Supporting Information for

Catalytic nitrene transfer by a zirconium(IV) redox-active ligand

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General Considerations. The complexes described below are air- and moisture-sensitive. All manipulations were carried out under an atmosphere of argon or nitrogen gas using standard Schlenk, vacuum-line, and glovebox techniques. High-purity solvents initially were sparged with argon and then passed through activated alumina and Q5 columns to remove water and oxygen, respectively. The reagents 4-methoxy-2-nitroaniline, 1-iodo-4-methoxy-2-nitrobenzene, pyridine, and *tert*-butylisocyanide were obtained from Alfa-Aesar and used as received. Dichloroiodobenzene,[1] aryl azides[2] , and alkyl azides [3], were prepared according to published procedures.

Physical Methods. All complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, UV-vis and elemental analysis. NMR spectra were collected on Bruker Avance 500 or 600 MHz spectrometers in either $CDCl_3$ or C_6D_6 solvents that were degassed by several freeze-pump-thaw cycles, dried over sodium benzophenone-ketyl radical (for C_6D_6), dried over calcium hydride (for $CDCl_3$), and vacuum-distilled before use. ^{1}H and ^{13}C NMR spectra were referenced to TMS using the residual ^{1}H and natural abundance ^{13}C impurities of the solvent. All chemical shift values are reported using the standard δ notation in ppm. Infrared spectra (450-4000 cm-1) were recorded on a Perkin-Elmer Spectrum One spectrophotometer as KBr pellets. UV-vis absorbance spectra (270-900 nm) were recorded on a Perkin-Elmer Lambda 800 double-beam spectrophotometer equipped with a PMT detector. EPR spectra were collected on a Bruker EMX X-band spectrometer equipped with an ER041XG microwave bridge. Spectra for EPR samples were collected using the following spectrometer settings: attenuation = 20 dB, microwave power = 2.021 mW, frequency = 9.762 GHz, sweep width = 50 G, modulation amplitude = 0.2 G, gain = 8.93×10^4, conversion time = 10.24 ms, time constant = 81.92 ms, and resolution = 2048 points. Elemental analyses were done on a Perkin-Elmer 2400 Series II CHNS/O analyzer. Gas-chromatography mass-spectrometry was with a Waters GCT Premier using chemical-ionization method with ammonia reagent gas.

Preparation of [NNN^{cat}]ZrCl(THF)$_2$ (1a). [NNN^{cat}]H$_3$ (0.521 g, 1.52 mmol, 1 equiv) was dissolved in diethyl ether (15 mL) with one drop of tetrahydrofuran added, and the solution was frozen. On thawing, *n*-BuLi solution was added (1510 µL, 3.01 M in diethyl ether) and stirred at room temperature for 30 min. The reaction mixture was frozen, and upon thawing, solid $ZrCl_4(THF)_2$ was added. Stirred overnight at room temperature, and filtered. The filtrate was dried *in vacuo* and washed with pentane (10 mL) to yield an orange powder (0.820 g, 88%).

^{1}H NMR (600 MHz, C_6D_6) δ 1.02 (m, 8H, THF), 1.44 (d, 12H, $^3J_{HH}$ = 6.8, CH(CH_3)$_2$), 3.59 (s, 6H, OCH_3), 3.97 (m, 8H, THF), 4.50 (br, 2H, CH(CH$_3$)$_2$), 6.36 (dd, 2H, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 2.4, aryl-H), 6.47 (d, 2H, $^4J_{HH}$ = 2.4, aryl-H), 7.55 (d, 2H, $^3J_{HH}$ = 8.6, aryl-H). ^{13}C NMR (125.8 MHz, C_6D_6) δ 22.6 (CH(*C*H$_3$)$_2$), 23.3 (THF), 48.9 (*C*H(CH$_3$)$_2$), 55.4 (OCH_3), 75.0 (THF), 98.8 (aryl-C), 99.9 (aryl-C), 110.6 (aryl-C), 137.8 (aryl-C), 151.1 (aryl-C), 154.7 (aryl-C). IR (KBr) ν/cm^{-1}: 2961, 2928, 1585, 1482, 1267, 1205, 1153, 1038, 924, 820, 625. UV–vis (THF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 306 (14 000).

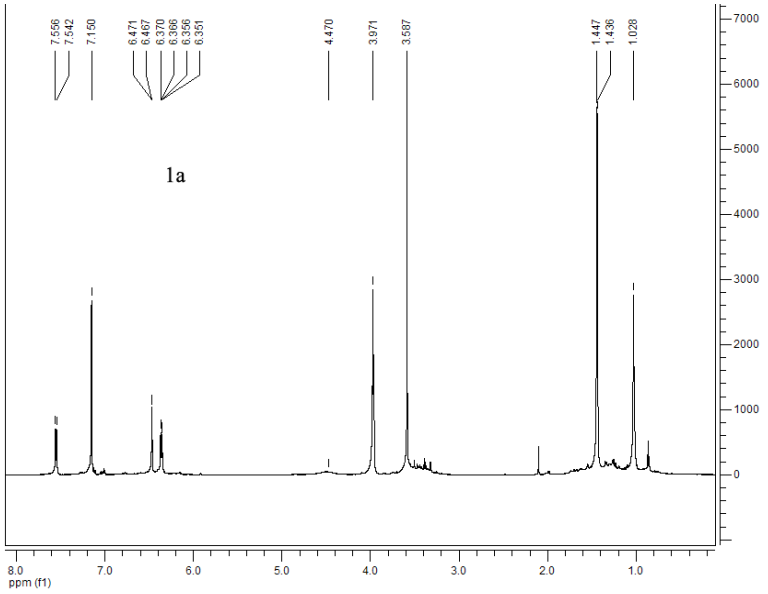

Figure S1. ^{1}H NMR spectrum of [NNN^{cat}]ZrCl(THF)$_2$ **(1a)** at 298 K in C_6D_6.

Preparation of [NNN^{cat}]ZrCl(CN^{t}Bu)$_2$ (1b). To a slurry of **1a** (0.1003 g, 0.164 mmol, 1 equiv) in diethyl ether (2 mL) was added *tert*-butylisocyanide (39 μL, 0.344 mmol, 2.1 equiv). Reacted for 10 min, and the wine-red solution was dried *in vacuo* to yield a wine-red solid (0.0998 g, 96%).

^{1}H NMR (500 MHz, C_6D_6) δ 0.73 (s, 18H, C(CH_3)$_3$), 1.65 (br, 12H, CH(CH_3)$_2$), 3.52 (s, 6H, OCH_3), 3.82 (br, 2H, CH(CH_3)$_2$), 6.28 (dd, 2H, $^{3}J_{HH}$ = 8.6, $^{4}J_{HH}$ = 2.0, aryl-H), 6.41 (d, 2H, $^{4}J_{HH}$ = 2.0, aryl-H), 7.49 (d, 2H, $^{3}J_{HH}$ = 8.6, aryl-H). ^{13}C NMR (125.8 MHz, C_6D_6) δ 23.5 (CH(CH_3)$_2$), 25.4 (C(CH_3)$_3$), 29.3 (C(CH_3)$_3$), 49.3 (CH(CH_3)$_2$), 55.3 (OCH_3), 98.0 (aryl-C), 100.9 (aryl-C), 111.0 (aryl-C), 129.3 (CN), 138.5 (aryl-C), 152.3 (aryl-C), 155.1 (aryl-C). IR (KBr) ν/cm^{-1}: 2962, 2931, 2200, 1578, 1499, 1467, 1267, 1231, 1203, 1153, 1125, 1042, 940, 864, 821, 800.

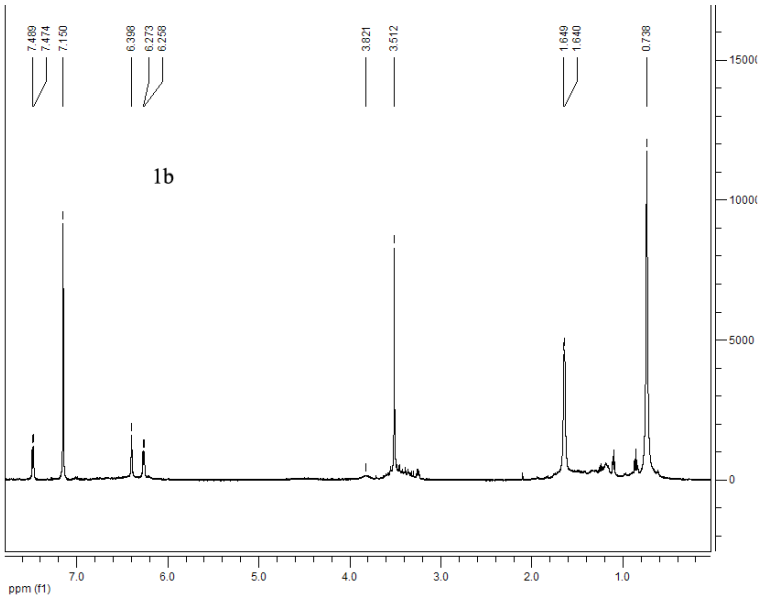

Figure S2. ^{1}H NMR spectrum of [NNN^{cat}]ZrCl(CN^{t}Bu)$_2$ **(1b)** at 298 K in C_6D_6.

Preparation of [NNN^{cat}]ZrCl(py)$_2$ (1c). To a slurry of **1a** (0.101 g, 0.166 mmol, 1 equiv) in diethyl ether (3 mL) was added pyridine (28 μL, 0.348 mmol, 2.1 equiv). Reacted for 10 min, and the brown-red solution was dried *in vacuo* to yield a brown solid (0.0889 g, 86%).

^{1}H NMR (600 MHz, C_6D_6) δ 1.20 (d, 12H, $^3J_{HH}$ = 6.8, CH(CH_3)$_2$), 3.49 (s, 6H, OCH_3), 4.70 (br, 2H, CH(CH$_3$)$_2$), 6.34 (d, 2H, $^4J_{HH}$ = 2.8, aryl-H), 6.34 (m, 4H, pyridine), 6.37 (dd, 2H, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 2.8, aryl-H), 6.58 (t, 2H, $^3J_{HH}$ = 7.3, pyridine), 7.70 (d, 2H, $^3J_{HH}$ = 8.6, aryl-H), 9.13 (d, 4H, $^3J_{HH}$ = 5.0). ^{13}C NMR (125.8 MHz, C_6D_6) δ 22.9 (CH(*C*H$_3$)$_2$), 48.7 (*C*H(CH$_3$)$_2$), 55.2 (OCH_3), 99.0 (aryl-C), 100.7 (aryl-C), 110.3 (pyridine-C), 111.2 (aryl-C), 124.6 (pyridine-C), 138.4 (aryl-C), 150.2 (aryl-C), 154.8 (aryl-C), 168.6 (pyridine-C).

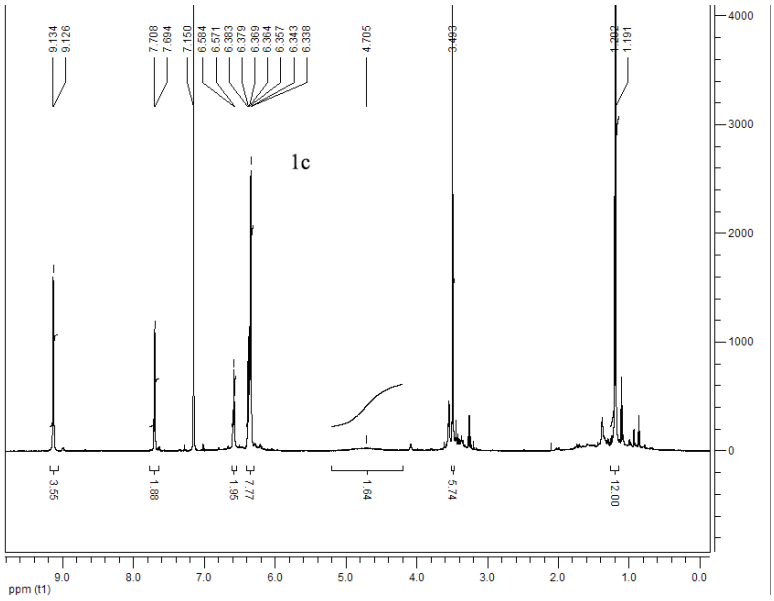

Figure S3. ^{1}H NMR spectrum of [NNN^{cat}]ZrCl(py)$_2$ **(1c)** at 298 K in C_6D_6.

Preparation of [NNN$^{sq\cdot}$]ZrCl$_2$(THF) (2). **1a** (0.100 g, 0.164 mmol, 1 equiv) was dissolved in a 1:1 solution of diethyl ether and tetrahydrofuran (5 mL). Iodobenzene dichloride (0.023 g, 0.083 mmol, 0.5 equiv) was added as a diethyl ether solution (2 mL) to **1a** at –35°C, and allowed to react overnight at –35°C. The solution reaction was filtered, dried *in vacuo*, and washed with pentane to yield a purple-red solid (0.0823 g, 87%).

Anal. Calcd for $C_{24}H_{34}Cl_2N_3O_3Zr$: C, 50.16; H, 5.96; N, 7.31. Found: C, 49.89; H, 5.97; N, 7.02. IR (KBr) ν/cm^{-1}: 2964, 2929, 1591, 1497, 1465, 1260, 1216, 1171, 1112, 1019, 801. UV–vis (THF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 305 (13 000), 408 (2000).

Preparation of [NNN^{q}]ZrCl$_3$ (3). A solution of **1a** (0.100 g, 0.164 mmol, 1 equiv) in diethyl ether (10 mL) was made and frozen. On thawing, iodobenzene dichloride (0.059 g, 0.214 mmol, 1.3 equiv) was added as a solution in diethyl ether (3 mL). The solution was reacted overnight at –35°C. The green solid was collected by filtration and washed with 10 mL diethyl ether (0.059 g, 67%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.81 (d, 12H, $^3J_{HH}$ = 6.6, CH(CH_3)$_2$), 3.94 (s, 6H, OCH_3), 5.20 (br, 2H, CH(CH$_3$)$_2$), 6.36 (s, 2H, aryl-H), 6.70 (d, 2H, $^3J_{HH}$ = 9.7, aryl-H), 7.62 (d, 2H, $^3J_{HH}$ = 9.7, aryl-H). ^{13}C NMR (125.8 MHz, C_6D_6) δ 21.1 (CH(*C*H$_3$)$_2$), 51.0 (*C*H(CH$_3$)$_2$), 56.1 (OCH_3), 94.9 (aryl-C), 121.4 (aryl-C), 125.5 (aryl-C), 138.4 (aryl-C), 164.1 (aryl-C), 165.9 (aryl-C). IR (KBr) ν/cm^{-1}: 2962, 2929, 1589, 1484, 1452, 1361, 1256, 1212, 1112, 1018, 821, 802. UV–vis (THF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 304 (11 000), 480 (4000), 865 (4000).

Preparation of {[NNN^{q}]Zr(μ–N(*p*-C$_6$H$_4$^{t}Bu)Cl}$_2$ (4). An ethereal solution (2 mL) containing *p-tert*-butylphenylazide (0.031 g, 0.180 mmol, 1 equiv) was added to a slurry of **1a** (0.108 g, 0.177 mmol, 1 equiv) in diethyl ether (10 mL). Immediate color change from orange to dark green-brown and N_2 effervescence was observed. The solution was allowed to react for 5h and the solid was collected by filtration. Benzene (3 mL) was added to re-dissolve the solid and dried *in vacuo*. Dark green-brown solid was obtained (0.0357 g, 33%).

Anal. Calcd for $C_{60}H_{78}Cl_2N_8O_4Zr_2$: C, 58.65; H, 6.40; N, 9.12. Found: C, 58.04; H, 6.60; N, 9.43. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (s, 9H, C(CH_3)$_3$), 1.27 (s, 9H, C(CH_3)$_3$), 1.44 (br, 12H, CH(CH_3)$_2$), 1.65 (br, 12H, CH(CH_3)$_2$), 3.79 (s, 12H, OCH_3), 4.45 (br, 4H, CH(CH$_3$)$_2$), 5.57 (br, 2H, aryl-H), 5.93 (br, 4H, aryl-H), 5.94 (br, 4H, aryl-H), 6.20 (br, 4H, aryl-H), 6.39 (br, 2H, aryl-H), 7.02 (br, 2H, aryl-H), 7.15 (br, 2H, aryl-H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 21.1 (CH(*C*H$_3$)$_2$), 31.7 (C(*C*H$_3$)$_2$), 33.6 (*C*(CH$_3$)$_3$), 33.9 (*C*(CH$_3$)$_3$), 50.8 (*C*H(CH$_3$)$_2$), 55.4 (OCH_3), 96.2 (aryl-C), 109.9 (aryl-C), 115.9 (aryl-C), 118.8 (aryl-C), 121.9 (aryl-C), 122.4 (aryl-C), 123.9 (aryl-C), 126.0 (aryl-C), 137.5 (aryl-C), 139.4 (aryl-C), 140.8 (aryl-C), 163.7 (aryl-C), 164.2 (aryl-C), 168.3 (aryl-C). IR (KBr) ν/cm^{-1}: 2961, 2868, 1593, 1486, 1454, 1360, 1259, 1218, 1113, 1017, 869, 817, 642, 584, 535. UV–vis (THF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 308 (18 000), 430 (7000).

Control reaction of 1-adamantylazide and *tert*-butylisocyanide. A J. Young tube was loaded with 1-adamantylazide (100 μL, 1.0 M in C_6D_6), *tert*-butylisocyanide (100 μL, 0.995 M in C_6D_6), and 400 μL of C_6D_6. The tube was sealed and heated at 80°C overnight. No reaction was observed by ^{1}H NMR.

Reaction of 1b with *p-tert*-butylphenylazide. **1b** was generated *in situ* by dissolving **1a** (0.0556 g, 0.0909 mmol, 1 equiv) in diethyl ether (5 mL) and adding *tert*-butylisocyanide (20.5 μL, 0.1812 mmol, 2 equiv). *p-tert*-Butylphenylazide (0.0156 g, 0.0890 mmol, 1 equiv) was then added. The reaction was allowed to run overnight, and pyridine (14.6 μL, 0.1812 mmol, 2 equiv) was added. An aliquot was analyzed by GC-MS and showed a peak with mass 231.2 m/Z (MH^+) consistent with formation of Ar–N=C=N–^{t}Bu (Ar = *p-tert*-butylphenyl). The remaining solution was dried *in vacuo*; ^{1}H NMR showed formation of **1c**.

Catalyzed reaction of 1-adamantylazide and *tert*-butylisocyanide. In a J. Young NMR tube **1a** (0.0129 g, 0.0211 mmol, 0.1 equiv) and *tert*-butylisocyanide (29 μL, 0.25 mmol, 1.2 equiv), were dissolved in ~600 μL C_6D_6 and then 1-adamantylazide (0.0370 g, 0.21 mmol, 1 equiv) was added. The tube was heated to 55°C for 2 h. ^{1}H NMR showed complete conversion to carbodiimide. Ad–N=C=N–^{t}Bu ^{1}H NMR (600 MHz, C_6D_6) δ 1.21 (s, 9H, $C(CH_3)_3$), 1.45 (s, 6H), 1.82 (s, 6H), 1.86 (s, 3H).

Catalyzed reaction of *tert*-butylazide and *tert*-butylisocyanide. In a J. Young NMR tube **1a** (0.013 g, 0.021 mmol, 0.1 equiv) and *tert*-butylisocyanide (29 μL, 0.25 mmol, 1.2 equiv) were dissolved in ~600 μL C_6D_6 and then *tert*-butylazide (0.021 g, 0.21 mmol, 1 equiv) was added. The tube was heated to 55°C for 2 h. ^{1}H NMR showed complete conversion to carbodiimide. ^{t}Bu –N=C=N–^{t}Bu ^{1}H NMR (600 MHz, C_6D_6) δ 1.23 (s, 9H, $C(CH_3)_3$).

Catalyzed reaction of mesitylazide and *tert*-butylisocyanide. In a J. Young NMR tube **1a** (0.0149 g, 0.024 mmol, 0.1 equiv) and *tert*-butylisocyanide (31 μL, 0.27 mmol, 1.2 equiv) were dissolved in ~600 μL C_6D_6 and then mesitylazide (0.039 g, 0.24 mmol, 1 equiv) was added. The

tube was heated to 55°C. ^{1}H NMR showed 40% conversion to carbodiimide[4] after 1 h, and 44% after 20 h.

Kinetics Procedures. All reactions were carried out in J. Young NMR tubes and monitored by ^{1}H NMR spectroscopy (600 MHz) at 25°C. Stock solutions of 1-adamantylazide (1.0 M), *tert*-butylisocyanide (0.995 M), and **1b** (0.0955 M) in C_6D_6 were used to add the reagents and all reaction mixtures were diluted to a total volume to 700 μL with C_6D_6. 1H NMR spectra were collected every 303 seconds. To determine the concentration dependence on the reaction rate, the method of initial rates was used over the first 10% conversion. The data is presented below in Table S1. The reactions were then monitored to completion to ensure complete conversion to the products. Non-linear least squares curve fitting of disappearance of azide over at least four half-lives gave identical results to the initial rates method.

Table S1. Initial rates data for the reaction of AdN_3 and ^{t}BuNC catalyzed by **1b** at 298 K.

Rate / M s^{-1}	[**1b**] / M	[AdN_3] / M	[^{t}BuNC] / M
1.60E-03	1.36E-02	1.43E-01	1.43E-01
8.17E-04	1.36E-02	7.15E-02	1.43E-01
9.01E-04	1.36E-02	1.43E-01	2.86E-01
3.26E-03	2.72E-02	1.43E-01	1.43E-01

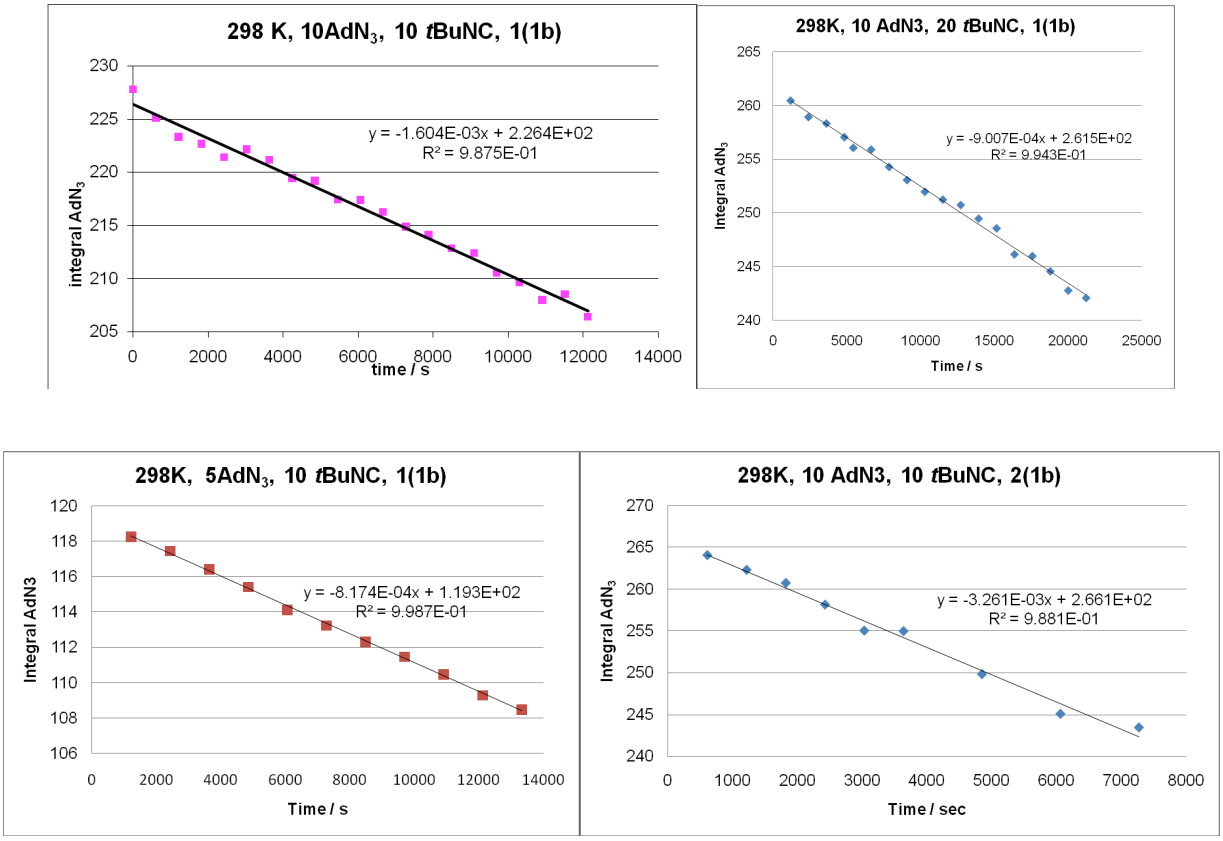

Figure S4. Plots of [RN_3] vs time over the first 10% of the reaction between AdN_3 and ^{t}BuNC catalyzed by **1b** at 298 K.

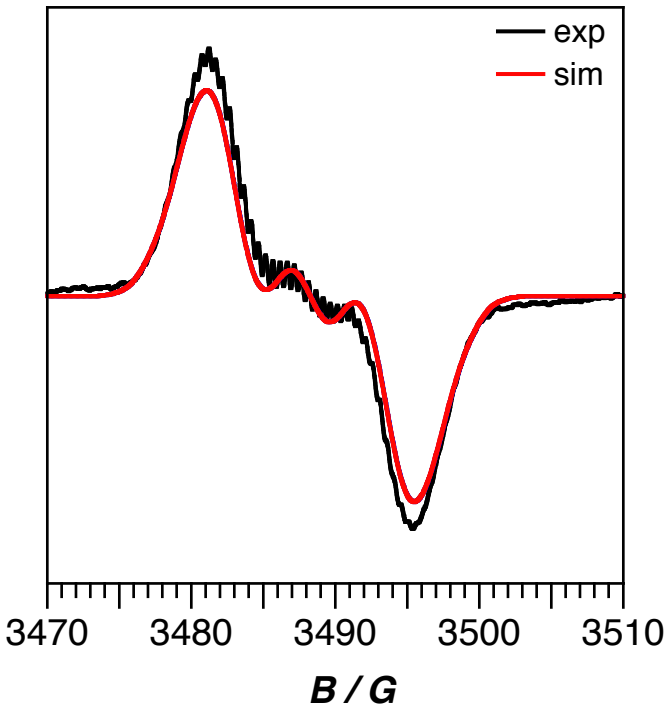

Figure S5. EPR Spectrum of [NNN$^{sq\cdot}$]$ZrCl_2$(THF) **(2)** at 298 K in THF. The spectrum was modeled assuming an isotropic signal with g = 1.9990 and hyperfine coupling to one nitrogen atom (a_N = 14 G).

Crystallographic Procedure. A green crystal of approximate dimensions 0.30 x 0.22 x 0.10 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[5] program package was used to determine the unit-cell parameters and for data collection (35 sec/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

At convergence, wR2 = 0.0892 and Goof = 1.034 for 751 variables refined against 15603 data (0.70 Å), R1 = 0.0376 for those 13280 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter[10].

Table S2. X-Ray Diffraction Data

Empirical formula	$C_{60}H_{78}Cl_2N_8O_4Zr_2 \bullet (C_4H_{10}O)$	
Formula weight	1302.76	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 14.7192(7) Å	α= 90°.
	b = 20.6103(9) Å	β= 90°.
	c = 21.1775(9) Å	γ = 90°.
	Volume	6424.6(5) $Å^3$
Z	4	
Density (calculated)	1.347 Mg/m^3	
Absorption coefficient	0.461 mm^{-1}	
F(000)	2728	
Crystal color	green	
Crystal size	0.30 x 0.22 x 0.10 mm^3	
Theta range for data collection	1.38 to 28.82°	
Index ranges	$-19 \le h \le 19$, $-27 \le k \le 27$, $-26 \le l \le 28$	
Reflections collected	57996	
Independent reflections	15603 [R(int) = 0.0419]	
Completeness to theta = 28.82°	95.7 %	
Data / restraints / parameters	15603 / 0 / 751	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2σ(I) = 13280 data]	R1 = 0.0376, wR2 = 0.0829	
R indices (all data, .70 Å)	R1 = 0.0518, wR2 = 0.0892	
Largest diff. peak and hole	0.765 and -0.335 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	3619(1)	4038(1)	1754(1)	17(1)
Zr(2)	3764(1)	4070(1)	3281(1)	16(1)
Cl(1)	4605(1)	3876(1)	792(1)	23(1)
Cl(2)	4713(1)	3520(1)	4122(1)	29(1)
O(1)	2740(2)	6986(1)	389(1)	27(1)
O(2)	-259(2)	2625(1)	698(1)	31(1)
O(3)	3274(2)	7104(1)	4511(1)	26(1)
O(4)	-368(2)	3051(1)	4384(1)	34(1)
N(1)	2391(2)	4448(1)	1158(1)	18(1)
N(2)	3838(2)	5089(1)	1514(1)	21(1)
N(3)	2771(2)	3210(1)	1401(1)	20(1)
N(4)	2622(2)	4547(1)	3915(1)	17(1)
N(5)	4232(2)	5038(1)	3618(1)	22(1)
N(6)	2715(2)	3323(1)	3589(1)	21(1)
N(7)	2868(2)	4320(1)	2556(1)	17(1)
N(8)	4518(2)	3767(1)	2480(1)	18(1)
C(1)	2431(2)	5062(1)	962(1)	20(1)
C(2)	3247(2)	5416(1)	1162(1)	20(1)
C(3)	3349(2)	6081(1)	969(1)	23(1)
C(4)	2708(2)	6361(1)	593(1)	24(1)
C(5)	1948(2)	6007(2)	357(1)	23(1)
C(6)	1820(2)	5386(1)	538(1)	22(1)
C(7)	4723(2)	5363(1)	1701(2)	27(1)
C(8)	4651(2)	5913(2)	2187(2)	34(1)
C(9)	5351(2)	5521(2)	1148(2)	38(1)
C(10)	3514(2)	7364(2)	564(2)	33(1)

C(11)	1688(2)	4021(2)	1088(1)	20(1)
C(12)	1930(2)	3350(1)	1190(1)	20(1)
C(13)	1260(2)	2872(2)	1041(1)	24(1)
C(14)	406(2)	3051(2)	858(1)	24(1)
C(15)	146(2)	3705(2)	832(2)	27(1)
C(16)	772(2)	4178(2)	946(1)	24(1)
C(17)	3073(2)	2518(1)	1360(1)	22(1)
C(18)	3930(2)	2414(1)	1741(2)	25(1)
C(19)	3244(2)	2321(2)	672(1)	25(1)
C(20)	-50(2)	1950(2)	719(2)	33(1)
C(21)	2761(2)	5177(1)	4087(1)	19(1)
C(22)	3624(2)	5437(1)	3905(1)	19(1)
C(23)	3798(2)	6105(1)	4043(1)	23(1)
C(24)	3187(2)	6462(1)	4386(1)	23(1)
C(25)	2404(2)	6169(1)	4651(1)	21(1)
C(26)	2198(2)	5554(1)	4502(1)	22(1)
C(27)	5203(2)	5261(2)	3651(2)	24(1)
C(28)	5815(2)	4838(2)	3250(2)	28(1)
C(29)	5537(2)	5253(2)	4338(2)	34(1)
C(30)	4015(2)	7443(2)	4222(2)	31(1)
C(31)	1848(2)	4214(1)	3966(1)	19(1)
C(32)	1944(2)	3513(2)	3840(1)	21(1)
C(33)	1181(2)	3112(1)	4016(1)	24(1)
C(34)	391(2)	3385(2)	4213(2)	27(1)
C(35)	257(2)	4072(2)	4220(2)	30(1)
C(36)	962(2)	4470(2)	4097(1)	24(1)
C(37)	2916(2)	2636(1)	3450(2)	26(1)
C(38)	3018(3)	2217(2)	4036(2)	35(1)
C(39)	2287(2)	2352(2)	2946(2)	33(1)

C(40)	-345(2)	2362(2)	4334(2)	35(1)
C(41)	1984(2)	4570(1)	2549(2)	18(1)
C(42)	1222(2)	4166(1)	2513(1)	19(1)
C(43)	350(2)	4420(1)	2466(2)	24(1)
C(44)	188(2)	5086(1)	2454(2)	27(1)
C(45)	946(2)	5483(1)	2518(2)	29(1)
C(46)	1820(2)	5238(1)	2572(2)	24(1)
C(47)	-761(2)	5381(2)	2346(2)	36(1)
C(48)	-739(3)	5818(2)	1748(2)	61(1)
C(49)	-1011(3)	5802(3)	2909(3)	86(2)
C(50)	-1478(2)	4877(2)	2236(3)	58(1)
C(51)	5378(2)	3467(1)	2440(1)	17(1)
C(52)	6096(2)	3736(1)	2089(1)	20(1)
C(53)	6947(2)	3444(1)	2069(1)	22(1)
C(54)	7134(2)	2860(1)	2376(1)	21(1)
C(55)	6404(2)	2582(1)	2694(1)	24(1)
C(56)	5565(2)	2876(1)	2735(1)	22(1)
C(57)	8060(2)	2520(1)	2350(1)	24(1)
C(58)	8063(2)	2051(2)	1788(2)	29(1)
C(59)	8234(2)	2129(2)	2949(2)	33(1)
C(60)	8831(2)	3007(2)	2272(2)	40(1)
O(5)	7877(2)	4708(1)	4517(2)	69(1)
C(62)	7556(3)	4054(2)	4450(2)	54(1)
C(61)	7739(3)	3826(2)	3792(2)	65(1)
C(63)	7700(4)	4962(3)	5116(3)	92(2)
C(64)	8027(5)	5661(3)	5159(4)	154(4)

Table S4. Bond lengths (Å) for **4**.

Zr(1)-N(8)	2.103(2)
Zr(1)-N(7)	2.107(2)
Zr(1)-N(3)	2.244(2)
Zr(1)-N(2)	2.248(2)
Zr(1)-N(1)	2.362(2)
Zr(1)-Cl(1)	2.5230(8)
Zr(1)-Zr(2)	3.2405(4)
Zr(2)-N(7)	2.088(2)
Zr(2)-N(8)	2.121(2)
Zr(2)-N(5)	2.229(2)
Zr(2)-N(6)	2.276(2)
Zr(2)-N(4)	2.365(2)
Zr(2)-Cl(2)	2.5316(8)
O(1)-C(4)	1.358(3)
O(1)-C(10)	1.431(4)
O(2)-C(14)	1.357(4)
O(2)-C(20)	1.426(4)
O(3)-C(24)	1.355(4)
O(3)-C(30)	1.433(4)
O(4)-C(34)	1.361(4)
O(4)-C(40)	1.424(4)
N(1)-C(1)	1.333(4)
N(1)-C(11)	1.366(4)
N(2)-C(2)	1.329(4)
N(2)-C(7)	1.473(4)
N(3)-C(12)	1.347(4)
N(3)-C(17)	1.497(4)

N(4)-C(31)	1.334(4)
N(4)-C(21)	1.364(4)
N(5)-C(22)	1.360(4)
N(5)-C(27)	1.503(4)
N(6)-C(32)	1.313(4)
N(6)-C(37)	1.476(4)
N(7)-C(41)	1.400(3)
N(8)-C(51)	1.412(3)
C(1)-C(6)	1.435(4)
C(1)-C(2)	1.467(4)
C(2)-C(3)	1.439(4)
C(3)-C(4)	1.363(4)
C(4)-C(5)	1.425(4)
C(5)-C(6)	1.350(4)
C(7)-C(9)	1.528(5)
C(7)-C(8)	1.535(4)
C(11)-C(16)	1.419(4)
C(11)-C(12)	1.445(4)
C(12)-C(13)	1.430(4)
C(13)-C(14)	1.365(4)
C(14)-C(15)	1.403(4)
C(15)-C(16)	1.363(4)
C(17)-C(18)	1.511(4)
C(17)-C(19)	1.534(4)
C(21)-C(22)	1.431(4)
C(21)-C(26)	1.435(4)
C(22)-C(23)	1.430(4)
C(23)-C(24)	1.371(4)
C(24)-C(25)	1.417(4)

C(25)-C(26)	1.342(4)
C(27)-C(28)	1.515(4)
C(27)-C(29)	1.534(4)
C(31)-C(36)	1.435(4)
C(31)-C(32)	1.474(4)
C(32)-C(33)	1.443(4)
C(33)-C(34)	1.359(4)
C(34)-C(35)	1.428(5)
C(35)-C(36)	1.348(4)
C(37)-C(38)	1.519(4)
C(37)-C(39)	1.530(4)
C(41)-C(46)	1.399(4)
C(41)-C(42)	1.400(4)
C(42)-C(43)	1.390(4)
C(43)-C(44)	1.394(4)
C(44)-C(45)	1.391(4)
C(44)-C(47)	1.541(4)
C(45)-C(46)	1.387(4)
C(47)-C(50)	1.499(5)
C(47)-C(49)	1.520(5)
C(47)-C(48)	1.554(5)
C(51)-C(56)	1.396(4)
C(51)-C(52)	1.406(4)
C(52)-C(53)	1.390(4)
C(53)-C(54)	1.397(4)
C(54)-C(55)	1.392(4)
C(54)-C(57)	1.533(4)
C(55)-C(56)	1.379(4)
C(57)-C(60)	1.523(4)

C(57)-C(59)	1.524(4)
C(57)-C(58)	1.532(4)
O(5)-C(63)	1.398(7)
O(5)-C(62)	1.435(5)
C(62)-C(61)	1.495(6)
C(63)-C(64)	1.523(8)

Table S5. Bond Angles (°) for **4**.

N(8)-Zr(1)-N(7)	79.29(9)
N(8)-Zr(1)-N(3)	112.99(8)
N(7)-Zr(1)-N(3)	100.72(9)
N(8)-Zr(1)-N(2)	109.34(8)
N(7)-Zr(1)-N(2)	89.54(8)
N(3)-Zr(1)-N(2)	137.57(9)
N(8)-Zr(1)-N(1)	165.30(9)
N(7)-Zr(1)-N(1)	86.05(8)
N(3)-Zr(1)-N(1)	70.62(9)
N(2)-Zr(1)-N(1)	69.18(8)
N(8)-Zr(1)-Cl(1)	101.12(7)
N(7)-Zr(1)-Cl(1)	171.34(6)
N(3)-Zr(1)-Cl(1)	87.14(7)
N(2)-Zr(1)-Cl(1)	82.14(6)
N(1)-Zr(1)-Cl(1)	93.21(6)
N(8)-Zr(1)-Zr(2)	40.09(6)
N(7)-Zr(1)-Zr(2)	39.21(6)
N(3)-Zr(1)-Zr(2)	112.57(6)
N(2)-Zr(1)-Zr(2)	101.34(6)
N(1)-Zr(1)-Zr(2)	125.22(6)
Cl(1)-Zr(1)-Zr(2)	140.37(2)
N(7)-Zr(2)-N(8)	79.33(9)
N(7)-Zr(2)-N(5)	102.09(9)
N(8)-Zr(2)-N(5)	110.95(8)
N(7)-Zr(2)-N(6)	87.12(9)
N(8)-Zr(2)-N(6)	112.68(8)
N(5)-Zr(2)-N(6)	136.36(9)
N(7)-Zr(2)-N(4)	82.33(9)

N(8)-Zr(2)-N(4)	161.48(9)
N(5)-Zr(2)-N(4)	70.47(8)
N(6)-Zr(2)-N(4)	68.67(9)
N(7)-Zr(2)-Cl(2)	167.51(6)
N(8)-Zr(2)-Cl(2)	98.22(7)
N(5)-Zr(2)-Cl(2)	90.25(7)
N(6)-Zr(2)-Cl(2)	82.53(7)
N(4)-Zr(2)-Cl(2)	100.25(6)
N(7)-Zr(2)-Zr(1)	39.65(6)
N(8)-Zr(2)-Zr(1)	39.69(6)
N(5)-Zr(2)-Zr(1)	110.94(7)
N(6)-Zr(2)-Zr(1)	103.20(6)
N(4)-Zr(2)-Zr(1)	121.90(6)
Cl(2)-Zr(2)-Zr(1)	136.86(2)
C(4)-O(1)-C(10)	117.5(2)
C(14)-O(2)-C(20)	117.9(2)
C(24)-O(3)-C(30)	117.7(2)
C(34)-O(4)-C(40)	117.7(3)
C(1)-N(1)-C(11)	127.8(3)
C(1)-N(1)-Zr(1)	118.14(19)
C(11)-N(1)-Zr(1)	113.98(18)
C(2)-N(2)-C(7)	122.4(2)
C(2)-N(2)-Zr(1)	121.36(19)
C(7)-N(2)-Zr(1)	115.79(17)
C(12)-N(3)-C(17)	117.3(2)
C(12)-N(3)-Zr(1)	117.28(19)
C(17)-N(3)-Zr(1)	125.39(18)
C(31)-N(4)-C(21)	126.6(3)
C(31)-N(4)-Zr(2)	116.00(19)

C(21)-N(4)-Zr(2)	116.18(18)
C(22)-N(5)-C(27)	114.8(2)
C(22)-N(5)-Zr(2)	118.75(18)
C(27)-N(5)-Zr(2)	125.71(18)
C(32)-N(6)-C(37)	122.8(3)
C(32)-N(6)-Zr(2)	119.98(19)
C(37)-N(6)-Zr(2)	117.05(19)
C(41)-N(7)-Zr(2)	133.3(2)
C(41)-N(7)-Zr(1)	125.5(2)
Zr(2)-N(7)-Zr(1)	101.15(9)
C(51)-N(8)-Zr(1)	129.6(2)
C(51)-N(8)-Zr(2)	130.2(2)
Zr(1)-N(8)-Zr(2)	100.22(9)
N(1)-C(1)-C(6)	127.4(3)
N(1)-C(1)-C(2)	114.7(3)
C(6)-C(1)-C(2)	117.6(3)
N(2)-C(2)-C(3)	125.0(3)
N(2)-C(2)-C(1)	116.6(3)
C(3)-C(2)-C(1)	118.4(3)
C(4)-C(3)-C(2)	119.9(3)
O(1)-C(4)-C(3)	124.3(3)
O(1)-C(4)-C(5)	113.7(3)
C(3)-C(4)-C(5)	122.0(3)
C(6)-C(5)-C(4)	119.7(3)
C(5)-C(6)-C(1)	122.0(3)
N(2)-C(7)-C(9)	114.2(3)
N(2)-C(7)-C(8)	113.7(2)
C(9)-C(7)-C(8)	113.5(3)
N(1)-C(11)-C(16)	126.5(3)

N(1)-C(11)-C(12)	114.5(2)
C(16)-C(11)-C(12)	119.0(3)
N(3)-C(12)-C(13)	124.0(3)
N(3)-C(12)-C(11)	118.8(3)
C(13)-C(12)-C(11)	117.2(3)
C(14)-C(13)-C(12)	120.8(3)
O(2)-C(14)-C(13)	124.1(3)
O(2)-C(14)-C(15)	114.5(3)
C(13)-C(14)-C(15)	121.5(3)
C(16)-C(15)-C(14)	119.8(3)
C(15)-C(16)-C(11)	121.1(3)
N(3)-C(17)-C(18)	110.6(2)
N(3)-C(17)-C(19)	110.8(2)
C(18)-C(17)-C(19)	109.4(2)
N(4)-C(21)-C(22)	114.7(2)
N(4)-C(21)-C(26)	126.3(3)
C(22)-C(21)-C(26)	118.3(3)
N(5)-C(22)-C(23)	123.7(3)
N(5)-C(22)-C(21)	118.6(2)
C(23)-C(22)-C(21)	117.7(3)
C(24)-C(23)-C(22)	120.4(3)
O(3)-C(24)-C(23)	124.4(3)
O(3)-C(24)-C(25)	114.6(3)
C(23)-C(24)-C(25)	121.0(3)
C(26)-C(25)-C(24)	119.5(3)
C(25)-C(26)-C(21)	121.7(3)
N(5)-C(27)-C(28)	111.2(2)
N(5)-C(27)-C(29)	110.3(3)
C(28)-C(27)-C(29)	109.6(3)

N(4)-C(31)-C(36)	127.1(3)
N(4)-C(31)-C(32)	114.1(3)
C(36)-C(31)-C(32)	118.8(3)
N(6)-C(32)-C(33)	127.2(3)
N(6)-C(32)-C(31)	116.6(3)
C(33)-C(32)-C(31)	116.1(3)
C(34)-C(33)-C(32)	120.5(3)
C(33)-C(34)-O(4)	125.1(3)
C(33)-C(34)-C(35)	122.1(3)
O(4)-C(34)-C(35)	112.7(3)
C(36)-C(35)-C(34)	119.7(3)
C(35)-C(36)-C(31)	120.9(3)
N(6)-C(37)-C(38)	113.7(3)
N(6)-C(37)-C(39)	112.5(3)
C(38)-C(37)-C(39)	114.4(3)
C(46)-C(41)-C(42)	116.7(2)
C(46)-C(41)-N(7)	121.5(2)
C(42)-C(41)-N(7)	121.8(2)
C(43)-C(42)-C(41)	121.3(2)
C(42)-C(43)-C(44)	122.0(3)
C(45)-C(44)-C(43)	116.2(3)
C(45)-C(44)-C(47)	120.6(2)
C(43)-C(44)-C(47)	123.1(3)
C(46)-C(45)-C(44)	122.5(3)
C(45)-C(46)-C(41)	121.0(3)
C(50)-C(47)-C(49)	110.3(4)
C(50)-C(47)-C(44)	112.8(3)
C(49)-C(47)-C(44)	109.2(3)
C(50)-C(47)-C(48)	106.8(3)

C(49)-C(47)-C(48)	108.3(4)
C(44)-C(47)-C(48)	109.3(3)
C(56)-C(51)-C(52)	115.6(2)
C(56)-C(51)-N(8)	122.2(3)
C(52)-C(51)-N(8)	122.2(2)
C(53)-C(52)-C(51)	121.6(3)
C(52)-C(53)-C(54)	122.4(3)
C(55)-C(54)-C(53)	115.4(3)
C(55)-C(54)-C(57)	121.0(3)
C(53)-C(54)-C(57)	123.6(3)
C(56)-C(55)-C(54)	122.7(3)
C(55)-C(56)-C(51)	122.2(3)
C(60)-C(57)-C(59)	108.2(3)
C(60)-C(57)-C(58)	109.3(3)
C(59)-C(57)-C(58)	108.1(3)
C(60)-C(57)-C(54)	111.4(2)
C(59)-C(57)-C(54)	111.2(2)
C(58)-C(57)-C(54)	108.5(2)
C(63)-O(5)-C(62)	112.3(4)
O(5)-C(62)-C(61)	109.2(4)
O(5)-C(63)-C(64)	110.4(6)

Table S6. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	18(1)	18(1)	14(1)	0(1)	-1(1)	2(1)
Zr(2)	16(1)	19(1)	14(1)	0(1)	0(1)	2(1)
Cl(1)	26(1)	23(1)	20(1)	-2(1)	3(1)	1(1)
Cl(2)	27(1)	39(1)	20(1)	5(1)	-1(1)	9(1)
O(1)	38(1)	19(1)	23(1)	5(1)	1(1)	4(1)
O(2)	22(1)	43(1)	27(1)	-1(1)	-5(1)	-8(1)
O(3)	35(1)	21(1)	22(1)	-6(1)	2(1)	-2(1)
O(4)	27(1)	35(1)	41(1)	10(1)	5(1)	-7(1)
N(1)	22(1)	19(1)	12(1)	0(1)	-1(1)	3(1)
N(2)	20(1)	20(1)	21(1)	-1(1)	-2(1)	3(1)
N(3)	22(1)	21(1)	17(1)	-2(1)	0(1)	0(1)
N(4)	18(1)	21(1)	12(1)	1(1)	-1(1)	2(1)
N(5)	17(1)	25(1)	22(1)	-5(1)	1(1)	-2(1)
N(6)	28(1)	20(1)	16(1)	1(1)	-2(1)	-1(1)
N(7)	18(1)	17(1)	17(1)	0(1)	0(1)	2(1)
N(8)	18(1)	17(1)	19(1)	-1(1)	1(1)	3(1)
C(1)	23(2)	22(2)	15(2)	-3(1)	-1(1)	3(1)
C(2)	24(2)	21(1)	14(2)	1(1)	3(1)	4(1)
C(3)	27(2)	22(2)	19(2)	-3(1)	2(1)	0(1)
C(4)	36(2)	20(2)	16(2)	-1(1)	5(1)	6(1)
C(5)	26(1)	26(2)	17(1)	1(1)	1(1)	9(1)
C(6)	21(2)	27(2)	18(2)	-2(1)	0(1)	6(1)
C(7)	25(2)	19(1)	36(2)	2(1)	-6(2)	3(1)
C(8)	39(2)	21(2)	41(2)	-4(1)	-15(2)	2(2)
C(9)	28(2)	27(2)	61(3)	-5(2)	9(2)	-2(1)

C(10)	47(2)	22(2)	29(2)	5(1)	-1(2)	-3(1)
C(11)	21(1)	25(2)	14(1)	-1(1)	0(1)	2(1)
C(12)	23(2)	26(2)	13(1)	-4(1)	2(1)	1(1)
C(13)	24(2)	26(2)	22(2)	-3(1)	2(1)	-4(1)
C(14)	23(2)	35(2)	15(2)	2(1)	-1(1)	-6(1)
C(15)	18(2)	42(2)	22(2)	5(1)	-1(1)	1(1)
C(16)	27(2)	26(2)	18(2)	4(1)	1(1)	5(1)
C(17)	24(2)	17(1)	24(2)	2(1)	-1(1)	-3(1)
C(18)	28(2)	20(1)	29(2)	0(1)	-2(1)	2(1)
C(19)	29(2)	22(2)	24(2)	-3(1)	-6(1)	1(1)
C(20)	33(2)	33(2)	33(2)	-5(2)	-4(2)	-7(1)
C(21)	19(1)	23(2)	14(2)	-1(1)	-1(1)	2(1)
C(22)	20(1)	23(1)	14(1)	0(1)	0(1)	-1(1)
C(23)	24(2)	24(2)	19(2)	-1(1)	3(1)	-3(1)
C(24)	30(2)	22(2)	16(2)	0(1)	-2(1)	2(1)
C(25)	23(2)	22(1)	18(2)	0(1)	0(1)	6(1)
C(26)	20(2)	25(2)	20(2)	4(1)	-1(1)	2(1)
C(27)	18(1)	28(2)	27(2)	-10(1)	0(1)	-2(1)
C(28)	20(1)	31(2)	32(2)	-10(2)	3(1)	-3(1)
C(29)	24(2)	45(2)	32(2)	-10(2)	-7(1)	2(1)
C(30)	34(2)	27(2)	31(2)	-1(1)	1(2)	-6(1)
C(31)	20(1)	23(2)	14(1)	2(1)	-1(1)	-1(1)
C(32)	20(2)	27(2)	15(2)	5(1)	0(1)	-2(1)
C(33)	29(2)	21(2)	22(2)	3(1)	-1(1)	-6(1)
C(34)	20(2)	36(2)	24(2)	6(1)	1(1)	-8(1)
C(35)	23(2)	35(2)	32(2)	1(2)	2(1)	-1(2)
C(36)	24(2)	24(2)	24(2)	1(1)	1(1)	0(1)
C(37)	30(2)	20(2)	28(2)	-1(1)	6(1)	0(1)
C(38)	45(2)	26(2)	35(2)	1(1)	6(2)	8(2)

C(39)	38(2)	26(2)	34(2)	-5(1)	6(2)	-6(1)
C(40)	33(2)	40(2)	34(2)	5(2)	-4(2)	-14(2)
C(41)	21(1)	21(1)	13(1)	0(1)	-1(1)	2(1)
C(42)	22(1)	16(1)	18(1)	0(1)	1(1)	3(1)
C(43)	19(1)	24(1)	28(2)	0(1)	3(1)	-2(1)
C(44)	21(2)	22(1)	38(2)	-1(2)	-1(2)	7(1)
C(45)	27(2)	20(1)	40(2)	-2(2)	-1(2)	4(1)
C(46)	23(2)	17(1)	32(2)	-3(1)	-2(1)	-1(1)
C(47)	26(2)	27(2)	57(3)	-2(2)	-3(2)	7(1)
C(48)	41(2)	58(3)	85(3)	21(3)	-12(2)	14(2)
C(49)	56(3)	120(5)	83(4)	-54(3)	-20(3)	54(3)
C(50)	19(2)	43(2)	113(4)	8(2)	-11(2)	6(2)
C(51)	19(1)	16(1)	16(1)	-2(1)	0(1)	2(1)
C(52)	22(2)	16(1)	21(2)	3(1)	-1(1)	0(1)
C(53)	19(1)	22(2)	26(2)	0(1)	3(1)	-3(1)
C(54)	21(1)	20(1)	22(2)	-2(1)	-1(1)	2(1)
C(55)	26(2)	15(1)	30(2)	1(1)	-3(1)	1(1)
C(56)	20(2)	25(2)	22(2)	3(1)	-1(1)	-3(1)
C(57)	19(1)	27(2)	26(2)	-2(1)	0(1)	3(1)
C(58)	29(2)	27(2)	30(2)	-3(1)	3(2)	8(1)
C(59)	27(2)	42(2)	31(2)	1(2)	-1(1)	11(2)
C(60)	19(2)	34(2)	66(3)	-4(2)	5(2)	3(1)
O(5)	57(2)	43(2)	107(3)	0(2)	-34(2)	2(2)
C(62)	47(2)	38(2)	77(3)	3(2)	-8(2)	-4(2)
C(61)	48(3)	65(3)	82(4)	-4(3)	-12(3)	7(2)
C(63)	105(5)	66(3)	105(5)	-30(3)	-75(4)	23(3)
C(64)	132(6)	76(4)	253(10)	-52(5)	-136(7)	8(4)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4**.

	x	y	z	U(eq)
H(3A)	3862	6324	1103	27
H(5A)	1534	6207	73	27
H(6A)	1310	5155	379	27
H(7A)	5036	5003	1931	32
H(8A)	4219	5790	2519	50
H(8B)	4438	6309	1978	50
H(8C)	5249	5992	2376	50
H(9A)	5344	5161	846	58
H(9B)	5971	5586	1304	58
H(9C)	5140	5918	938	58
H(10A)	3472	7794	370	49
H(10B)	4069	7147	418	49
H(10C)	3534	7409	1025	49
H(13A)	1410	2424	1068	29
H(15A)	-464	3818	735	33
H(16A)	592	4621	930	28
H(17A)	2583	2235	1537	26
H(18A)	3815	2524	2184	38
H(18B)	4415	2692	1575	38
H(18C)	4116	1958	1710	38
H(19A)	3414	1862	654	37
H(19B)	3737	2586	497	37
H(19C)	2690	2391	424	37
H(20A)	-595	1698	615	49
H(20B)	157	1834	1144	49
H(20C)	430	1853	413	49

H(23A)	4341	6302	3895	27
H(25A)	2028	6406	4933	25
H(26A)	1666	5362	4674	26
H(27A)	5237	5716	3490	29
H(28A)	5591	4833	2815	42
H(28B)	5815	4395	3419	42
H(28C)	6435	5011	3259	42
H(29A)	5181	5563	4587	51
H(29B)	6180	5376	4351	51
H(29C)	5462	4817	4513	51
H(30A)	3968	7907	4319	46
H(30B)	3993	7381	3764	46
H(30C)	4591	7274	4386	46
H(33A)	1233	2653	3994	29
H(35A)	-325	4247	4312	36
H(36A)	870	4926	4097	29
H(37A)	3533	2640	3251	31
H(38A)	3449	2421	4327	52
H(38B)	3244	1787	3915	52
H(38C)	2427	2172	4244	52
H(39A)	2232	2659	2594	49
H(39B)	1685	2274	3129	49
H(39C)	2539	1942	2790	49
H(40A)	-939	2184	4451	53
H(40B)	122	2190	4618	53
H(40C)	-202	2239	3899	53
H(42A)	1302	3708	2520	23
H(43A)	-152	4130	2443	28
H(45A)	862	5940	2526	35

H(46A)	2316	5529	2624	29
H(48A)	-1352	5979	1660	92
H(48B)	-521	5565	1387	92
H(48C)	-330	6186	1821	92
H(49A)	-1635	5961	2860	129
H(49B)	-594	6171	2934	129
H(49C)	-967	5544	3297	129
H(50A)	-2064	5090	2164	87
H(50B)	-1521	4595	2607	87
H(50C)	-1317	4617	1865	87
H(52A)	5997	4126	1861	24
H(53A)	7418	3651	1837	27
H(55A)	6488	2172	2892	28
H(56A)	5099	2669	2971	27
H(58A)	7995	2297	1395	43
H(58B)	7557	1745	1831	43
H(58C)	8638	1812	1781	43
H(59A)	8180	2413	3318	50
H(59B)	8847	1944	2933	50
H(59C)	7787	1778	2980	50
H(60A)	8815	3319	2621	59
H(60B)	8760	3237	1871	59
H(60C)	9414	2777	2276	59
H(62A)	6896	4036	4538	65
H(62B)	7871	3769	4756	65
H(61A)	7448	3404	3726	98
H(61B)	8396	3784	3728	98
H(61C)	7493	4141	3490	98
H(63A)	8012	4696	5440	111

H(63B)	7039	4944	5201	111
H(64A)	7849	5845	5568	231
H(64B)	7752	5916	4818	231
H(64C)	8690	5673	5118	231

Table S8. Torsion angles (°) for **4**.

N(8)-Zr(1)-Zr(2)-N(7)	-178.37(12)
N(3)-Zr(1)-Zr(2)-N(7)	-78.99(11)
N(2)-Zr(1)-Zr(2)-N(7)	75.00(11)
N(1)-Zr(1)-Zr(2)-N(7)	2.59(12)
Cl(1)-Zr(1)-Zr(2)-N(7)	166.36(10)
N(7)-Zr(1)-Zr(2)-N(8)	178.37(12)
N(3)-Zr(1)-Zr(2)-N(8)	99.38(11)
N(2)-Zr(1)-Zr(2)-N(8)	-106.63(11)
N(1)-Zr(1)-Zr(2)-N(8)	-179.04(12)
Cl(1)-Zr(1)-Zr(2)-N(8)	-15.28(9)
N(8)-Zr(1)-Zr(2)-N(5)	97.95(11)
N(7)-Zr(1)-Zr(2)-N(5)	-83.68(11)
N(3)-Zr(1)-Zr(2)-N(5)	-162.66(9)
N(2)-Zr(1)-Zr(2)-N(5)	-8.68(9)
N(1)-Zr(1)-Zr(2)-N(5)	-81.09(10)
Cl(1)-Zr(1)-Zr(2)-N(5)	82.68(7)
N(8)-Zr(1)-Zr(2)-N(6)	-109.72(11)
N(7)-Zr(1)-Zr(2)-N(6)	68.65(11)
N(3)-Zr(1)-Zr(2)-N(6)	-10.34(10)
N(2)-Zr(1)-Zr(2)-N(6)	143.65(9)
N(1)-Zr(1)-Zr(2)-N(6)	71.24(10)
Cl(1)-Zr(1)-Zr(2)-N(6)	-125.00(7)
N(8)-Zr(1)-Zr(2)-N(4)	177.38(11)
N(7)-Zr(1)-Zr(2)-N(4)	-4.25(11)
N(3)-Zr(1)-Zr(2)-N(4)	-83.24(10)
N(2)-Zr(1)-Zr(2)-N(4)	70.75(9)
N(1)-Zr(1)-Zr(2)-N(4)	-1.66(10)

Cl(1)-Zr(1)-Zr(2)-N(4)	162.10(7)
N(8)-Zr(1)-Zr(2)-Cl(2)	-16.57(9)
N(7)-Zr(1)-Zr(2)-Cl(2)	161.80(10)
N(3)-Zr(1)-Zr(2)-Cl(2)	82.82(7)
N(2)-Zr(1)-Zr(2)-Cl(2)	-123.20(7)
N(1)-Zr(1)-Zr(2)-Cl(2)	164.39(8)
Cl(1)-Zr(1)-Zr(2)-Cl(2)	-31.84(5)
N(8)-Zr(1)-N(1)-C(1)	88.9(4)
N(7)-Zr(1)-N(1)-C(1)	92.9(2)
N(3)-Zr(1)-N(1)-C(1)	-164.3(2)
N(2)-Zr(1)-N(1)-C(1)	1.91(19)
Cl(1)-Zr(1)-N(1)-C(1)	-78.4(2)
Zr(2)-Zr(1)-N(1)-C(1)	91.3(2)
N(8)-Zr(1)-N(1)-C(11)	-87.4(4)
N(7)-Zr(1)-N(1)-C(11)	-83.36(19)
N(3)-Zr(1)-N(1)-C(11)	19.46(18)
N(2)-Zr(1)-N(1)-C(11)	-174.4(2)
Cl(1)-Zr(1)-N(1)-C(11)	105.29(19)
Zr(2)-Zr(1)-N(1)-C(11)	-85.00(19)
N(8)-Zr(1)-N(2)-C(2)	-166.7(2)
N(7)-Zr(1)-N(2)-C(2)	-88.3(2)
N(3)-Zr(1)-N(2)-C(2)	17.2(3)
N(1)-Zr(1)-N(2)-C(2)	-2.3(2)
Cl(1)-Zr(1)-N(2)-C(2)	94.2(2)
Zr(2)-Zr(1)-N(2)-C(2)	-125.9(2)
N(8)-Zr(1)-N(2)-C(7)	20.8(2)
N(7)-Zr(1)-N(2)-C(7)	99.3(2)
N(3)-Zr(1)-N(2)-C(7)	-155.22(19)
N(1)-Zr(1)-N(2)-C(7)	-174.8(2)

Cl(1)-Zr(1)-N(2)-C(7)	-78.3(2)
Zr(2)-Zr(1)-N(2)-C(7)	61.7(2)
N(8)-Zr(1)-N(3)-C(12)	148.5(2)
N(7)-Zr(1)-N(3)-C(12)	65.7(2)
N(2)-Zr(1)-N(3)-C(12)	-35.5(3)
N(1)-Zr(1)-N(3)-C(12)	-16.2(2)
Cl(1)-Zr(1)-N(3)-C(12)	-110.6(2)
Zr(2)-Zr(1)-N(3)-C(12)	104.9(2)
N(8)-Zr(1)-N(3)-C(17)	-33.6(2)
N(7)-Zr(1)-N(3)-C(17)	-116.4(2)
N(2)-Zr(1)-N(3)-C(17)	142.3(2)
N(1)-Zr(1)-N(3)-C(17)	161.7(2)
Cl(1)-Zr(1)-N(3)-C(17)	67.2(2)
Zr(2)-Zr(1)-N(3)-C(17)	-77.3(2)
N(7)-Zr(2)-N(4)-C(31)	70.7(2)
N(8)-Zr(2)-N(4)-C(31)	78.7(3)
N(5)-Zr(2)-N(4)-C(31)	176.5(2)
N(6)-Zr(2)-N(4)-C(31)	-19.21(19)
Cl(2)-Zr(2)-N(4)-C(31)	-96.95(19)
Zr(1)-Zr(2)-N(4)-C(31)	73.4(2)
N(7)-Zr(2)-N(4)-C(21)	-97.4(2)
N(8)-Zr(2)-N(4)-C(21)	-89.3(3)
N(5)-Zr(2)-N(4)-C(21)	8.43(19)
N(6)-Zr(2)-N(4)-C(21)	172.8(2)
Cl(2)-Zr(2)-N(4)-C(21)	95.02(19)
Zr(1)-Zr(2)-N(4)-C(21)	-94.62(19)
N(7)-Zr(2)-N(5)-C(22)	66.9(2)
N(8)-Zr(2)-N(5)-C(22)	150.0(2)
N(6)-Zr(2)-N(5)-C(22)	-31.7(3)

N(4)-Zr(2)-N(5)-C(22)	-10.3(2)
Cl(2)-Zr(2)-N(5)-C(22)	-111.1(2)
Zr(1)-Zr(2)-N(5)-C(22)	107.3(2)
N(7)-Zr(2)-N(5)-C(27)	-123.4(2)
N(8)-Zr(2)-N(5)-C(27)	-40.4(3)
N(6)-Zr(2)-N(5)-C(27)	137.9(2)
N(4)-Zr(2)-N(5)-C(27)	159.3(3)
Cl(2)-Zr(2)-N(5)-C(27)	58.5(2)
Zr(1)-Zr(2)-N(5)-C(27)	-83.0(2)
N(7)-Zr(2)-N(6)-C(32)	-69.9(2)
N(8)-Zr(2)-N(6)-C(32)	-147.1(2)
N(5)-Zr(2)-N(6)-C(32)	34.6(3)
N(4)-Zr(2)-N(6)-C(32)	13.0(2)
Cl(2)-Zr(2)-N(6)-C(32)	117.1(2)
Zr(1)-Zr(2)-N(6)-C(32)	-106.4(2)
N(7)-Zr(2)-N(6)-C(37)	105.7(2)
N(8)-Zr(2)-N(6)-C(37)	28.5(2)
N(5)-Zr(2)-N(6)-C(37)	-149.79(19)
N(4)-Zr(2)-N(6)-C(37)	-171.4(2)
Cl(2)-Zr(2)-N(6)-C(37)	-67.3(2)
Zr(1)-Zr(2)-N(6)-C(37)	69.2(2)
N(8)-Zr(2)-N(7)-C(41)	175.5(2)
N(5)-Zr(2)-N(7)-C(41)	-75.2(2)
N(6)-Zr(2)-N(7)-C(41)	61.7(2)
N(4)-Zr(2)-N(7)-C(41)	-7.1(2)
Cl(2)-Zr(2)-N(7)-C(41)	95.7(4)
Zr(1)-Zr(2)-N(7)-C(41)	176.5(3)
N(8)-Zr(2)-N(7)-Zr(1)	-1.06(8)
N(5)-Zr(2)-N(7)-Zr(1)	108.31(9)

N(6)-Zr(2)-N(7)-Zr(1)	-114.79(10)
N(4)-Zr(2)-N(7)-Zr(1)	176.36(10)
Cl(2)-Zr(2)-N(7)-Zr(1)	-80.8(3)
N(8)-Zr(1)-N(7)-C(41)	-175.8(2)
N(3)-Zr(1)-N(7)-C(41)	-64.2(2)
N(2)-Zr(1)-N(7)-C(41)	74.4(2)
N(1)-Zr(1)-N(7)-C(41)	5.2(2)
Cl(1)-Zr(1)-N(7)-C(41)	90.6(5)
Zr(2)-Zr(1)-N(7)-C(41)	-176.9(3)
N(8)-Zr(1)-N(7)-Zr(2)	1.07(8)
N(3)-Zr(1)-N(7)-Zr(2)	112.71(9)
N(2)-Zr(1)-N(7)-Zr(2)	-108.72(9)
N(1)-Zr(1)-N(7)-Zr(2)	-177.88(9)
Cl(1)-Zr(1)-N(7)-Zr(2)	-92.5(4)
N(7)-Zr(1)-N(8)-C(51)	178.8(2)
N(3)-Zr(1)-N(8)-C(51)	81.6(2)
N(2)-Zr(1)-N(8)-C(51)	-95.5(2)
N(1)-Zr(1)-N(8)-C(51)	-177.0(3)
Cl(1)-Zr(1)-N(8)-C(51)	-10.0(2)
Zr(2)-Zr(1)-N(8)-C(51)	179.9(3)
N(7)-Zr(1)-N(8)-Zr(2)	-1.05(8)
N(3)-Zr(1)-N(8)-Zr(2)	-98.25(9)
N(2)-Zr(1)-N(8)-Zr(2)	84.65(10)
N(1)-Zr(1)-N(8)-Zr(2)	3.1(4)
Cl(1)-Zr(1)-N(8)-Zr(2)	170.14(6)
N(7)-Zr(2)-N(8)-C(51)	-178.8(2)
N(5)-Zr(2)-N(8)-C(51)	82.2(2)
N(6)-Zr(2)-N(8)-C(51)	-96.5(2)
N(4)-Zr(2)-N(8)-C(51)	173.1(2)

Cl(2)-Zr(2)-N(8)-C(51)	-11.2(2)
Zr(1)-Zr(2)-N(8)-C(51)	-179.9(3)
N(7)-Zr(2)-N(8)-Zr(1)	1.06(8)
N(5)-Zr(2)-N(8)-Zr(1)	-97.92(10)
N(6)-Zr(2)-N(8)-Zr(1)	83.34(10)
N(4)-Zr(2)-N(8)-Zr(1)	-7.0(3)
Cl(2)-Zr(2)-N(8)-Zr(1)	168.64(6)
C(11)-N(1)-C(1)-C(6)	-12.1(5)
Zr(1)-N(1)-C(1)-C(6)	172.2(2)
C(11)-N(1)-C(1)-C(2)	174.3(3)
Zr(1)-N(1)-C(1)-C(2)	-1.4(3)
C(7)-N(2)-C(2)-C(3)	-5.9(4)
Zr(1)-N(2)-C(2)-C(3)	-177.8(2)
C(7)-N(2)-C(2)-C(1)	174.4(3)
Zr(1)-N(2)-C(2)-C(1)	2.5(3)
N(1)-C(1)-C(2)-N(2)	-0.6(4)
C(6)-C(1)-C(2)-N(2)	-174.9(3)
N(1)-C(1)-C(2)-C(3)	179.6(2)
C(6)-C(1)-C(2)-C(3)	5.4(4)
N(2)-C(2)-C(3)-C(4)	178.4(3)
C(1)-C(2)-C(3)-C(4)	-1.9(4)
C(10)-O(1)-C(4)-C(3)	2.2(4)
C(10)-O(1)-C(4)-C(5)	-175.5(3)
C(2)-C(3)-C(4)-O(1)	179.6(3)
C(2)-C(3)-C(4)-C(5)	-2.9(4)
O(1)-C(4)-C(5)-C(6)	-178.0(3)
C(3)-C(4)-C(5)-C(6)	4.2(4)
C(4)-C(5)-C(6)-C(1)	-0.4(4)
N(1)-C(1)-C(6)-C(5)	-177.7(3)

C(2)-C(1)-C(6)-C(5)	-4.3(4)
C(2)-N(2)-C(7)-C(9)	-61.9(4)
Zr(1)-N(2)-C(7)-C(9)	110.5(2)
C(2)-N(2)-C(7)-C(8)	70.5(4)
Zr(1)-N(2)-C(7)-C(8)	-117.1(2)
C(1)-N(1)-C(11)-C(16)	-17.9(5)
Zr(1)-N(1)-C(11)-C(16)	158.0(2)
C(1)-N(1)-C(11)-C(12)	163.8(3)
Zr(1)-N(1)-C(11)-C(12)	-20.4(3)
C(17)-N(3)-C(12)-C(13)	11.8(4)
Zr(1)-N(3)-C(12)-C(13)	-170.2(2)
C(17)-N(3)-C(12)-C(11)	-166.2(3)
Zr(1)-N(3)-C(12)-C(11)	11.8(3)
N(1)-C(11)-C(12)-N(3)	6.6(4)
C(16)-C(11)-C(12)-N(3)	-171.9(3)
N(1)-C(11)-C(12)-C(13)	-171.6(3)
C(16)-C(11)-C(12)-C(13)	9.9(4)
N(3)-C(12)-C(13)-C(14)	176.8(3)
C(11)-C(12)-C(13)-C(14)	-5.1(4)
C(20)-O(2)-C(14)-C(13)	-0.3(4)
C(20)-O(2)-C(14)-C(15)	-179.4(3)
C(12)-C(13)-C(14)-O(2)	178.8(3)
C(12)-C(13)-C(14)-C(15)	-2.2(5)
O(2)-C(14)-C(15)-C(16)	-176.1(3)
C(13)-C(14)-C(15)-C(16)	4.8(5)
C(14)-C(15)-C(16)-C(11)	0.4(5)
N(1)-C(11)-C(16)-C(15)	174.0(3)
C(12)-C(11)-C(16)-C(15)	-7.8(4)
C(12)-N(3)-C(17)-C(18)	-167.5(3)

Zr(1)-N(3)-C(17)-C(18)	14.7(3)
C(12)-N(3)-C(17)-C(19)	71.0(3)
Zr(1)-N(3)-C(17)-C(19)	-106.8(2)
C(31)-N(4)-C(21)-C(22)	-172.3(3)
Zr(2)-N(4)-C(21)-C(22)	-5.7(3)
C(31)-N(4)-C(21)-C(26)	17.8(5)
Zr(2)-N(4)-C(21)-C(26)	-175.6(2)
C(27)-N(5)-C(22)-C(23)	20.4(4)
Zr(2)-N(5)-C(22)-C(23)	-168.8(2)
C(27)-N(5)-C(22)-C(21)	-159.2(3)
Zr(2)-N(5)-C(22)-C(21)	11.6(3)
N(4)-C(21)-C(22)-N(5)	-3.4(4)
C(26)-C(21)-C(22)-N(5)	167.4(3)
N(4)-C(21)-C(22)-C(23)	177.0(2)
C(26)-C(21)-C(22)-C(23)	-12.2(4)
N(5)-C(22)-C(23)-C(24)	-173.9(3)
C(21)-C(22)-C(23)-C(24)	5.7(4)
C(30)-O(3)-C(24)-C(23)	5.3(4)
C(30)-O(3)-C(24)-C(25)	-175.8(3)
C(22)-C(23)-C(24)-O(3)	-176.5(3)
C(22)-C(23)-C(24)-C(25)	4.6(4)
O(3)-C(24)-C(25)-C(26)	172.8(3)
C(23)-C(24)-C(25)-C(26)	-8.2(4)
C(24)-C(25)-C(26)-C(21)	1.2(4)
N(4)-C(21)-C(26)-C(25)	178.6(3)
C(22)-C(21)-C(26)-C(25)	9.0(4)
C(22)-N(5)-C(27)-C(28)	-172.7(3)
Zr(2)-N(5)-C(27)-C(28)	17.3(4)
C(22)-N(5)-C(27)-C(29)	65.5(3)

Zr(2)-N(5)-C(27)-C(29)	-104.5(3)
C(21)-N(4)-C(31)-C(36)	12.6(5)
Zr(2)-N(4)-C(31)-C(36)	-154.0(2)
C(21)-N(4)-C(31)-C(32)	-170.4(3)
Zr(2)-N(4)-C(31)-C(32)	22.9(3)
C(37)-N(6)-C(32)-C(33)	-0.4(5)
Zr(2)-N(6)-C(32)-C(33)	174.9(2)
C(37)-N(6)-C(32)-C(31)	178.6(3)
Zr(2)-N(6)-C(32)-C(31)	-6.1(4)
N(4)-C(31)-C(32)-N(6)	-11.7(4)
C(36)-C(31)-C(32)-N(6)	165.5(3)
N(4)-C(31)-C(32)-C(33)	167.4(3)
C(36)-C(31)-C(32)-C(33)	-15.4(4)
N(6)-C(32)-C(33)-C(34)	-173.4(3)
C(31)-C(32)-C(33)-C(34)	7.6(4)
C(32)-C(33)-C(34)-O(4)	179.5(3)
C(32)-C(33)-C(34)-C(35)	3.7(5)
C(40)-O(4)-C(34)-C(33)	-2.2(5)
C(40)-O(4)-C(34)-C(35)	173.9(3)
C(33)-C(34)-C(35)-C(36)	-7.6(5)
O(4)-C(34)-C(35)-C(36)	176.2(3)
C(34)-C(35)-C(36)-C(31)	-0.8(5)
N(4)-C(31)-C(36)-C(35)	-170.9(3)
C(32)-C(31)-C(36)-C(35)	12.3(4)
C(32)-N(6)-C(37)-C(38)	-67.6(4)
Zr(2)-N(6)-C(37)-C(38)	116.9(3)
C(32)-N(6)-C(37)-C(39)	64.5(4)
Zr(2)-N(6)-C(37)-C(39)	-111.0(2)
Zr(2)-N(7)-C(41)-C(46)	87.1(4)

Zr(1)-N(7)-C(41)-C(46)	-97.0(3)
Zr(2)-N(7)-C(41)-C(42)	-93.6(3)
Zr(1)-N(7)-C(41)-C(42)	82.2(3)
C(46)-C(41)-C(42)-C(43)	3.4(5)
N(7)-C(41)-C(42)-C(43)	-175.9(3)
C(41)-C(42)-C(43)-C(44)	0.0(5)
C(42)-C(43)-C(44)-C(45)	-2.7(5)
C(42)-C(43)-C(44)-C(47)	174.6(3)
C(43)-C(44)-C(45)-C(46)	2.0(6)
C(47)-C(44)-C(45)-C(46)	-175.4(3)
C(44)-C(45)-C(46)-C(41)	1.4(6)
C(42)-C(41)-C(46)-C(45)	-4.1(5)
N(7)-C(41)-C(46)-C(45)	175.2(3)
C(45)-C(44)-C(47)-C(50)	175.3(4)
C(43)-C(44)-C(47)-C(50)	-1.9(5)
C(45)-C(44)-C(47)-C(49)	-61.7(5)
C(43)-C(44)-C(47)-C(49)	121.1(4)
C(45)-C(44)-C(47)-C(48)	56.6(5)
C(43)-C(44)-C(47)-C(48)	-120.6(4)
Zr(1)-N(8)-C(51)-C(56)	-121.8(3)
Zr(2)-N(8)-C(51)-C(56)	58.0(3)
Zr(1)-N(8)-C(51)-C(52)	56.8(3)
Zr(2)-N(8)-C(51)-C(52)	-123.4(3)
C(56)-C(51)-C(52)-C(53)	-3.2(4)
N(8)-C(51)-C(52)-C(53)	178.1(3)
C(51)-C(52)-C(53)-C(54)	2.1(5)
C(52)-C(53)-C(54)-C(55)	1.2(4)
C(52)-C(53)-C(54)-C(57)	178.7(3)
C(53)-C(54)-C(55)-C(56)	-3.3(4)

C(57)-C(54)-C(55)-C(56)	179.2(3)
C(54)-C(55)-C(56)-C(51)	2.2(5)
C(52)-C(51)-C(56)-C(55)	1.2(4)
N(8)-C(51)-C(56)-C(55)	179.8(3)
C(55)-C(54)-C(57)-C(60)	-152.9(3)
C(53)-C(54)-C(57)-C(60)	29.8(4)
C(55)-C(54)-C(57)-C(59)	-32.1(4)
C(53)-C(54)-C(57)-C(59)	150.6(3)
C(55)-C(54)-C(57)-C(58)	86.8(3)
C(53)-C(54)-C(57)-C(58)	-90.5(3)
C(63)-O(5)-C(62)-C(61)	177.9(4)
C(62)-O(5)-C(63)-C(64)	-178.4(4)

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