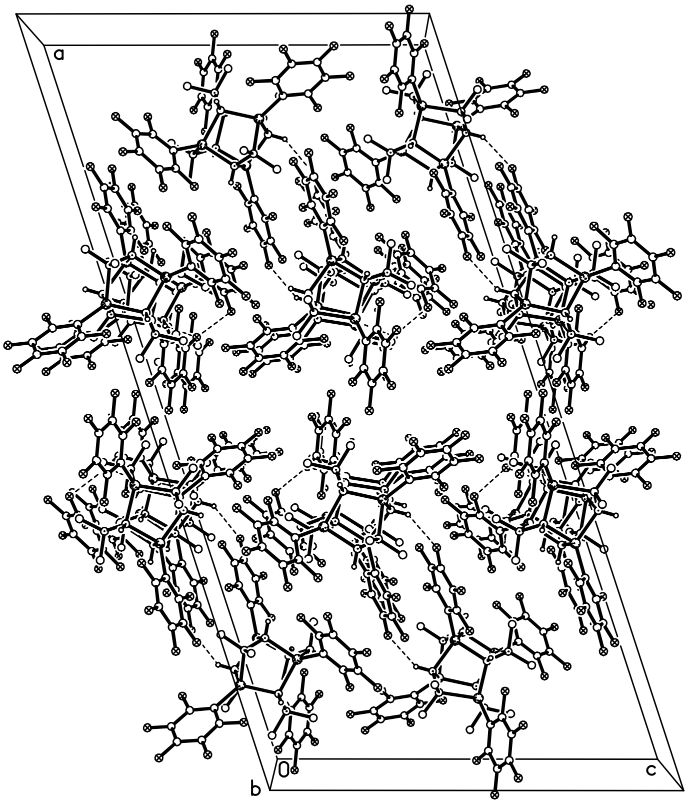

Figure S1: Packing plot showing 1-D, H-bonded, tapes of **I** (R = Me, $R^/$ = C_6F_5).

Example of type **II** (R = Ph, $R^/$ = C_6F_5):

1-Me,1-$PhNNH_2$ (0.18 cm^3, 1.53 mmol), $(C_6F_5)_2Zn$.toluene (1.0 g, 2.03 mmol) and H_2O (0.1 cm^3, 0.55 mmol) were heated in toluene for 2 h. Work-up as in method for **I** above afforded colourless prisms in 70 - 75 yields.. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.18 (m, 7H, aryl*H*), 6.78 (m, 8H, aryl*H*), 2.91 (s, 9H. N*Me*), 1.95 (overlapping signals, 12H, *Me*CN + N*H*). ^{19}F NMR (acetone-d_6, 282 MHz) δ: -140.47 (m, 8F, *o*-F), -156.35 (m, 4F, *p*-F), 164.28 (m, 8F, *m*-F). IR: 3468bw (OH), 3168w (NH), 1630w, 1599w, 1545w, 1535w, 1262s, 1096bs, 1021bs, 871w, 801s, 723w, 690w. $[(C_6F_5Zn)_4(OH)(NHNMe_2)_3]$.3MeCN requires C, 42.7; H, 2.6; N, 8.8 %. Found, C, 42.6, H, 2.6, N, 8.8 %.

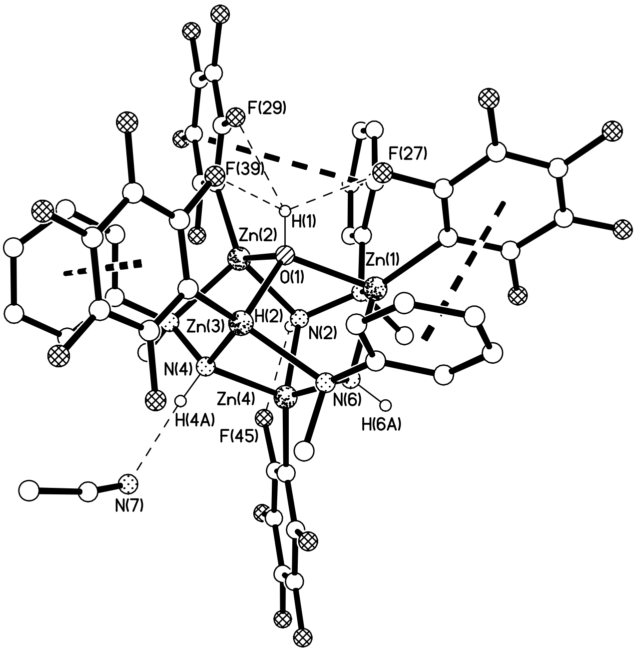

Figure S2: The mono-solvated structure **II** ((R = Ph, $R^{/}$ = C_6F_5). Selected bond lengths (Å) and angles (^{o}) with estimated standard deviations: Zn(1) – O(1) 2.061(7), Zn(1) – N(1) 2.131(9), Zn(1) – N(6) 2.007(9), Zn(2) – O(1) 2.059(8), Zn(2) – N(2) 2.010(9), Zn(2) – N(3) 2.120(10), Zn(3) – O(1) 2.062(7), Zn(3) – N(4) 2.007(10), Zn(3) – N(5) 2.125(10), Zn(4) – N(2) 2.067(9), Zn(4) – N(4) 2.085(10), Zn(4) – N(6) 2.059(10); O(1) – Zn(1) – N(1) 94.4(3), O(1) – Zn(1) – N(6) 92.3(3), Zn(2) – O(1) – Zn(3) 106.5(3).

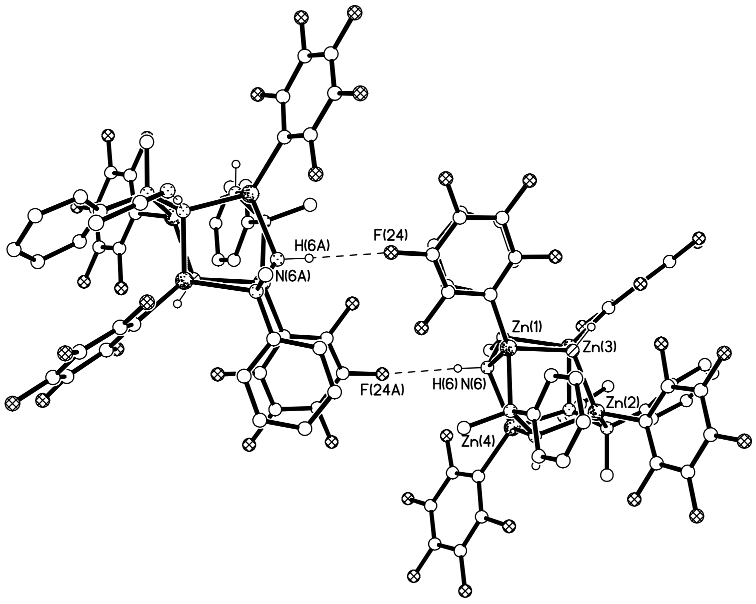

Figure S3: Pairs of head-to-tail H-bonded molecules of **II**.

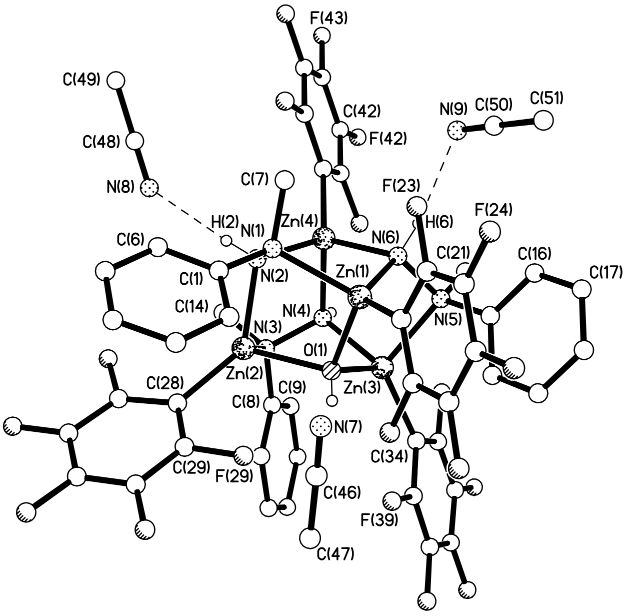

Figure S4: The tris-solvated structure **II** ((R = Ph, $R^{/} = C_6F_5$) Selected bond lengths (Å) and angles (^{o}) for tris-solvate with estimated standard deviations: Zn(1) – O(1) 2.0710(16), Zn(1) – N(1) 2.1174(19), Zn(1) – N(6) 2.0210(19), Zn(2) – O(1) 2.0726(17), Zn(2) – N(2) 2.010(2), Zn(2) – N(3) 2.1207(19), Zn(3) – O(1) 2.0508(17), Zn(3) – N(4) 2.004(2), Zn(3) – N(5) 2.1166(19), Zn(4) – N(2) 2.044(2), Zn(4) – N(4) 2.0762(19), Zn(4) – N(6) 2.078(2); O(1) – Zn(1) – N(1) 96.38(7), O(1) – Zn(1) – N(6) 91.19(7), Zn(2) – O(1) – Zn(3) 106.63(7).

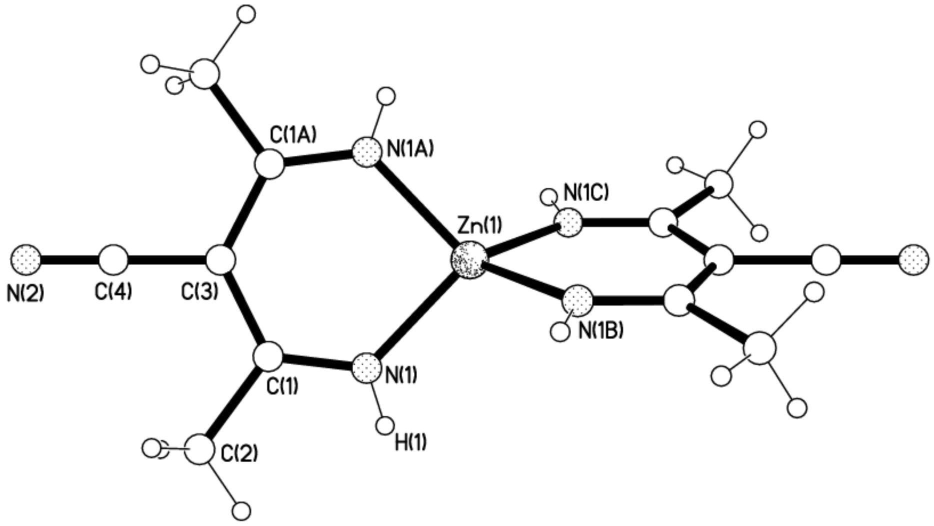

Figure S5: Nitrile coupled complex **III**. Selected bond lengths (Å) and angles (^{o}) with estimated standard deviations: Zn(1) – N(1) 1.9787(13), N(1) – C(1) 1.3056(19), C(1) – C(3) 1.4316(18); N(1) – Zn(1) – N(1B) 133.03(8), N(1) – Zn(1) – N(1A) 92.76(8). Symmetry operators: –x+1/4, y, –

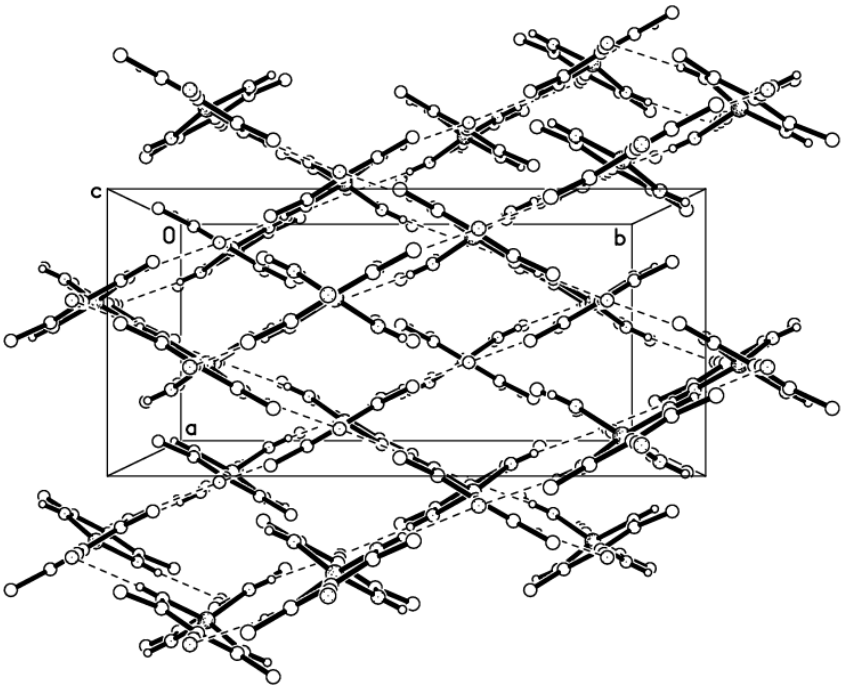

Figure S6: Diamondoid network in **III**.

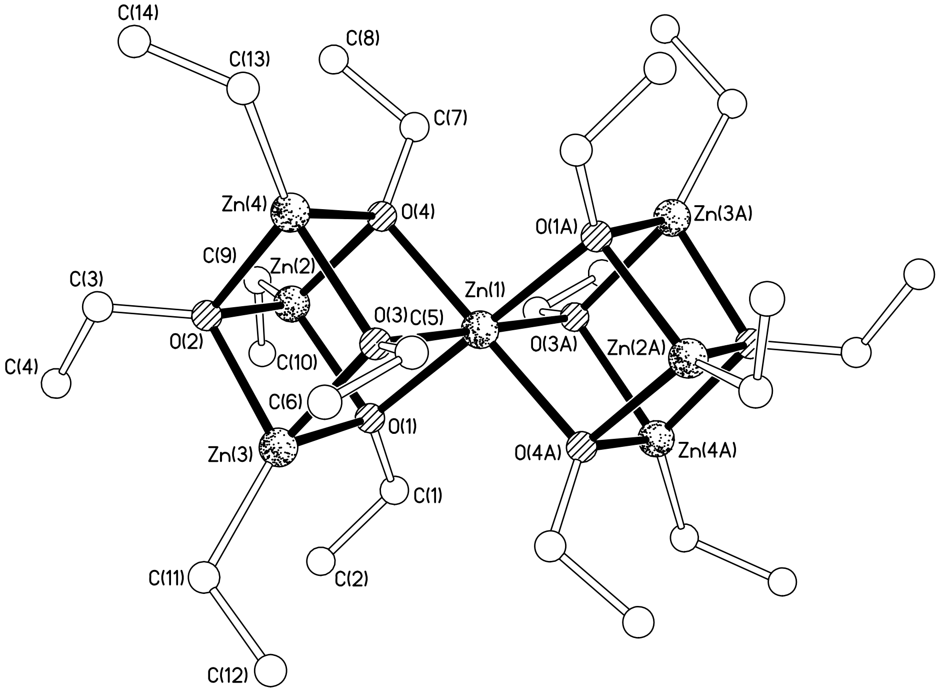

Figure S7: Double cube structure **IV**. One of two similar molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (^{o}) with estimated standard deviations: Zn(1) – O(1) 2.1356(19), Zn(1) – O(3) 2.1247(18), Zn(1) – O(4) 2.1011(19), Zn(2) – O(1) 2.0643(19), Zn(2) – O(2) 2.0619(19), Zn(2) – O(4) 2.069(2); O(1) – Zn(1) – O(1A) 180.0, Zn(1) – O(1) – Zn(2) 95.86(7). Symmetry operator: A = –x+1, –y+1, -z. For spectroscopic characterization see reference [2].

Example of type **V** complex:

*t*BuLi (1.5 cm^3, 2.55 mmol; 1.7 M in solution in pentane) was added to the *n*-hexane (20 cm^3) solution of [(EtZn)$_4$(NHNMe$_2$)$_4$] (1.5 g, 2.44 mmol) at -78 °C and stir for 3 h. MeAlCl$_2$ (1.275 mmol) was added slowly to this mixture and stir for overnight at ambient temperature. The volatiles were removed under vacuum and the residue was filtered using n-hexane (20 cm^3). The clear, colourless filtrate, when stored at -20 °C, afforded colourless crystals. Yield 40 – 45 %.

$C_{14}H_{39}ClN_8Zn_4$ requires C 27.3, H 6.4, N 18.2; found: C 26.9, H 6.3, N 18.3; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.04 (m, 12H, $\mathrm{N}Me_2$), 2.67 (m, 12H, $\mathrm{N}Me_2$), 2.35, 2.40, 2.52, 2.63 (4x s, 4H, N*H*), 1.46 (m, 9H, $\mathrm{ZnCH_2C}H_3$), 0.16 (q, 2H, 2H, $^2J_{HH}$ 8.0 Hz, $\mathrm{ZnC}H_2\mathrm{CH_3}$), 0.10 (q, 2H, J obscured, $\mathrm{ZnC}H_2\mathrm{CH_3}$), 0.03 (q, 2H, $^2J_{HH}$ 8.0 Hz, $\mathrm{ZnC}H_2\mathrm{CH_3}$). IR: 3176w, 2360w, 2341w, 1558w, 1262s, 1160s, 1090bs, 1040s, 991s, 951w, 870m, 819bs, 661m, 599m, 569m, 482m, 459w.

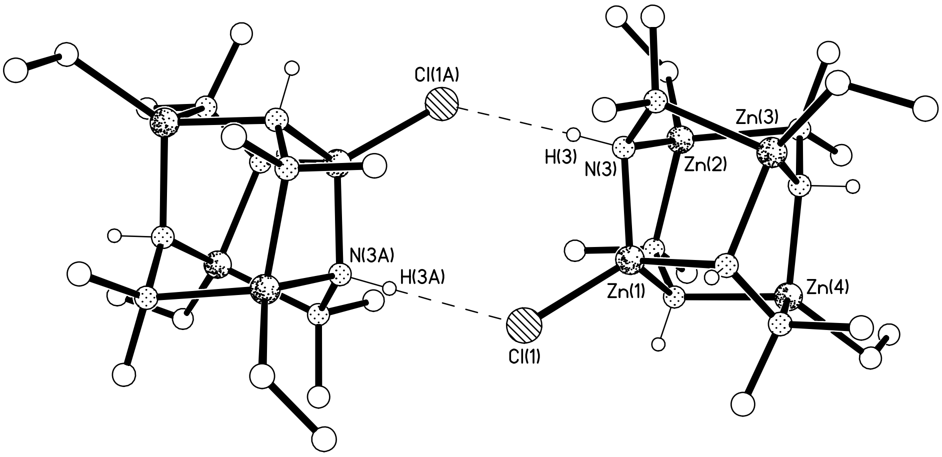

Figure S8: Head-to-tails pairs of H-bonded molecules in **V**.

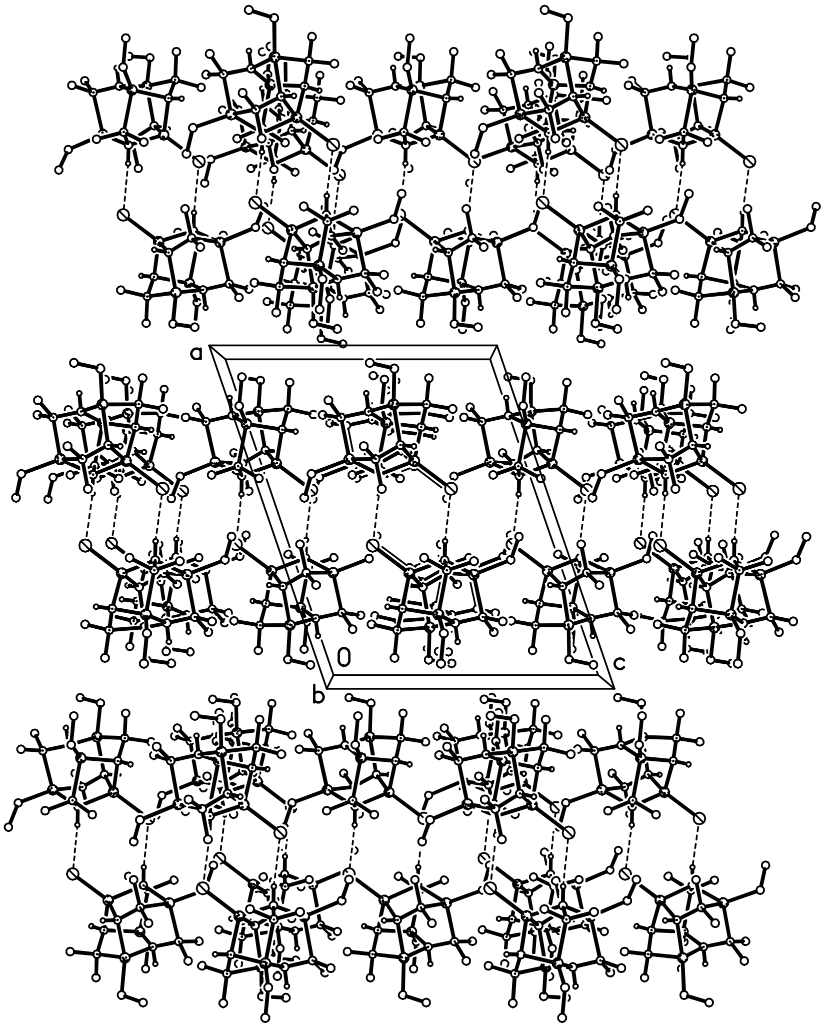

Figure S9: Layered structure of **V**.

Example of type **VI** (R = Me, R$^{/}$ = Et):

To [(EtZn)$_4$(OH)(NHNMe$_2$)$_3$] (1.0 g, 1.75 mmol) in hexane at -78 ^{o}C was added *tert*-butyllithium (1.06 cm^3, 1.7M, 1.80 mmol), and the system was slowly allowed to warm to ambient temperature and stirred for 6 h. Following removal of volatiles *in vacuo*, the residue was extracted into hexane (20 cm^3). The colourless solution was stored at -20 °C to afford colourless block shaped crystals of **VI** in 40 – 45 % yield. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 2.79 – 2.42 (overlapping m, 21H N*Me*$_2$ + N*H*), 1.22 (m, 12H, ZnCH$_2$C*H*$_3$), 0.55 (m, 8H, ZnC*H*$_2$CH$_3$). IR: 3185w, 1636m, 1607w, 1532w, 1503s, 1340m, 1260s, 1170w, 1097s, 1068s, 1050s, 1021s, 947s, 847m, 809s, 734w, 698w. [(EtZn)$_4$(OLi)(NHNMe$_2$)$_3$]$_2$ requires C, 29.1; H, 7.2; N, 14.5 %. Found, C, 28.9, H, 7.0, N, 14.5 %.

References

[1] D.A. Walker, T.J. Woodman, D.L. Hughes and M. Bochmann *Organometallics* **2001**, *20*, 3772.

[2] S. Jana, R.J.F. Berger, R. Fröhlich, T. Pape and N.W. Mitzel, *Inorg. Chem*. **2007**, *46*, 4293.