Electronic Supplementary Material (ESI) for Dalton Transactions.

Formation of Novel Mononuclear N,O-chelate Zirconium Complexes by Direct Insertion of Epoxide into Tetrakis(dimethylamido)zirconium: Highly Promising Approach for Developing ALD Precursor of ZrO_2 Thin Film

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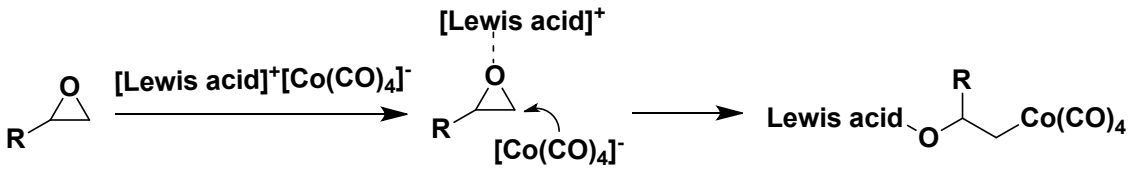
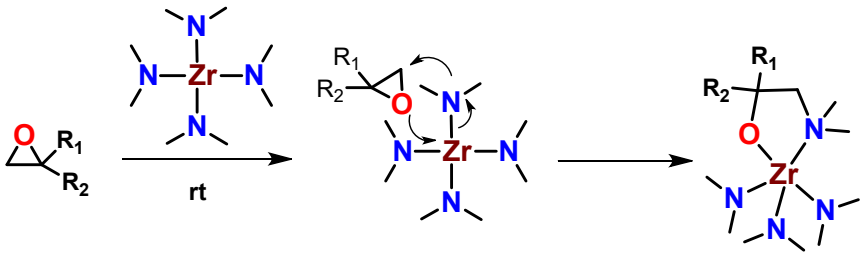
Supporting Information

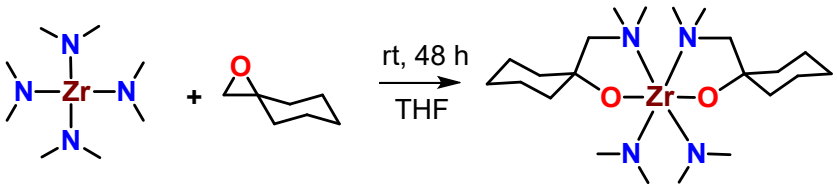
Coates and our previous work



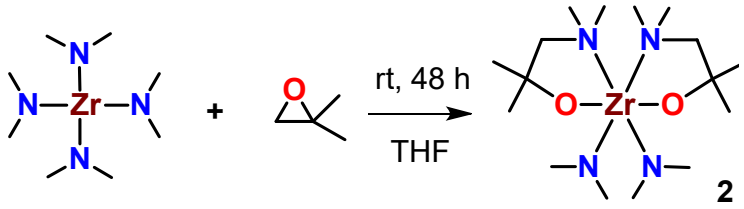
Our inspiration



Scheme S1 Proposed mechanism for the formation of N,O-chelate Zr complex.



Scheme S2 Synthetic procedure of complex **1.**



Scheme S3 Synthetic procedure of complex **2.**

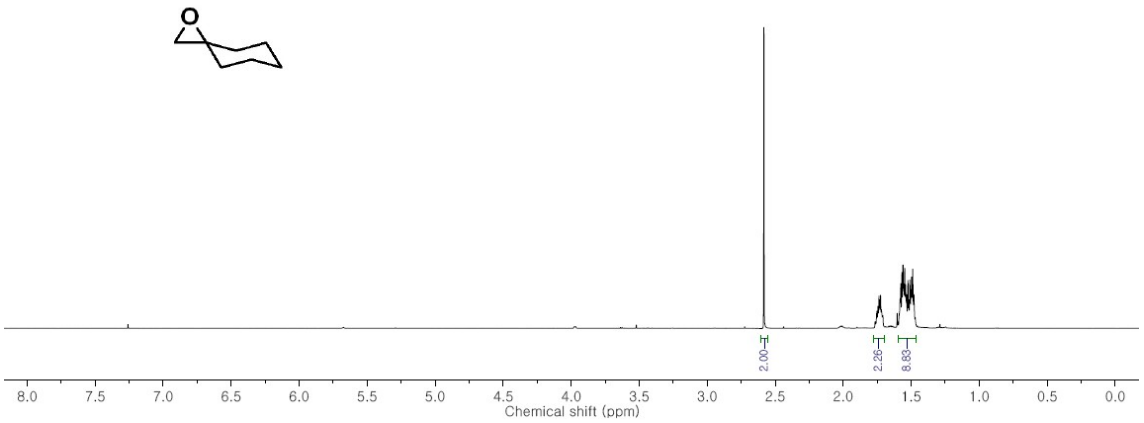


Fig. S1 ^{1}H NMR spectrum of MCO in $CDCl_3$.

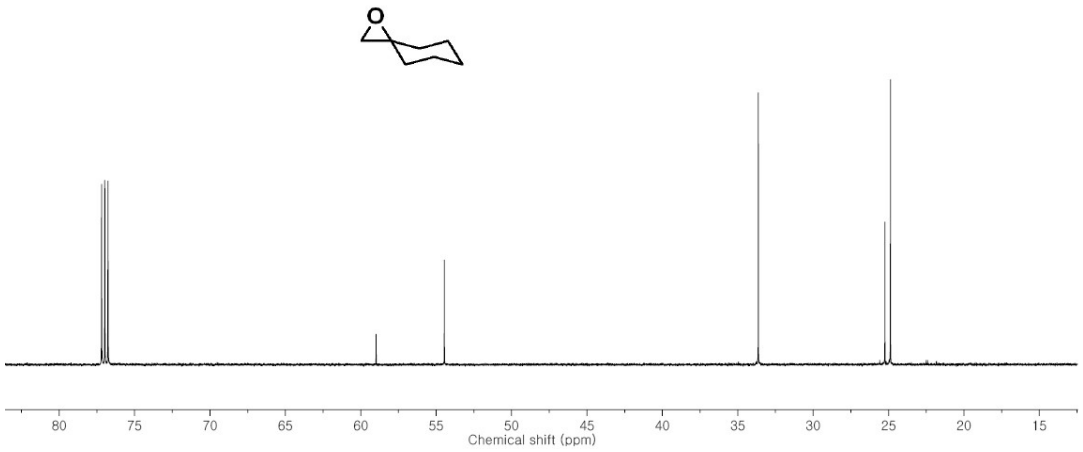


Fig. S2 ^{13}C NMR spectrum of MCO in $CDCl_3$.

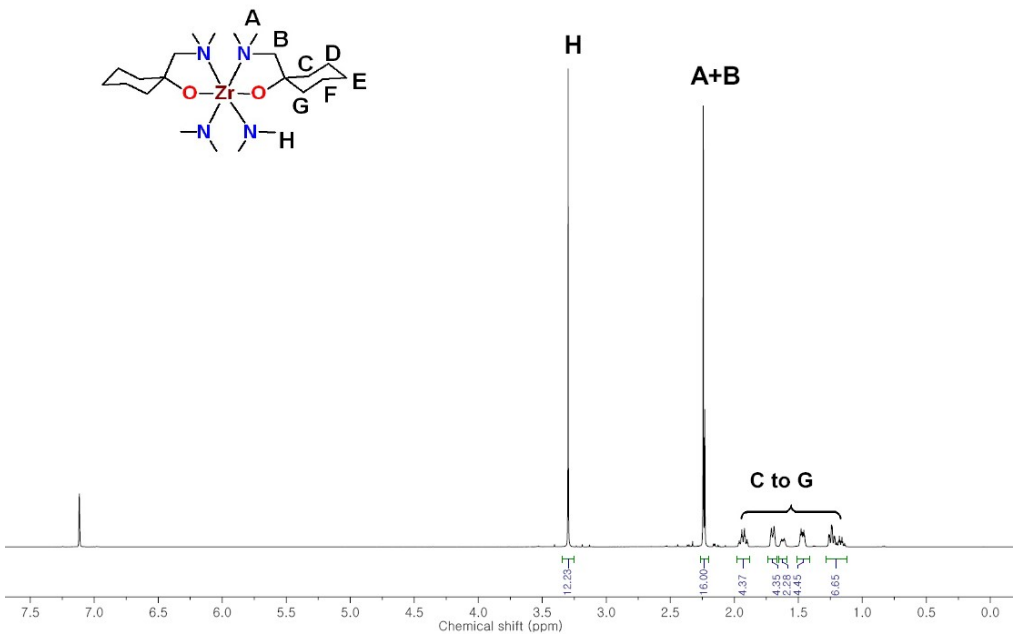


Fig. S3 ^{1}H NMR spectrum of complex **1** in C_6D_6.

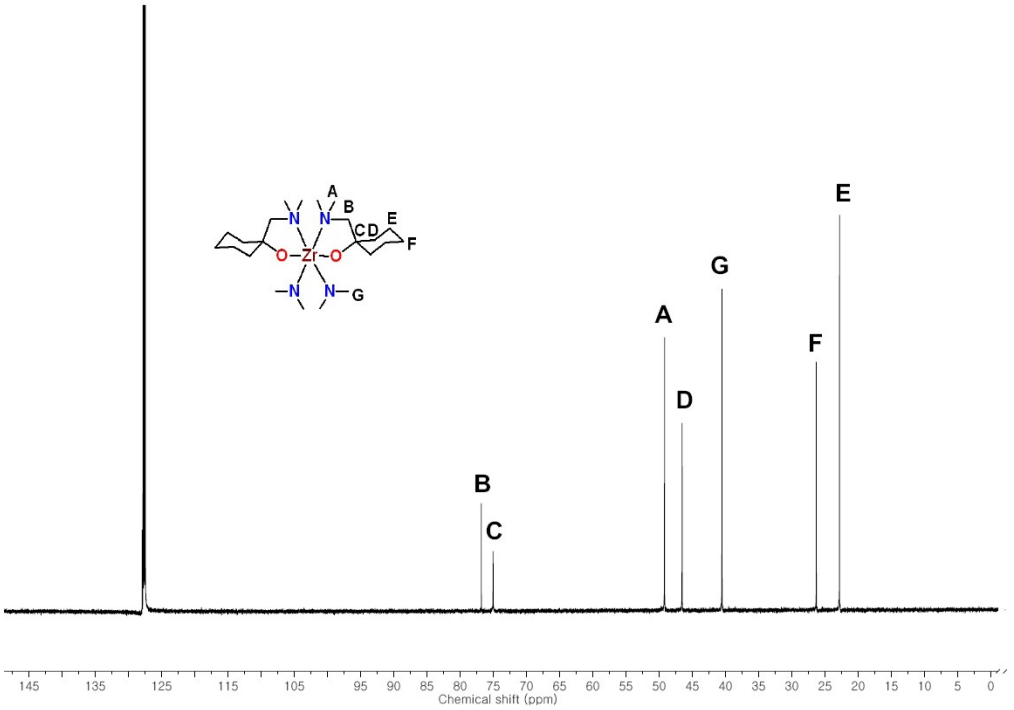


Fig. S4 ^{13}C NMR spectrum of complex **1** in C_6D_6.

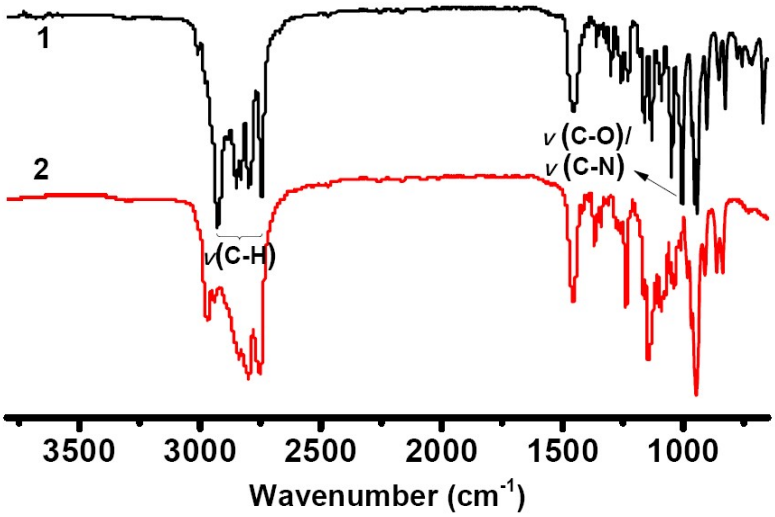


Fig. S5 FTIR spectra of complex **1** and complex **2**.

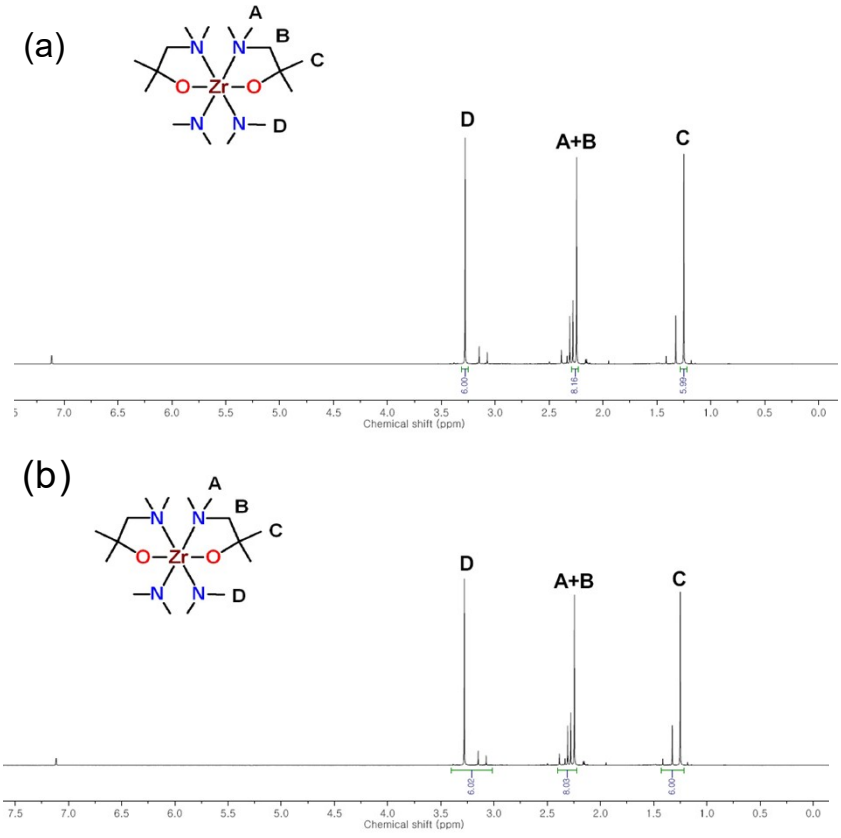


Fig. S6 ^{1}H NMR spectrum of complex **2** in C_6D_6. (a) Integration area of one set of peaks (b) Integration area of several sets of peaks.

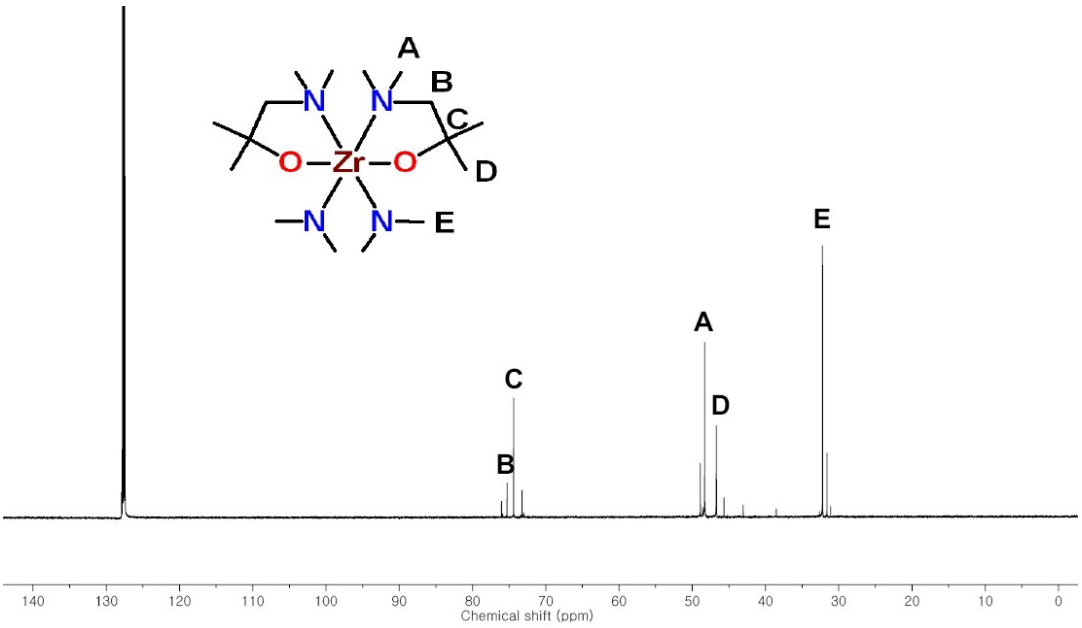


Fig. S7 ^{13}C NMR spectrum of complex **2** in C_6D_6.

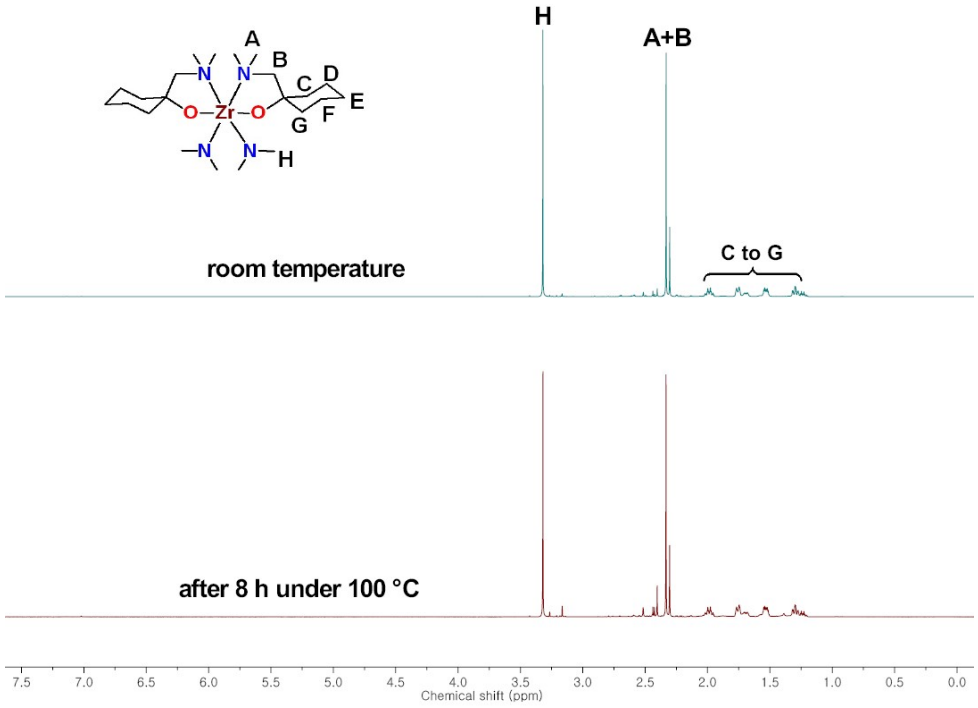


Fig. S8 ^{1}H NMR spectra of complex **1** before and after heating in toluene-d_8 under 100 °C for 8 h.

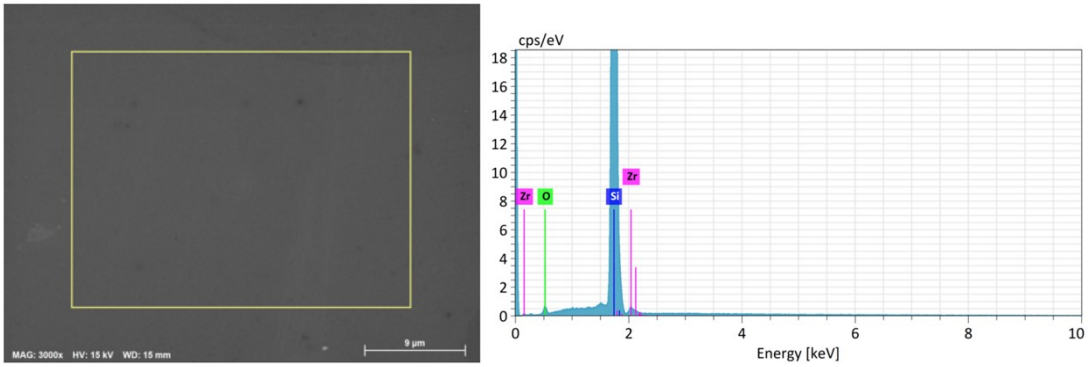


Fig. S9 The plan-view SEM and EDX images of the film prepared using **1**.

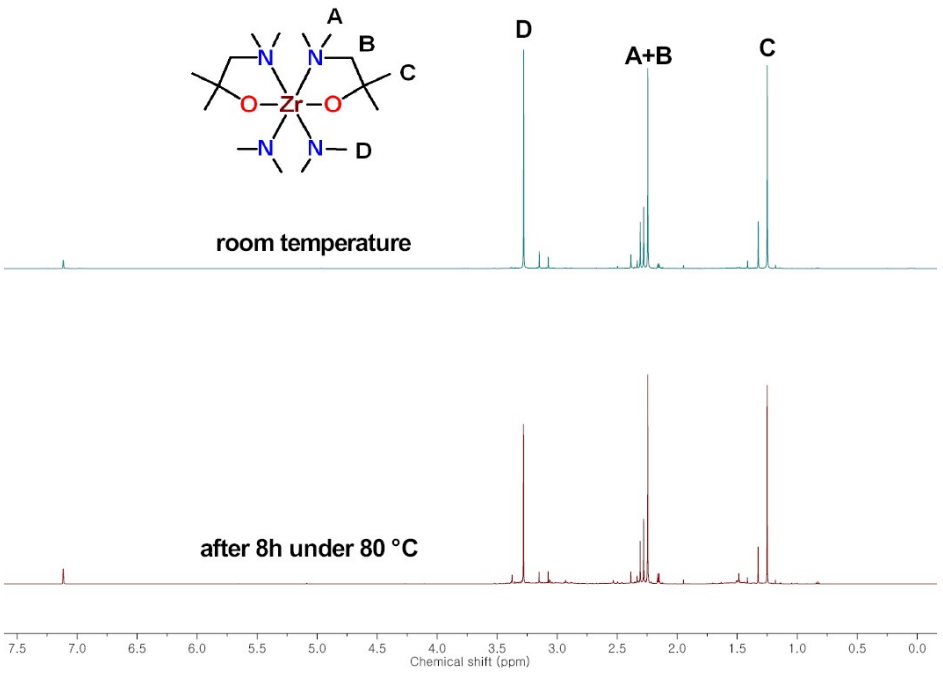


Fig. S10 ^{1}H NMR spectra of complex **2** before and after heating in toluene-d_8 under 80 °C for 8 h.

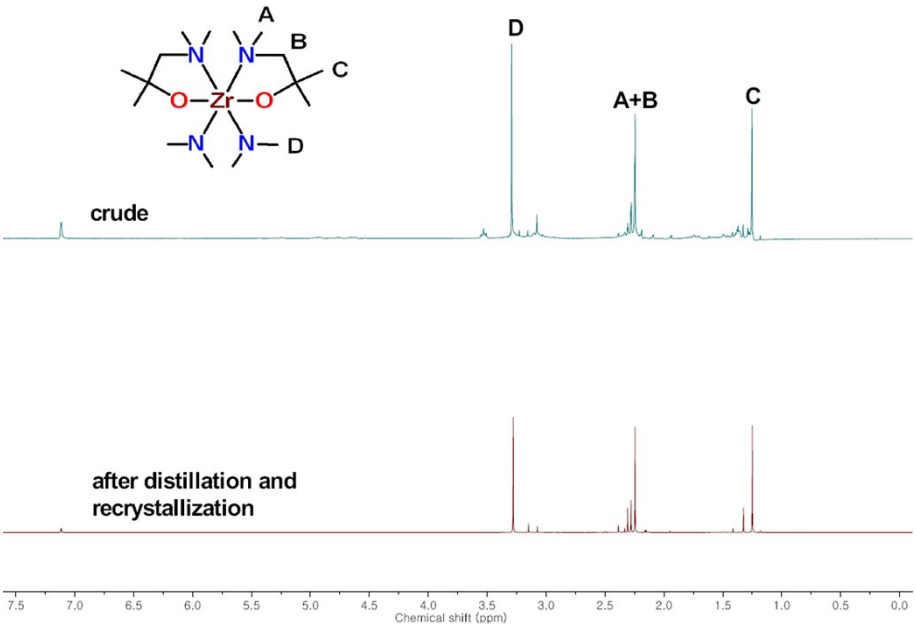


Fig. S11 ^{1}H NMR spectra of complex **2** before and after purification.

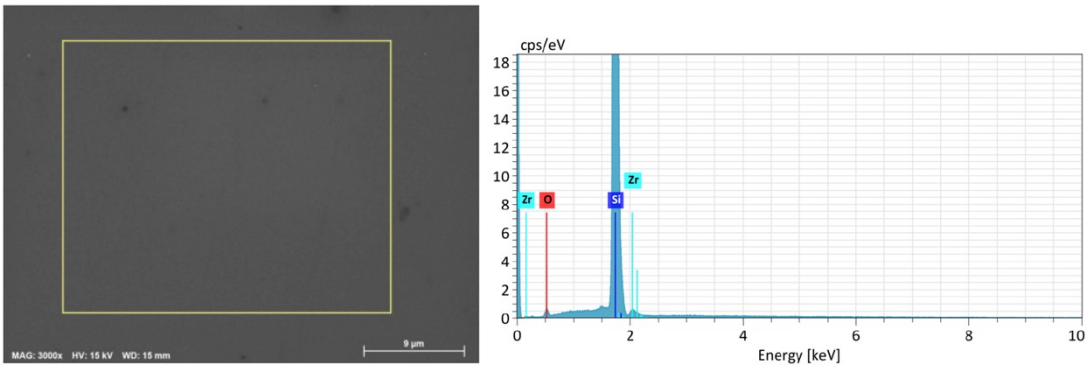
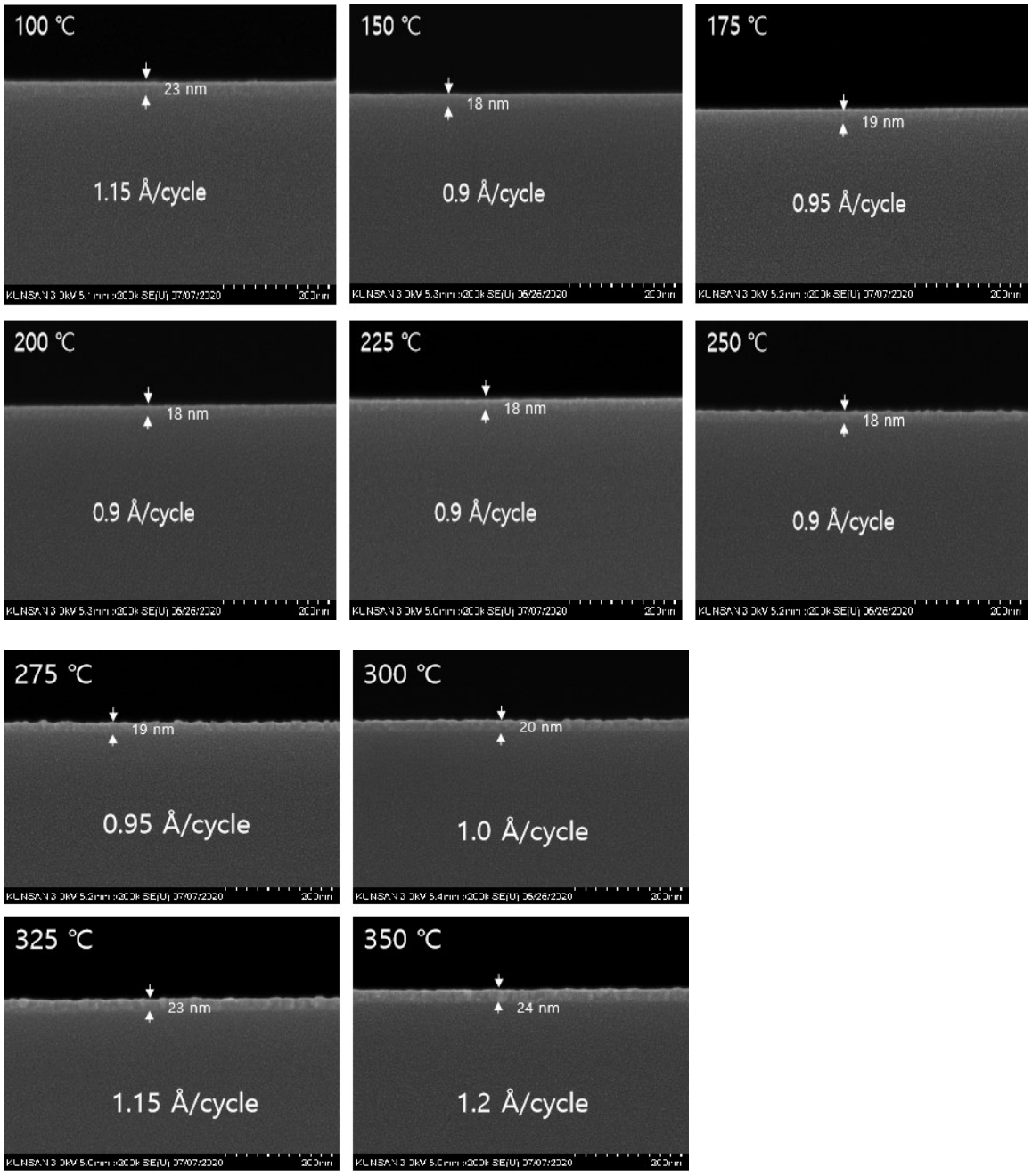


Fig. S12 The plan-view SEM and EDX images of the film prepared using **2**.


100 ℃
23 nm
1.15 Å/cycle
150 ℃
18 nm
0.9 Å/cycle
175 ℃
19 nm
0.95 Å/cycle
200 ℃
18 nm
0.9 Å/cycle
225 ℃
18 nm
0.9 Å/cycle
250 ℃
18 nm
0.9 Å/cycle
275 ℃
19 nm
0.95 Å/cycle
300 ℃
20 nm
1.0 Å/cycle
325 ℃
23 nm
1.15 Å/cycle
350 ℃
24 nm
1.2 Å/cycle

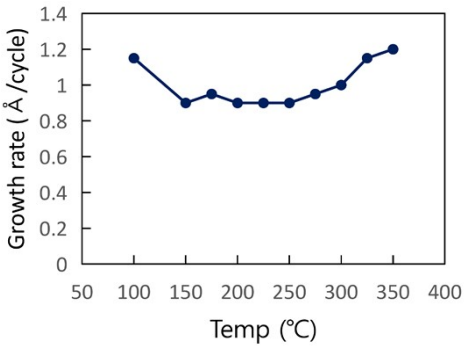

Growth rate (Å /cycle)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
50
100
150
200
250
300
350
400
Temp (℃)

Fig. S13-1 Cross-sectional SEM images of ZrO_2 thin film deposited using standard $CpZr(NMe_2)_3$ precursor and O_3 on silicon at various temperatures through 200 cycles. (Bottom) The growth rate of ZrO_2 thin film as a function of temperature.

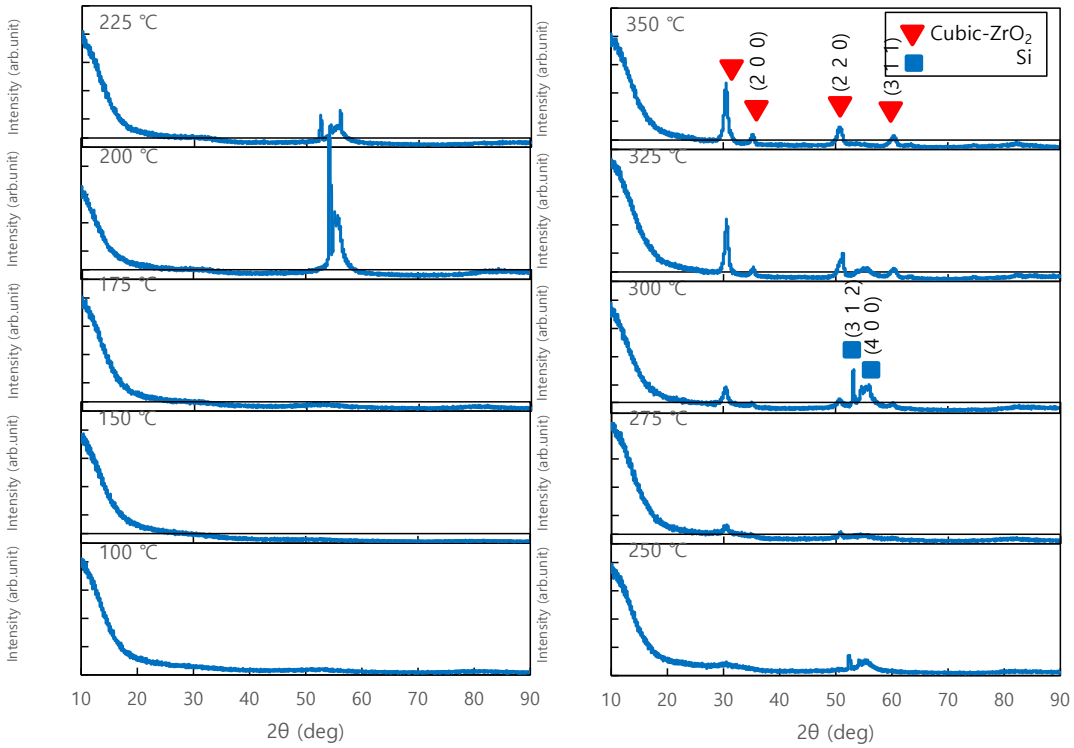


Fig. S13-2 XRD images of ZrO_2 thin film deposited using $CpZr(NMe_2)_3$ and O_3 on silicon at various temperatures through 200 cycles.

Table S1 Summary of X-ray Crystallographic data.

Compound	$[(Me_2N)_2Zr(OC(C_5H_{10})CH_2NMe_2)_2]$ (complex **1**)	$[(Me_2N)_2Zr(OCMe_2CH_2NMe_2)_2]$ (complex **2**)
Empirical formula	$ZrO_2N_4C_{22}H_{48}$	$ZrO_2N_4C_{16}H_{40}$
Formula weight	491.86	413.75
Temperature	193(2) K	293(2) K
Wavelength	1.54178 Å	1.54184 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Unit cell dimensions	a = 15.9734(3) Å α = 90°. b = 9.57200(19) Å β = 91.5782(16)°. c = 16.6128(3) Å γ = 90°.	a = 8.8032(2) Å α = 75.6210(10)°. b = 9.05680(10) Å β = 86.3200(10)°. c = 15.4925(2) Å γ = 65.266(2)°.
Volume	2539.09(8) Å3	1085.63(3) Å3
Z	4	2
Density (calculated)	1.287 Mg/m^3	1.266 Mg/m3
Absorption coefficient	3.719 mm^{-1}	4.249 mm-1
F(000)	1056	444
Crystal size	0.133 x 0.067 x 0.054 mm3	0.235 x 0.146 x 0.108 mm3
Theta range for data collection	5.327 to 79.037°..	5.539 to 79.130°
Index ranges	-20<=h<=19, -7<=k<=11, -18<=l<=21	-11<=h<=11, -11<=k<=11, -19<=l<=15
Reflections collected	20701	14033
Independent reflections	5328 [R(int) = 0.0331]	4560 [R(int) = 0.0455]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F2
Goodness-of-fit on F2	1.111	1.147
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1307	R1 = 0.0327, wR2 = 0.0893
R indices (all data)	R1 = 0.0529, wR2 = 0.1322	R1 = 0.0337, wR2 = 0.0899

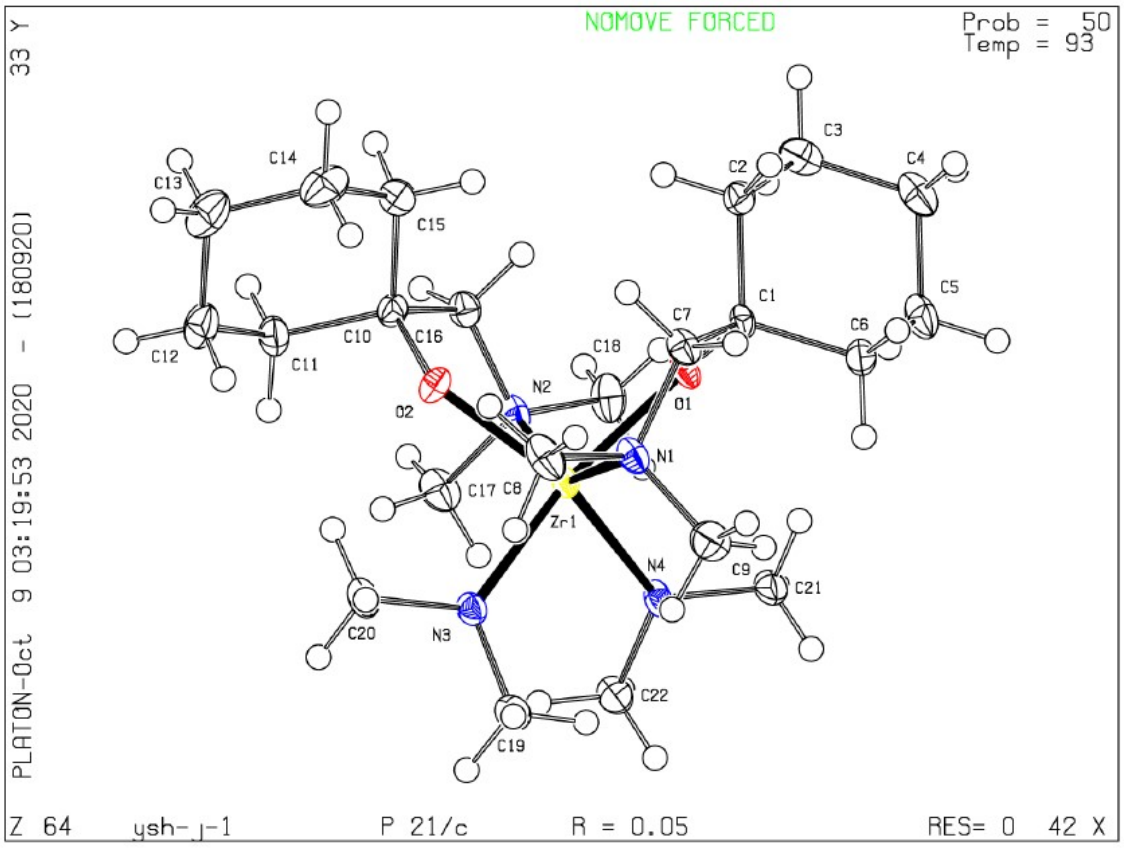


Fig. S14 Structure of complex **1** ([$(Me_2N)_2Zr(OC(C_5H_{10})CH_2NMe_2)_2$])

Table S2. Selected Angles (deg) and Interatomic Distances (Å) for complex **1** ($[(Me_2N)_2Zr(OC(C_5H_{10})CH_2NMe_2)_2]$)

Bond angles and lengths			
O(2)-Zr(1)-O(1)	100.30(11)	Zr(1)-O(2)	2.038(3)
O(2)-Zr(1)-N(4)	152.71(12)	Zr(1)-O(1)	2.043(2)
O(1)-Zr(1)-N(4)	92.81(11)	Zr(1)-N(4)	2.117(3)
O(2)-Zr(1)-N(3)	87.81(11)	Zr(1)-N(3)	2.139(3)
O(1)-Zr(1)-N(3)	156.48(11)	Zr(1)-N(1)	2.415(3)
N(4)-Zr(1)-N(3)	89.56(12)	Zr(1)-N(2)	2.437(3)
O(2)-Zr(1)-N(1)	95.62(11)		
O(1)-Zr(1)-N(1)	71.97(10)		
N(4)-Zr(1)-N(1)	111.23(12)		
N(3)-Zr(1)-N(1)	85.37(11)		
O(2)-Zr(1)-N(2)	71.43(11)		
O(1)-Zr(1)-N(2)	84.98(10)		
N(4)-Zr(1)-N(2)	86.15(12)		
N(3)-Zr(1)-N(2)	118.53(11)		
N(1)-Zr(1)-N(2)	151.31(11)		
C(1)-O(1)-Zr(1)	129.8(2)		
C(9)-N(1)-Zr(1)	109.8(2)		
C(8)-N(1)-Zr(1)	112.2(2)		
C(7)-N(1)-Zr(1)	106.6(2)		
C(10)-O(2)-Zr(1)	129.4(2)		
C(16)-N(2)-Zr(1)	105.1(2)		
C(17)-N(2)-Zr(1)	109.3(2)		
C(18)-N(2)-Zr(1)	113.2(2)		
C(19)-N(3)-Zr(1)	125.5(2)		
C(20)-N(3)-Zr(1)	125.6(3)		
C(21)-N(4)-Zr(1)	125.8(2)		
C(22)-N(4)-Zr(1)	125.0(2)		

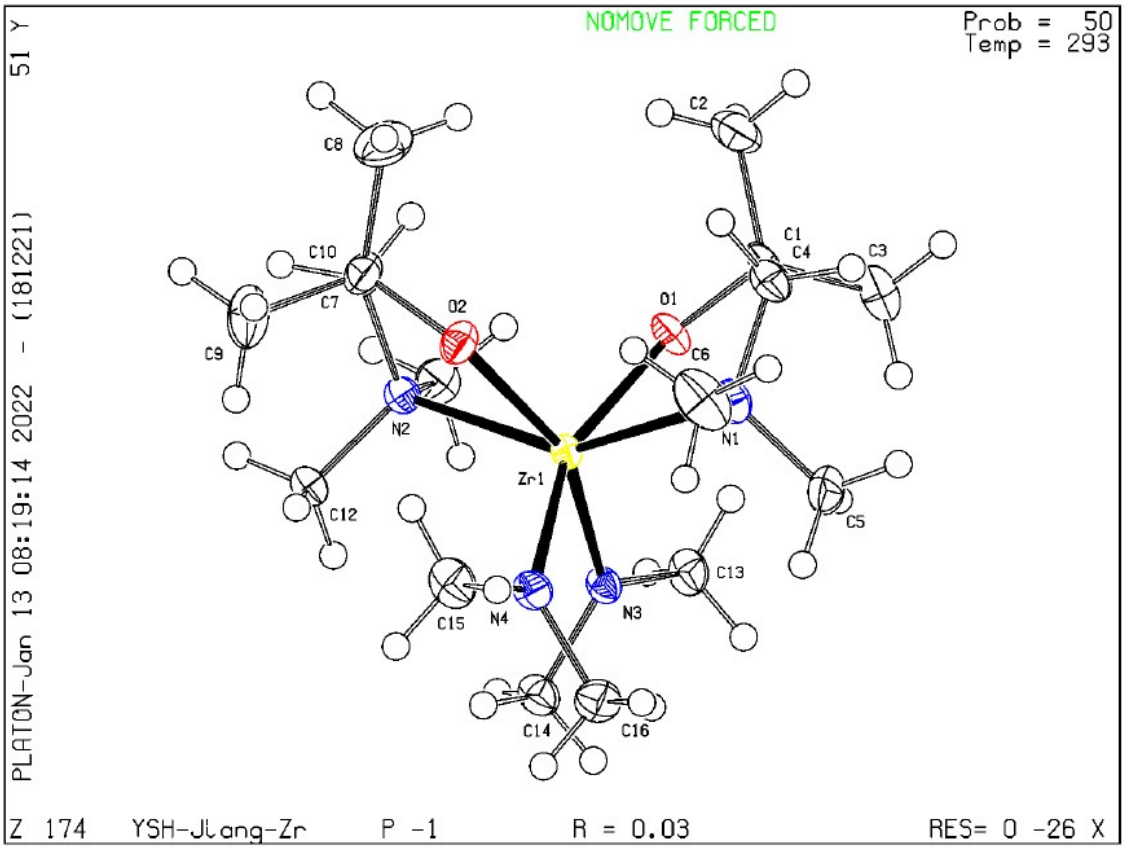


Fig. S15 Structure of complex **2** ([$(Me_2N)_2Zr(OCMe_2CH_2NMe_2)_2$]).

Table S3. Selected Angles (deg) and Interatomic Distances (Å) for complex **2** ([$(Me_2N)_2Zr(OCMe_2CH_2NMe_2)_2$]).

Bond angles and lengths			
O(2)-Zr(1)-O(1)	101.96(7)	Zr(1)-O(2)	2.0337(17)
O(2)-Zr(1)-N(3)	154.75(7)	Zr(1)-O(1)	2.0370(17)
O(1)-Zr(1)-N(3)	90.93(7)	Zr(1)-N(3)	2.1192(19)
O(2)-Zr(1)-N(4)	89.58(8)	Zr(1)-N(4)	2.125(2)
O(1)-Zr(1)-N(4)	154.61(8)	Zr(1)-N(1)	2.414(2)
N(3)-Zr(1)-N(4)	87.65(8)	Zr(1)-N(2)	2.418(2)
O(2)-Zr(1)-N(1)	90.69(7)		
O(1)-Zr(1)-N(1)	71.53(7)		
N(3)-Zr(1)-N(1)	114.11(7)		
N(4)-Zr(1)-N(1)	85.95(7)		
O(2)-Zr(1)-N(2)	71.98(7)		
O(1)-Zr(1)-N(2)	89.01(7)		
N(3)-Zr(1)-N(2)	86.82(7)		
N(4)-Zr(1)-N(2)	116.19(7)		
N(1)-Zr(1)-N(2)	150.93(7)		
C(1)-O(1)-Zr(1)	130.05(15)		
C(7)-O(2)-Zr(1)	129.75(15)		
C(14)-N(3)-Zr(1)	126.39(15)		
C(13)-N(3)-Zr(1)	124.48(16)		
C(16)-N(4)-C(15)	108.2(2)		
C(16)-N(4)-Zr(1)	125.67(16)		
C(15)-N(4)-Zr(1)	125.59(17)		
C(10)-N(2)-Zr(1)	105.75(14)		