A zwitterionic zirconium complex that catalyzes hydroamination of aminoalkenes at room temperature

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Experiment details.

General Procedures. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Dry, oxygen-free solvents were used throughout. Benzene, toluene, pentane, and tetrahydrofuran were degassed by sparging with nitrogen, filtered through activated alumina columns, and stored under N_2. Benzene-d_6 and toluene-d_8 were vacuum transferred from Na/K alloy and stored under N_2 in the glovebox. $Zr(NMe_2)_4$,[1] $Hf(NMe_2)_4$,[2] tetrakis(trimethylsilyl)silane,[3] and sodium cyclopentadienide,[4] 2,2-diphenyl-4-penten-1-amine (**5**),[5] 2,2-dimethyl-4-penten-1-amine (**6**),[6] 4-penten-1-amine (**7**),[7] (1-allylcyclohexyl)methylamine (**8**),[6] 1-(3-butenyl-cyclohexyl)methylamine (**9**),[6] and N-methyl-2,2-diphenyl-4-penten-1-amine (**10**)[8] were prepared by published procedures. Cyclooctane was purchased from Aldrich. Cyclooctane and all the aminoalkenes were degassed and stored with 4 Å molecular sieve in glovebox prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were collected on a Bruker DRX-400 spectrometer. ^{15}N chemical shifts were determined by ^1H-^{15}N HMBC experiments on a Bruker Avance II 700 spectrometer with a Bruker Z-gradient inverse TXI $^1H/^{13}C/^{15}N$ 5mm cryoprobe; ^{15}N chemical shifts were originally referenced to liquid NH_3 and recalculated to the CH_3NO_2 chemical shift scale by adding -381.9 ppm. ^{11}B NMR spectra were referenced to an external sample of $BF_3 \cdot Et_2O$. Elemental analysis was performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility.

H[PhB(C$_5$H$_5$)(Ox^{Me2})$_2$] (H[1]). A Schlenk flask was charged with $PhB(Ox^{Me2})_2$ (3.00 g, 10.5 mmol) and NaCp (0.581 g, 6.59 mmol) in the glovebox. The flask was attached to a Schlenk manifold, and THF (150 mL) was added via cannula addition to form a yellow solution. The flask was sealed and the resulting solution was stirred overnight. The solution was filtered to remove a precipitate that appeared overnight, and then the solvent was removed under reduced pressure to afford a brownish yellow solid. This crude product was purified by silica gel column chromatography (Hexane:EtOAc:Et$_3$N = 12:7:1; R_f = 0.50) to afford 3.13 g of H[PhB(C$_5$H$_5$)(Ox^{Me2})$_2$] (4.95 mmol, 47.1%) as a mixture of three isomers. The light yellow solid was dissolved in benzene and stirred over P_2O_5 to dry without any reduction in yield. ^1H NMR (acetonitrile-d_3, 400 MHz): δ 7.14-7.04 (m, 5 H, C_6H_5), 6.61-6.16 (m, 3 H, C_5H_5-sp^2), 4.09-4.00 (m, 4 H, $\overline{CNCMe_2CH_2O}$), 2.90-2.88 (m, 2 H, C_5H_5-sp^3), 1.35-1.34 (m, 12 H, $\overline{CNCMe_2CH_2O}$).

^{13}C{^{1}H} NMR (acetonitrile-d_3, 150 MHz): δ 190.50 ($\overline{C}$NCMe$_2$CH$_2$O), 158.8 (br, *ipso*-C$_5$H$_5$) 141.90 (C$_5$H$_5$-sp^2), 140.85 (C$_5$H$_5$-sp^2), 134.96 (C$_5$H$_5$-sp^2), 134.74 (C$_5$H$_5$-sp^2), 134.65 (*ortho*-C$_6$H$_5$), 134.37 (C$_5$H$_5$-sp^2), 134.30 (C$_5$H$_5$-sp^2), 131.81 (C$_5$H$_5$-sp^2), 129.71 (C$_5$H$_5$-sp^2), 128.51 (C$_5$H$_5$-sp^2), 128.34 (*meta*-C$_6$H$_5$), 126.48 (C$_5$H$_5$-sp^2), 126.24 (*para*-C$_6$H$_5$), 81.31 (CNCMe$_2$$\overline{C}H_2$O), 64.71 (CN$\overline{C}Me_2CH_2$O), 64.68 (CN$\overline{C}Me_2CH_2$O), 47.45 (C$_5H_5$-$sp^3$), 43.48 (C$_5H_5$-$sp^3$), 28.47 (CNC$\overline{Me}_2CH_2$O), 28.35 (CNC$\overline{Me}_2CH_2$O). ^{11}B NMR (acetonitrile-d_3, 128 MHz): δ -15.27, -15.63, -15.99. ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ -172 ($\overline{C}$NCMe$_2$CH$_2$O). IR (KBr, cm^{-1}): 3080 w, 3056 w, 3028 w, 2969 m, 2929 w, 2887 w, 1589 s (C=N), 1461 s, 1429 s, 1416 s, 1383 m, 1365 m, 1345 w, 1318 s, 1265 m, 1195 s, 1138 w, 1090 w, 1064 w, 1022 w, 965 s, 934 s, 891 s. Anal. Calcd for C$_{21}$H$_{27}$BO$_2$N$_2$: C, 72.01; H, 7.77; N, 8.00. Found: C, 71.99; H, 7.99; N, 7.84. mp 152-154 °C.

{PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$ (2). In the glovebox, H[PhB(C$_5$H$_5$)(Ox^{Me2})$_2$] (0.250 g, 0.714 mmol) and Zr(NMe$_2$)$_4$ (0.193 g, 0.721 mmol) were placed in a 100 mL Schlenk roundbottom flask. The solids were dissolved in benzene (50 mL), and the solution was stirred for 2 h. All volatile materials were removed under reduced pressure to afford a light yellow oil, which was washed with pentane to obtain a light yellow powder of {(PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$)}Zr(NMe$_2$)$_2$ (0.367 g, 0.696 mmol, 97.6 %). ^{1}H NMR (benzene-d_6, 400 MHz): δ 8.21 (d, ^3J = 7 Hz, 2 H, *ortho*-C$_6$H$_5$), 7.52 (t, ^{3}J = 7 Hz, 2 H, *meta*-C$_6$H$_5$), 7.32 (t, ^{3}J = 7 Hz, 1 H, *para*-C$_6$H$_5$), 6.52 (m, 2 H, Cp), 6.15 (m, 2 H, Cp), 3.64 (d, 2 H, ^2J = 8.0 Hz, CNCMe$_2$C$\overline{H}_2$O), 3.56 (d, 2 H, ^2J = 8.0 Hz, CNCMe$_2$C$\overline{H}_2$O), 2.69 (s, 12 H, NMe$_2$), 1.11 (s, 6 H, CNC$\overline{Me}_2$CH$_2$O), 1.01 (s, 6 H, CNC$\overline{Me}_2$CH$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz): δ 194.65 ($\overline{C}$NCMe$_2$CH$_2$O), 151.5 (br, *ipso*-C$_6$H$_5$), 143.01 (*ipso*-C$_5$H$_4$), 135.11 (*ortho*-C$_6$H$_5$), 127.67 (*meta*-C$_6$H$_5$), 125.47 (*para*-C$_6$H$_5$), 122.61(C$_5$H$_4$), 113.66 (C$_5$H$_4$), 78.91 (CNCMe$_2$$\overline{C}H_2$O), 67.16 (CN$\overline{C}Me_2CH_2$O), 43.94 (N$\overline{Me}_2$), 28.91 (CNC$\overline{Me}_2CH_2$O), 28.50 (CNC$\overline{Me}_2CH_2$O). ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ -135.4 ($\overline{C}$NCMe$_2$CH$_2$O); Zr(NMe$_2$)$_2$ was not detected. ^{11}B NMR (benzene-d_6, 128 MHz): δ -14.51. IR (KBr, cm^{-1}): 3064 w, 3040 w, 2962 s, 2927 s, 2863 s, 2819 s, 2771 s, 1595 s (C=N), 1491 s, 1461 s, 1444 w, 1429 m, 1369 m, 1360 m, 1283 s, 1249 s, 1195 s, 1165 s, 1139 s, 1118 s, 1050 s, 1037 w, 989 w, 963 s, 942 s, 927 s, 886 w, 871 w, 837 m, 815 m, 796 m, 783 w, 732 s, 705 s, 688 s. Anal. Calcd for C$_{25}$H$_{37}$BO$_2$N$_4$ Zr: C, 56.91; H, 7.07; N, 10.62. Found: C, 57.26; H, 6.99; N, 9.87. m.p. 107-110 °C, dec.

{PhBC$_5$H$_4$(Ox^{Me2})$_2$}Hf(NMe$_2$)$_2$] (3). A procedure analogous to that described for {PhBC$_5$H$_4$(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$, using H[PhB(C$_5$H$_5$)(Ox^{Me2})$_2$] (0.250 g, 0.714 mmol) and Hf(NMe$_2$)$_4$ (0.256 g, 0.721 mmol), provides {PhBC$_5$H$_4$(Ox^{Me2})$_2$}Hf(NMe$_2$)$_2$ as a light orange solid. Yield: 0.430 g (0.699 mmol, 97.9 %). ^{1}H NMR (benzene-d_6, 400 MHz): δ 8.21 (d, ^3J = 7

Hz, 2 H, *ortho*-C_6H_5), 7.52 (t, ^3J = 7 Hz, 2 H, *meta*-C_6H_5), 7.32 (t, ^3J = 7 Hz, 1 H, *para*-C_6H_5), 6.46 (m, 2 H, C_5H_4), 6.12 (m, 2 H, C_5H_4), 3.65 (d, 2 H, ^2J = 8.0 Hz, CNCMe$_2$CH_2O), 3.57 (d, 2 H, ^2J = 8.0 Hz, CNCMe$_2$CH_2O), 2.74 (s, 12 H, NMe_2), 1.12 (s, 6 H, CNCMe_2CH$_2$O), 1.00 (s, 6 H, CNCMe_2CH$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 400 MHz): δ 198.36 (CNCMe$_2$CH$_2$O), 150.75 (*ipso*-C_6H_5), 140.61 (*ipso*-C_5H_4), 134.79 (*ortho*-C_6H_5), 127.46 (*meta*-C_6H_5), 125.22 (*para*-C_6H_5), 120.88 (C_5H_4), 112.49 (C_5H_4), 78.91 (CNCMe$_2$$CH_2$O), 67.07 (CN$CMe_2CH_2$O), 43.77(s, N$Me_2$), 28.51 (CN$CMe_2CH_2$O), 27.90 (CN$CMe_2CH_2$O). ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ -132.3 (CNCMe$_2$CH$_2$O). ^{11}B NMR (benzene-d_6, 128 MHz): δ -14.6. IR (KBr, cm^{-1}): 3064 w, 3042 w, 3012 w, 2962 s, 2928 m, 2868 s, 2853 s, 2821 s, 2773 s, 1595 m (C=N), 1549 w, 1483 s, 1462 s, 1446 m, 1429 m, 1370 m, 1361 m, 1287 s, 1251 s, 1203 s, 1195 s, 1183 s, 1166 m, 1138 m, 1051 m, 1037 w, 963 s, 936 s, 908 w. Anal. Calcd for $C_{25}H_{37}BO_2N_4Hf(C_6H_6)_{0.5}$: C, 51.43; H, 6.17; N, 8.57. Found: C, 51.17; H, 6.20; N, 8.40. Mp: 90-95 °C, dec.

{PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$THF (4). Slow diffusion of pentane into a THF solution of **2** at -30 °C provided analytically pure, X-ray quality crystals of {PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$THF (**4**). The room temperature NMR spectroscopic data for **4** is identical to that of the THF-free species in addition to resonances due to uncoordinated THF. The structural difference is observed in the IR and in the analytical data. IR (KBr, cm^{-1}): 3063 w, 3042 m, 2995 m, 2966 s, 2930s, 2862 s, 2819 s, 2768 s, 1610 s (CN), 1533 s (CN), 1488 m, 1461 m, 1429 m, 1367 w, 1356 w, 1281 s, 1243 s, 1196 s, 1180 s, 1149 m, 1135 m, 1059 s, 1048 s, 1035 m, 1021 m, 991 s, 964 s, 950 s, 937 s, 873 s, 863 s, 817 s, 799 s, 774 w, 732 s, 704 s. Anal. Calcd for $C_{29}H_{45}BO_3N_4Zr$: C, 58.08; H, 7.56; N, 9.34. Found: C, 57.88; H, 7.51; N, 9.10.

Hydroamination Catalysis.

a) In a typical small-scale hydroamination experiment, a J. Young style NMR tube with a re-sealable with Teflon valve was charged with 100 μmol of aminoalkene substrate, 10 μmol of catalyst, and 0.5 mL of solvent (benzene-d_6). The vessel was sealed, and the reaction progress was monitored by ^{1}H NMR spectroscopy at regular intervals to determine the optimum conversion.

b) In a typical scaled up hydroamination experiment, a Schlenk flask equipped with a magnetic stir bar was charged with the catalyst {PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$ (**2**) (10 mol%) and a benzene solution (30 mL) of the aminoalkene (1.00 g). The flask was sealed, and the reaction mixture was stirred for 15 h at room temprerature. Then, the solution was concentrated under reduced pressure and subjected to silica gel column chromatography (CH$_2$Cl$_2$:MeOH = 9.5:0.5) to provide purified pyrrolidine or piperidine.

Kinetic measurements. All the kinetics measurements were conducted by monitoring the reactions with ^{1}H NMR spectroscopy using a Bruker DRX400 spectrometer. The conversion of 2,2-diphenyl-1-penten-1-amine to 2-methyl-4,4-diphenylpyrrolidine, and 2,2-dimethyl-1-penten-1-amine to 2-methyl-4,4-dimethylpyrrolidine was monitored at regular intervals with single scan acquisition of ^{1}H NMR spectra. The substrate concentration was determined by integration of appropriate resonances and comparison to integration of a cyclooctane or tetrakis(trimethylsilyl)silane internal standard of accurately known concentration.

Representative example: Catalytic conversion of 2,2-diphenyl-1-penten-1-amine into 2-methyl-4,4-diphenylpyrrolidine using 10 mol % {PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$ (**2**) as a catalyst is described. A 5 mL stock solution containing a known concentration of 2,2-diphenyl-1-penten-1-amine (0.237 g, 0.999 mmol, 0.20 M in benzene-d_6) and the appropriate internal standard cyclooctane (0.008 g, 0.071 mmol, 0.014 M) was prepared using a 5 mL volumetric flask. The stock solution (0.5 mL) was added by a 1 mL glass syringe to a known amount of catalyst **2** (0.005 g, 0.010 mmol) in a glass vial. The resultant solution was quickly transferred to a J-Young style re-sealable NMR tube. The NMR tube was immediately placed in the NMR probe, which was preset at 296 K. Single scan spectra were acquired automatically at preset time intervals. The concentration of substrate and product at any given time were determined by integration of substrate and product resonances relative to the integration of the internal standard. These values of substrate concentrations (M) at different times (s) were plotted for the determination of the order of the substrate.

Verification of first order substrate dependence using initial rates (Differential method).
Because plots of ln[substrate] versus time were complicated by severe product inhibition, the method of initial rates (a.k.a. the differential method) was used to verify first order dependence on substrate concentration. The initial rates for the hydroamination of 2,2-diphenyl-1-pentene-1-amine were measured for several substrate concentrations. Linear regression fits for [substrate] versus time for the first 3000 s of the reaction provided the initial rate (d[substrate]/dt) for a particular initial substrate concentration (Figure S3). Catalyst concentration was kept constant for these experiments.

Plots of ln(d[2,2-phenyl-1-penten-1-amine]/dt) vs. ln[2,2-phenyl-1-penten-1-amine] provides the value of the slope 0.94 (Figure S4). According to the rate equation: ln[rate] = ln$k$ + n ln[substrate], the order of the substrate 2,2-phenyl-1-penten-1-amine is 0.94, which is consistent with the first order dependence of substrate.

Isotope effect determination. k_H and k_D were measured from the slope of the curves obtained from plotting $k_{obs(H)}$ vs [catalyst] and $k_{obs(D)}$ vs [catalyst] for cyclization reactions of 2,2-diphenyl-

1-penten-1-amine. The ratio of the two slopes (Figure S5) provided the value of the isotope effect (k_H/k_D=5.4).

References:

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8. B. D. Stubbert and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 4253.

Figure S1. Plot of ln[substrate] vs. time, illustrating first-order dependence on [2,2-diphenyl-1-penten-1-amine] for catalyst [{PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$] [**2**] concentrations from 0.0068 – 0.0398 M.

ln[2,2-diphenyl-1-penten-1-amine] vs. time

Legend (in plot):

- y = -1.71 - 6.774E-5x   R= 0.9996
- y = -1.766 - 4.583E-5x   R= 0.9984
- y = -1.788 - 3.706E-5x   R= 0.9971
- y = -1.695 - 3.089E-5x   R= 0.9982
- y = -1.709 - 1.639E-5x   R= 0.9997

Data series labels: 6.82 mM, 14.0 mM, 18.8 mM, 25.8 mM, 39.8 mM

Axis labels: ln[aminoalkene] (y-axis), time (s) (x-axis)
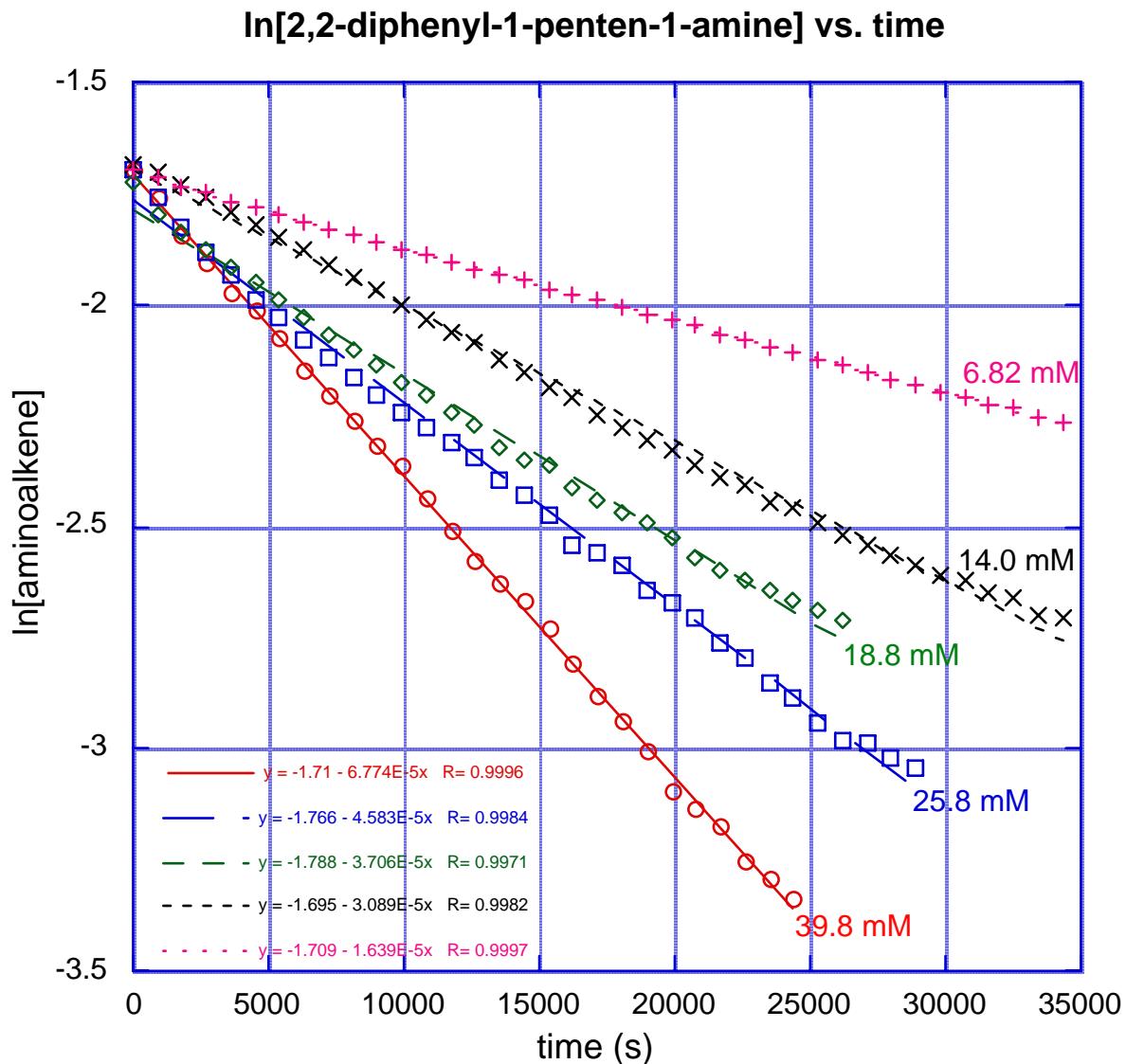
Figure S2. Plot of k_{obs} (from Figure S1) versus concentration of [(PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$] (**2**) for the cyclization of 2,2-diphenyl-1-penten-1-amine showing first order dependence on catalyst.

Plot of k_{obs} versus [catalyst]

$y = 7.685E\text{-}6 + 0.001514x$ R= 0.9973
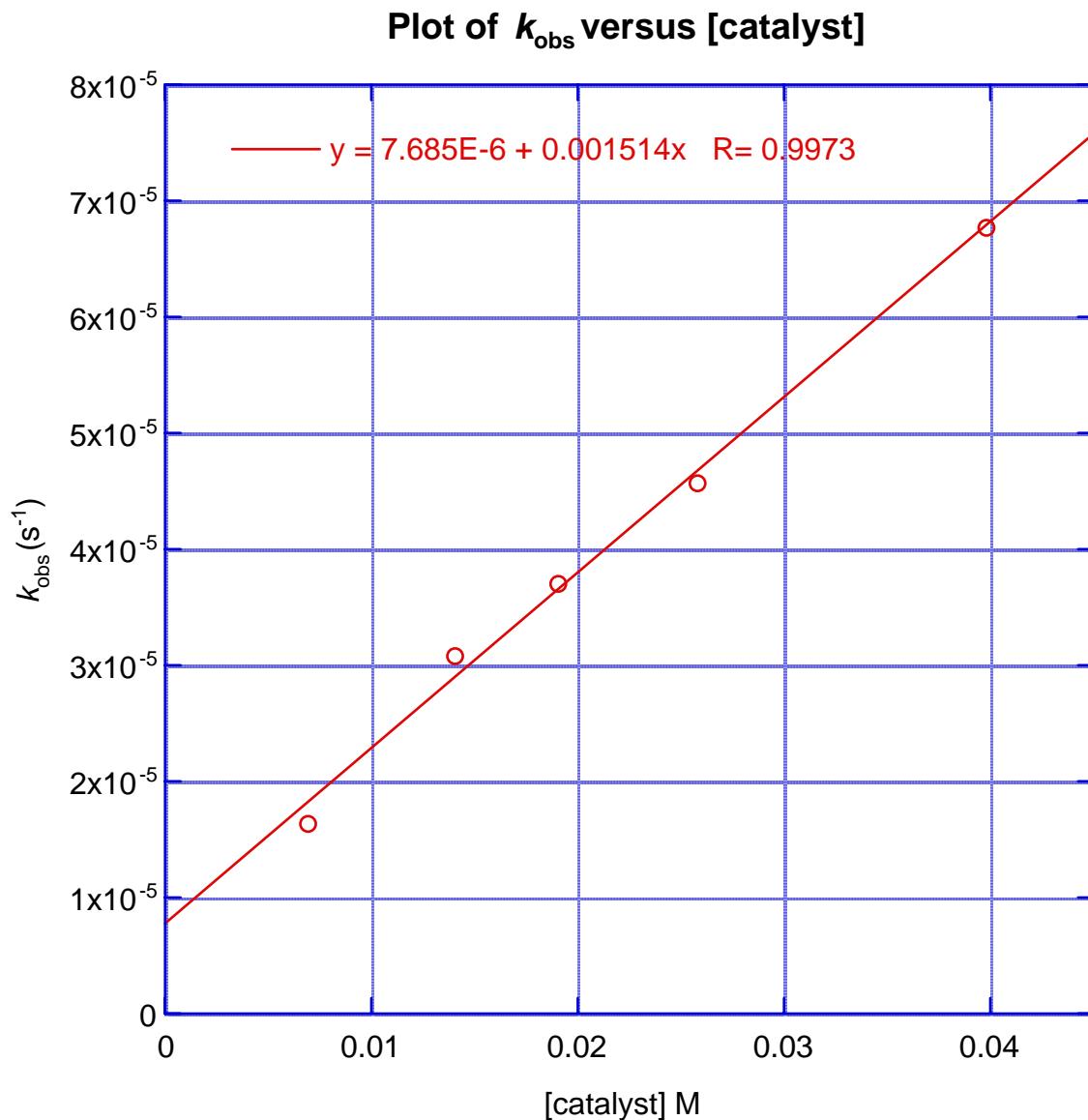
Figure S3. Initial rates for cyclization of 2,2-diphenyl-1-penten-1-amine catalyzed by **2**. The concentration of catalyst [**2**] is 0.0144 M.
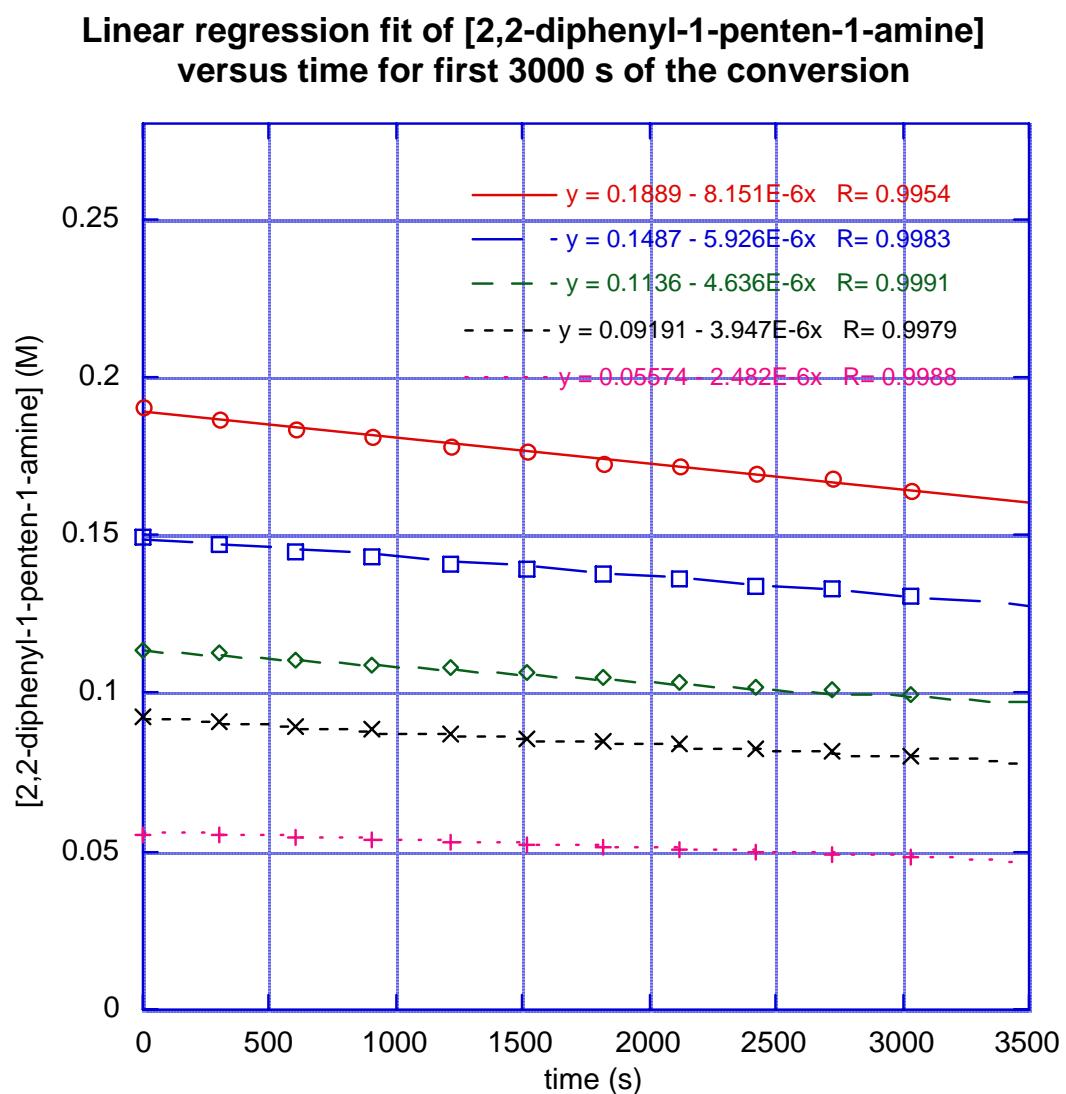

Linear regression fit of [2,2-diphenyl-1-penten-1-amine] versus time for first 3000 s of the conversion

Legend:
- y = 0.1889 - 8.151E-6x   R= 0.9954
- y = 0.1487 - 5.926E-6x   R= 0.9983
- y = 0.1136 - 4.636E-6x   R= 0.9991
- y = 0.09191 - 3.947E-6x   R= 0.9979
- y = 0.05574 - 2.482E-6x   R= 0.9988

x-axis: time (s)
y-axis: [2,2-diphenyl-1-penten-1-amine] (M)

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Figure S4. Plot of ln(d[substrate]/dt) versus ln[substrate]$_{ave}$ using initial rates shown in Figure S3. [substrate]$_{ave}$ is the average substrate concentration over 3000 s. A slope of 0.94 indicates first order [2,2-diphenyl-1-penten-1-amine] dependence.

ln(d[substrate]/dt) vs ln([substrate]$_{ave}$)

$y = -10.1 + 0.944x$ $R = 0.996$
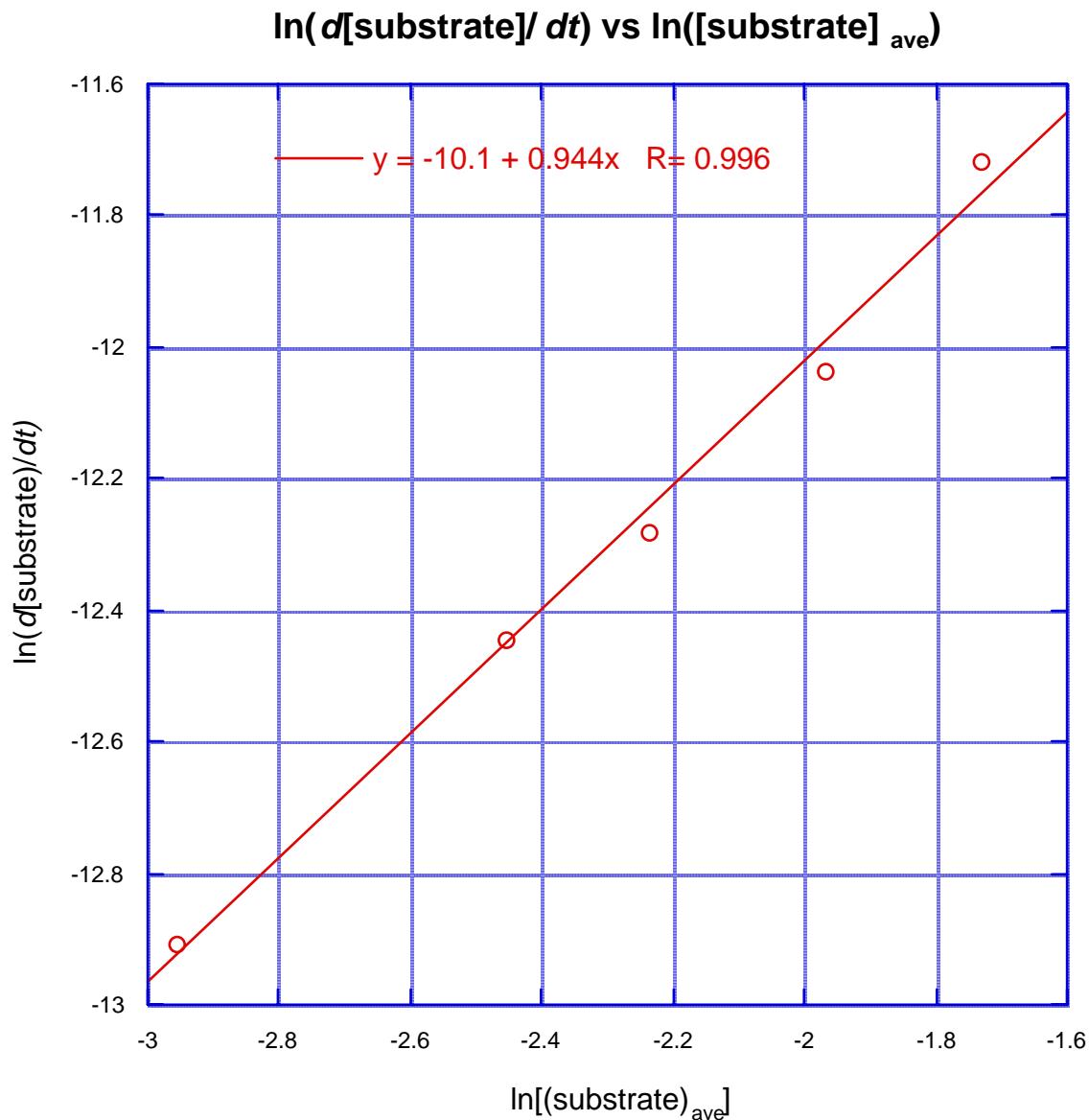
Figure S5. Primary isotope effect determination.

Kinetic Isotope Effect (k_H/k_D): plots of k_{obs} versus catalyst concentration for 2,2-diphenyl-1-pentene-amine and 2,2-diphenyl-1-pentene-amine-(N-d_2)

$y = 7.685E\text{-}6 + 0.001514x \quad R = 0.9973$

$y = 1.686E\text{-}6 + 0.0002778x \quad R = 0.9988$

RNH$_2$

RND$_2$

y-axis: k_{obs} (s^{-1})

x-axis: [catalyst] M
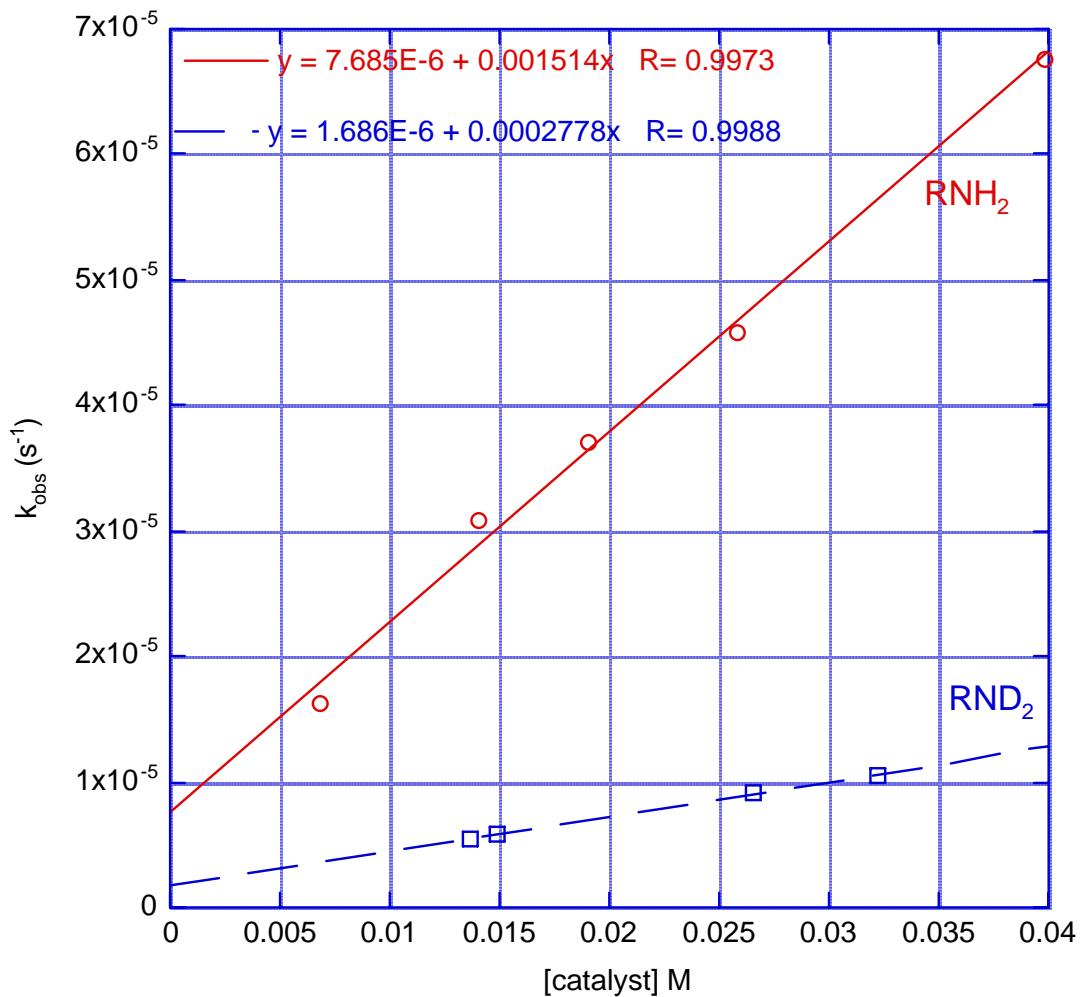
Figure S6. Plot of ln[substrate] vs. time, illustrating first-order dependence on [2,2-dimethyl-1-penten-1-amine] for catalyst [{PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$] [**2**] concentrations from 0.0088 – 0.0157 M.

ln[2,2-dimethyl-1-penten-1-amine] vs. time

$y = -2.193 - 8.814E-5x$ $R = 0.9969$

$-y = -2.162 - 6.821E-5x$ $R = 0.9979$

$-y = -2.124 - 5.027E-5x$ $R = 0.9979$

0.0157 M   0.012 M   0.0088 M

time (s)
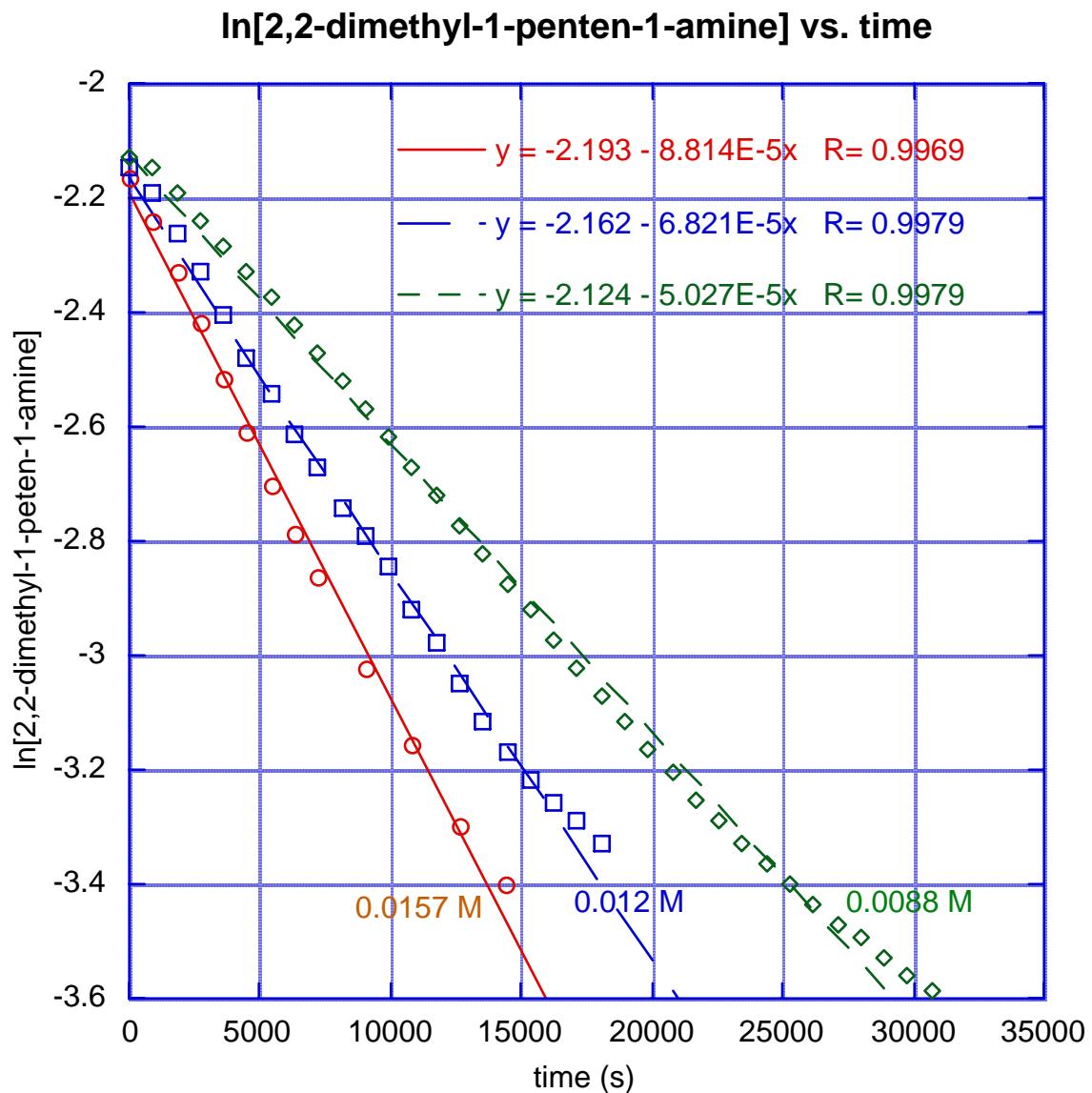
Figure S7. Plot of k_{obs} (from Figure S6) versus concentration of $[(PhB(\eta^5\text{-} C_5H_4)(Ox^{Me2})_2\}Zr(NMe_2)_2]$ (**2**) for the cyclization of 2,2-dimethyl-1-penten-1-amine showing first order dependence on catalyst.

Plot of k_{obs} versus [catalyst] for cyclization of 2,2-Me$_2$-1-penten-1-amine
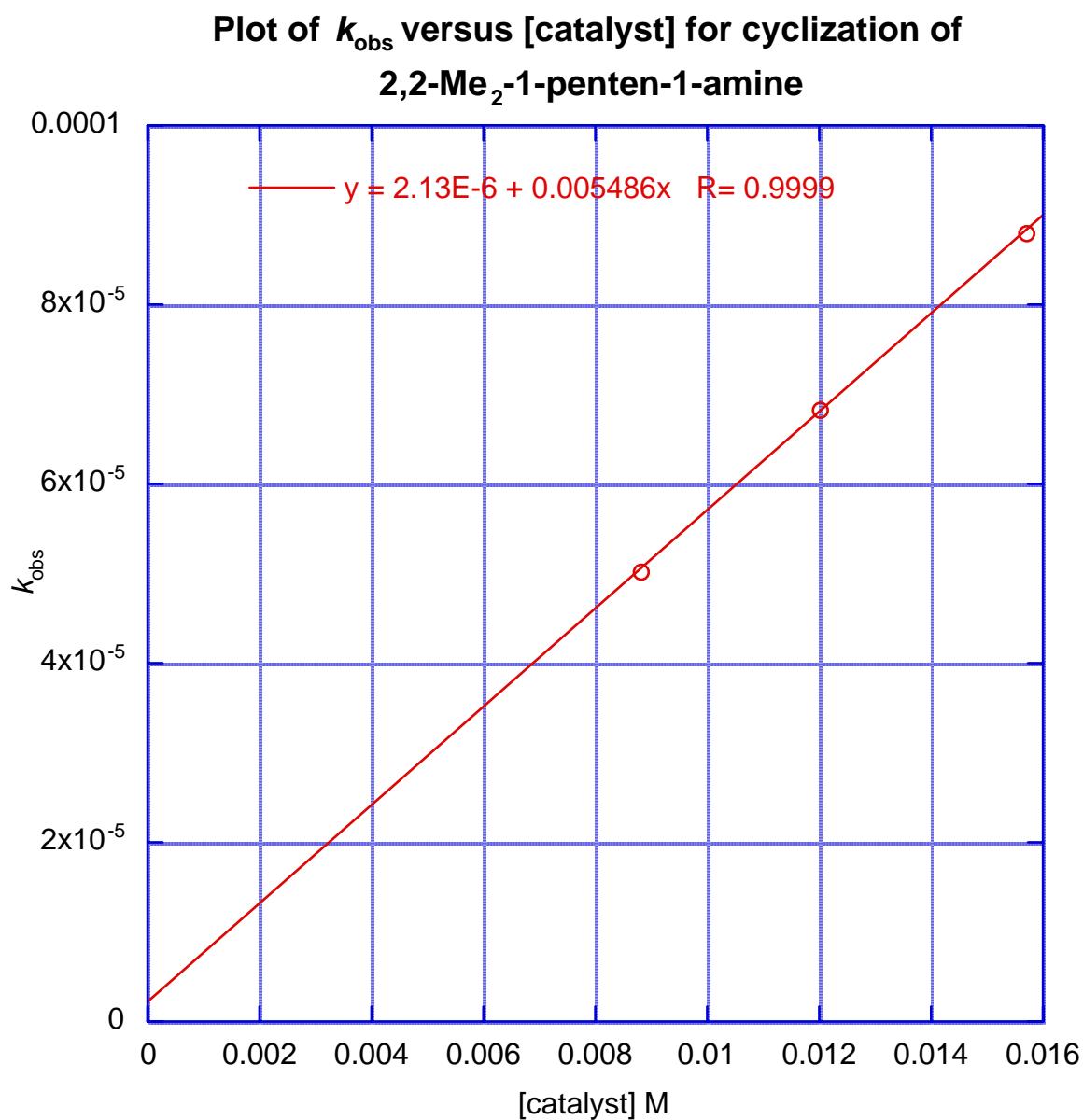
X-ray crystallography for {(PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$THF (4).
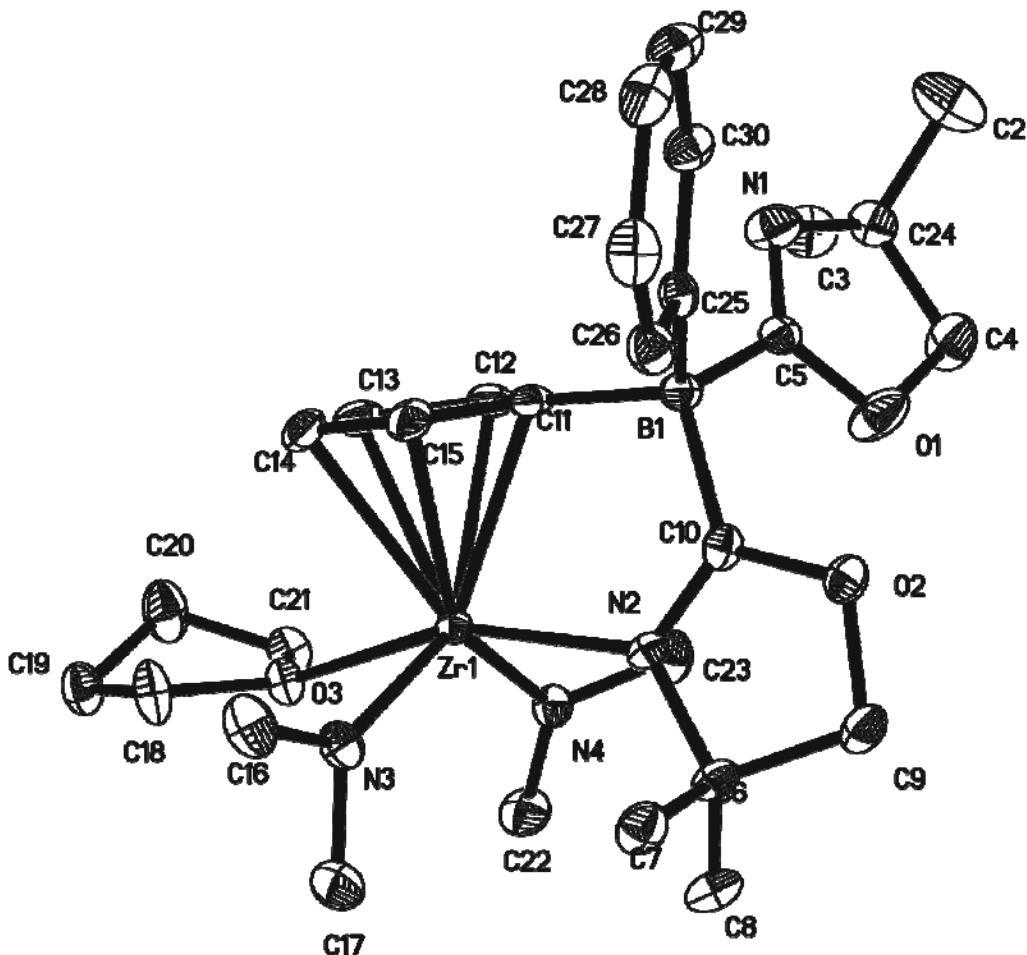
Table S1. Crystal data and structure refinement for {PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$THF (**4**).

Empirical formula	C$_{29}$H$_{45}$BN$_4$O$_3$Zr
Formula weight	599.72
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2$_1$/n
Unit cell dimensions	a = 12.7494(5) Å α= 90°.
	b = 17.2023(7) Å β= 93.9520(10)°.
	c = 13.5397(5) Å γ = 90°.
Volume	2962.5(2) Å^3
Z	4
Density (calculated)	1.345 Mg/m^3
Absorption coefficient	0.407 mm^{-1}
F(000)	1264
Crystal size	0.32 × 0.26 × 0.20 mm^3

Theta range for data collection	1.92 to 27.53°.
Index ranges	$-16 \leq h \leq 16$, $-22 \leq k \leq 22$, $-17 \leq l \leq 17$
Reflections collected	31553
Independent reflections	6824 [R(int) = 0.0382]
Completeness to theta = 27.53°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.74 and 0.63
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6824 / 0 / 351
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0681
R indices (all data)	R1 = 0.0357, wR2 = 0.0732
Largest diff. peak and hole	0.541 and -0.419 e.Å^{-3}

$R1 \ = \Sigma \, | \, |F_O| - |F_c| \, | \ / \, \Sigma \, |F_o|$ and $wR2 \ = \ \{ \, \Sigma \, [\, w(F_o^2 - F_c^2)^2 \,] \ / \, \Sigma \, [\, w(F_o^2)^2 \,] \, \}^{1/2}$

Table S2. Atomic coordinates $(\times 10^4)$ and equivalent isotropic displacement parameters $(\mathring{A}^2 \times 10^3)$ for $\{PhB(\eta^5\text{-}C_5H_4)(Ox^{Me2})_2\}Zr(NMe_2)_2THF$ (**4**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	6261(1)	1485(1)	7744(1)	13(1)
B(1)	4278(1)	2756(1)	8455(1)	16(1)
C(2)	3239(2)	5333(1)	7242(2)	42(1)
C(3)	4664(2)	4826(1)	6258(2)	34(1)
C(4)	4959(2)	4884(1)	8123(2)	32(1)
C(5)	4348(1)	3647(1)	8070(1)	17(1)
C(6)	6626(1)	2093(1)	10187(1)	19(1)
C(7)	6295(2)	1356(1)	10710(1)	23(1)
C(8)	7809(1)	2116(1)	10104(1)	26(1)
C(9)	6228(1)	2816(1)	10698(1)	22(1)
C(10)	5212(1)	2605(1)	9299(1)	17(1)
C(11)	4496(1)	2145(1)	7582(1)	17(1)
C(12)	4983(1)	2264(1)	6678(1)	19(1)
C(13)	5057(1)	1547(1)	6182(1)	24(1)
C(14)	4608(1)	970(1)	6764(1)	25(1)
C(15)	4269(1)	1338(1)	7615(1)	21(1)
C(16)	5714(2)	-190(1)	8689(2)	28(1)
C(17)	7503(2)	222(1)	8738(1)	27(1)
C(18)	6928(2)	-49(1)	6314(2)	30(1)
C(19)	7374(2)	-234(1)	5342(1)	29(1)
C(20)	7278(2)	544(1)	4808(2)	36(1)
C(21)	7556(2)	1117(1)	5627(1)	23(1)
C(22)	8656(1)	1991(1)	7520(2)	28(1)
C(23)	7453(2)	3028(1)	7694(1)	26(1)
C(24)	4157(1)	4777(1)	7238(1)	23(1)
C(25)	3135(1)	2553(1)	8859(1)	17(1)
C(26)	3003(1)	2010(1)	9612(1)	22(1)
C(27)	2012(2)	1788(1)	9884(1)	25(1)
C(28)	1117(1)	2107(1)	9416(1)	25(1)
C(29)	1223(1)	2649(1)	8670(1)	25(1)
C(30)	2215(1)	2862(1)	8399(1)	21(1)
N(1)	3794(1)	3966(1)	7370(1)	28(1)
N(2)	5999(1)	2138(1)	9206(1)	15(1)
N(3)	6420(1)	433(1)	8442(1)	20(1)

N(4)	7555(1)	2188(1)	7613(1)	19(1)
O(1)	5106(1)	4115(1)	8535(1)	37(1)
O(2)	5211(1)	2967(1)	10188(1)	22(1)
O(3)	7153(1)	766(1)	6519(1)	19(1)

Table S3. Bond lengths [Å] for {PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$THF **(4)**.

Zr(1)-N(3)	2.045(1)	C(6)-C(9)	1.527(2)	C(18)-C(19)	1.504(3)
Zr(1)-N(4)	2.062(1)	C(7)-H(7A)	0.9800	C(18)-H(18A)	0.9900
Zr(1)-N(2)	2.321(1)	C(7)-H(7B)	0.9800	C(18)-H(18B)	0.9900
Zr(1)-O(3)	2.415(1)	C(7)-H(7C)	0.9800	C(19)-C(20)	1.522(3)
Zr(1)-C(12)	2.492(2)	C(8)-H(8A)	0.9800	C(19)-H(19A)	0.9900
Zr(1)-C(11)	2.518(2)	C(8)-H(8B)	0.9800	C(19)-H(19B)	0.9900
Zr(1)-C(13)	2.528(2)	C(8)-H(8C)	0.9800	C(20)-C(21)	1.508(3)
Zr(1)-C(15)	2.547(2)	C(9)-O(2)	1.451(2)	C(20)-H(20A)	0.9900
Zr(1)-C(14)	2.569(2)	C(9)-H(9A)	0.9900	C(20)-H(20B)	0.9900
B(1)-C(10)	1.614(2)	C(9)-H(9B)	0.9900	C(21)-O(3)	1.473(2)
B(1)-C(11)	1.620(2)	C(10)-N(2)	1.298(2)	C(21)-H(21A)	0.9900
B(1)-C(5)	1.624(2)	C(10)-O(2)	1.355(2)	C(21)-H(21B)	0.9900
B(1)-C(25)	1.628(2)	C(11)-C(15)	1.420(2)	C(22)-N(4)	1.458(2)
C(2)-C(24)	1.512(3)	C(11)-C(12)	1.424(2)	C(22)-H(22A)	0.9800
C(2)-H(2A)	0.9800	C(12)-C(13)	1.410(2)	C(22)-H(22B)	0.9800
C(2)-H(2B)	0.9800	C(12)-H(12)	1.0000	C(22)-H(22C)	0.9800
C(2)-H(2C)	0.9800	C(13)-C(14)	1.413(3)	C(23)-N(4)	1.455(2)
C(3)-C(24)	1.519(3)	C(13)-H(13)	1.0000	C(23)-H(23A)	0.9800
C(3)-H(3A)	0.9800	C(14)-C(15)	1.409(2)	C(23)-H(23B)	0.9800
C(3)-H(3B)	0.9800	C(14)-H(14)	1.0000	C(23)-H(23C)	0.9800
C(3)-H(3C)	0.9800	C(15)-H(15)	1.0000	C(24)-N(1)	1.484(2)
C(4)-O(1)	1.443(2)	C(16)-N(3)	1.454(2)	C(25)-C(30)	1.395(2)
C(4)-C(24)	1.531(3)	C(16)-H(16A)	0.9800	C(25)-C(26)	1.403(2)
C(4)-H(4A)	0.9900	C(16)-H(16B)	0.9800	C(26)-C(27)	1.394(3)
C(4)-H(4B)	0.9900	C(16)-H(16C)	0.9800	C(26)-H(26)	0.9500
C(5)-N(1)	1.267(2)	C(17)-N(3)	1.457(2)	C(27)-C(28)	1.380(3)
C(5)-O(1)	1.377(2)	C(17)-H(17A)	0.9800	C(27)-H(27)	0.9500
C(6)-N(2)	1.505(2)	C(17)-H(17B)	0.9800	C(28)-C(29)	1.388(3)
C(6)-C(8)	1.520(2)	C(17)-H(17C)	0.9800	C(28)-H(28)	0.9500
C(6)-C(7)	1.525(2)	C(18)-O(3)	1.455(2)	C(29)-C(30)	1.390(2)

Table S3. Bond angles [°] for {PhB(η^5-C$_5$H$_4$)(Ox^{Me2})$_2$}Zr(NMe$_2$)$_2$THF **(4)**.

N(3)-Zr(1)-N(4)	120.26(6)	C(12)-Zr(1)-C(11)	33.03(5)	N(3)-Zr(1)-C(14)	89.16(6)
N(3)-Zr(1)-N(2)	92.84(5)	N(3)-Zr(1)-C(13)	117.35(6)	N(4)-Zr(1)-C(14)	142.21(6)
N(4)-Zr(1)-N(2)	87.26(5)	N(4)-Zr(1)-C(13)	110.29(6)	N(2)-Zr(1)-C(14)	116.49(5)
N(3)-Zr(1)-O(3)	80.11(5)	N(2)-Zr(1)-C(13)	125.29(5)	O(3)-Zr(1)-C(14)	82.97(5)
N(4)-Zr(1)-O(3)	79.87(5)	O(3)-Zr(1)-C(13)	74.65(5)	C(12)-Zr(1)-C(14)	53.55(6)
N(2)-Zr(1)-O(3)	159.40(4)	C(12)-Zr(1)-C(13)	32.61(6)	C(11)-Zr(1)-C(14)	54.12(6)
N(3)-Zr(1)-C(12)	141.58(6)	C(11)-Zr(1)-C(13)	54.55(5)	C(13)-Zr(1)-C(14)	32.17(6)
N(4)-Zr(1)-C(12)	97.48(6)	N(3)-Zr(1)-C(15)	90.60(6)	C(15)-Zr(1)-C(14)	31.97(6)
N(2)-Zr(1)-C(12)	96.11(5)	N(4)-Zr(1)-C(15)	148.43(6)	C(10)-B(1)-C(11)	104.9(1)
O(3)-Zr(1)-C(12)	101.42(5)	N(2)-Zr(1)-C(15)	84.52(5)	C(10)-B(1)-C(5)	109.0(1)
N(3)-Zr(1)-C(11)	119.94(6)	O(3)-Zr(1)-C(15)	114.66(5)	C(11)-B(1)-C(5)	111.2(1)
N(4)-Zr(1)-C(11)	116.32(6)	C(12)-Zr(1)-C(15)	53.43(6)	C(10)-B(1)-C(25)	111.2(1)
N(2)-Zr(1)-C(11)	71.04(5)	C(11)-Zr(1)-C(15)	32.56(5)	C(11)-B(1)-C(25)	108.0(1)
O(3)-Zr(1)-C(11)	129.19(5)	C(13)-Zr(1)-C(15)	53.24(6)	C(5)-B(1)-C(25)	112.4(1)

C(24)-C(2)-H(2A)	109.5	C(11)-C(12)-Zr(1)	74.48(9)	C(20)-C(21)-H(21B)	110.8
C(24)-C(2)-H(2B)	109.5	C(13)-C(12)-H(12)	124.9	H(21A)-C(21)-H(21B)	108.8
H(2A)-C(2)-H(2B)	109.5	C(11)-C(12)-H(12)	124.9	N(4)-C(22)-H(22A)	109.5
C(24)-C(2)-H(2C)	109.5	Zr(1)-C(12)-H(12)	124.9	N(4)-C(22)-H(22B)	109.5
H(2A)-C(2)-H(2C)	109.5	C(12)-C(13)-C(14)	107.83(15)	H(22A)-C(22)-H(22B)	109.5
H(2B)-C(2)-H(2C)	109.5	C(12)-C(13)-Zr(1)	72.28(9)	N(4)-C(22)-H(22C)	109.5
C(24)-C(3)-H(3A)	109.5	C(14)-C(13)-Zr(1)	75.5(1)	H(22A)-C(22)-H(22C)	109.5
C(24)-C(3)-H(3B)	109.5	C(12)-C(13)-H(13)	125.7	H(22B)-C(22)-H(22C)	109.5
H(3A)-C(3)-H(3B)	109.5	C(14)-C(13)-H(13)	125.7	N(4)-C(23)-H(23A)	109.5
C(24)-C(3)-H(3C)	109.5	Zr(1)-C(13)-H(13)	125.7	N(4)-C(23)-H(23B)	109.5
H(3A)-C(3)-H(3C)	109.5	C(15)-C(14)-C(13)	107.4(2)	H(23A)-C(23)-H(23B)	109.5
H(3B)-C(3)-H(3C)	109.5	C(15)-C(14)-Zr(1)	73.15(9)	N(4)-C(23)-H(23C)	109.5
O(1)-C(4)-C(24)	104.7(2)	C(13)-C(14)-Zr(1)	72.33(10)	H(23A)-C(23)-H(23C)	109.5
O(1)-C(4)-H(4A)	110.8	C(15)-C(14)-H(14)	126.1	H(23B)-C(23)-H(23C)	109.5
C(24)-C(4)-H(4A)	110.8	C(13)-C(14)-H(14)	126.1	N(1)-C(24)-C(2)	110.3(2)
O(1)-C(4)-H(4B)	110.8	Zr(1)-C(14)-H(14)	126.1	N(1)-C(24)-C(3)	108.2(2)
C(24)-C(4)-H(4B)	110.8	C(14)-C(15)-C(11)	109.79(16)	C(2)-C(24)-C(3)	110.1(2)
H(4A)-C(4)-H(4B)	108.9	C(14)-C(15)-Zr(1)	74.88(10)	N(1)-C(24)-C(4)	102.5(1)
N(1)-C(5)-O(1)	115.22(15)	C(11)-C(15)-Zr(1)	72.59(9)	C(2)-C(24)-C(4)	113.3(2)
N(1)-C(5)-B(1)	127.51(15)	C(14)-C(15)-H(15)	124.9	C(3)-C(24)-C(4)	112.1(2)
O(1)-C(5)-B(1)	117.25(14)	C(11)-C(15)-H(15)	124.9	C(30)-C(25)-C(26)	116.0(2)
N(2)-C(6)-C(8)	113.75(14)	Zr(1)-C(15)-H(15)	124.9	C(30)-C(25)-B(1)	120.9(2)
N(2)-C(6)-C(7)	107.83(13)	N(3)-C(16)-H(16A)	109.5	C(26)-C(25)-B(1)	122.8(2)
C(8)-C(6)-C(7)	111.34(15)	N(3)-C(16)-H(16B)	109.5	C(27)-C(26)-C(25)	122.1(2)
N(2)-C(6)-C(9)	100.68(13)	H(16A)-C(16)-H(16B)	109.5	C(27)-C(26)-H(26)	119.0
C(8)-C(6)-C(9)	111.98(15)	N(3)-C(16)-H(16C)	109.5	C(25)-C(26)-H(26)	119.0
C(7)-C(6)-C(9)	110.75(14)	H(16A)-C(16)-H(16C)	109.5	C(28)-C(27)-C(26)	120.4(2)
C(6)-C(7)-H(7A)	109.5	H(16B)-C(16)-H(16C)	109.5	C(28)-C(27)-H(27)	119.8
C(6)-C(7)-H(7B)	109.5	N(3)-C(17)-H(17A)	109.5	C(26)-C(27)-H(27)	119.8
H(7A)-C(7)-H(7B)	109.5	N(3)-C(17)-H(17B)	109.5	C(27)-C(28)-C(29)	118.8(2)
C(6)-C(7)-H(7C)	109.5	H(17A)-C(17)-H(17B)	109.5	C(27)-C(28)-H(28)	120.6
H(7A)-C(7)-H(7C)	109.5	N(3)-C(17)-H(17C)	109.5	C(29)-C(28)-H(28)	120.6
H(7B)-C(7)-H(7C)	109.5	H(17A)-C(17)-H(17C)	109.5	C(28)-C(29)-C(30)	120.4(2)
C(6)-C(8)-H(8A)	109.5	H(17B)-C(17)-H(17C)	109.5	C(28)-C(29)-H(29)	119.8
C(6)-C(8)-H(8B)	109.5	O(3)-C(18)-C(19)	106.8(2)	C(30)-C(29)-H(29)	119.8
H(8A)-C(8)-H(8B)	109.5	O(3)-C(18)-H(18A)	110.4	C(29)-C(30)-C(25)	122.3(2)
C(6)-C(8)-H(8C)	109.5	C(19)-C(18)-H(18A)	110.4	C(29)-C(30)-H(30)	118.8
H(8A)-C(8)-H(8C)	109.5	O(3)-C(18)-H(18B)	110.4	C(25)-C(30)-H(30)	118.8
H(8B)-C(8)-H(8C)	109.5	C(19)-C(18)-H(18B)	110.4	C(5)-N(1)-C(24)	109.5(2)
O(2)-C(9)-C(6)	104.1(1)	H(18A)-C(18)-H(18B)	108.6	C(10)-N(2)-C(6)	108.3(1)
O(2)-C(9)-H(9A)	110.9	C(18)-C(19)-C(20)	101.9(2)	C(10)-N(2)-Zr(1)	122.7(1)
C(6)-C(9)-H(9A)	110.9	C(18)-C(19)-H(19A)	111.4	C(6)-N(2)-Zr(1)	129.0(1)
O(2)-C(9)-H(9B)	110.9	C(20)-C(19)-H(19A)	111.4	C(16)-N(3)-C(17)	110.1(1)
C(6)-C(9)-H(9B)	110.9	C(18)-C(19)-H(19B)	111.4	C(16)-N(3)-Zr(1)	135.7(1)
H(9A)-C(9)-H(9B)	109.0	C(20)-C(19)-H(19B)	111.4	C(17)-N(3)-Zr(1)	114.2(1)
N(2)-C(10)-O(2)	114.8(1)	H(19A)-C(19)-H(19B)	109.2	C(23)-N(4)-C(22)	109.2(1)
N(2)-C(10)-B(1)	124.6(1)	C(21)-C(20)-C(19)	102.7(2)	C(23)-N(4)-Zr(1)	120.0(1)
O(2)-C(10)-B(1)	120.6(1)	C(21)-C(20)-H(20A)	111.2	C(22)-N(4)-Zr(1)	130.7(1)
C(15)-C(11)-C(12)	105.6(2)	C(19)-C(20)-H(20A)	111.2	C(5)-O(1)-C(4)	106.9(1)
C(15)-C(11)-B(1)	124.4(2)	C(21)-C(20)-H(20B)	111.2	C(10)-O(2)-C(9)	106.6(1)
C(12)-C(11)-B(1)	129.9(2)	C(19)-C(20)-H(20B)	111.2	C(18)-O(3)-C(21)	108.3(1)
C(15)-C(11)-Zr(1)	74.85(9)	H(20A)-C(20)-H(20B)	109.1	C(18)-O(3)-Zr(1)	121.90(1)
C(12)-C(11)-Zr(1)	72.49(9)	O(3)-C(21)-C(20)	104.9(1)	C(21)-O(3)-Zr(1)	124.08(9)
B(1)-C(11)-Zr(1)	115.2(1)	O(3)-C(21)-H(21A)	110.8		
C(13)-C(12)-C(11)	109.4(2)	C(20)-C(21)-H(21A)	110.8		
C(13)-C(12)-Zr(1)	75.1(1)	O(3)-C(21)-H(21B)	110.8		

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $\{PhB(\eta^5\text{-}C_5H_4)(Ox^{Me2})_2\}Zr(NMe_2)_2THF$ (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2\,a^{*2}U^{11} + \ldots + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	12(1)	14(1)	14(1)	1(1)	1(1)	0(1)
B(1)	15(1)	19(1)	14(1)	0(1)	1(1)	2(1)
C(2)	42(1)	45(1)	41(1)	19(1)	17(1)	16(1)
C(3)	32(1)	41(1)	29(1)	6(1)	8(1)	0(1)
C(4)	45(1)	21(1)	31(1)	5(1)	-5(1)	-8(1)
C(5)	13(1)	23(1)	16(1)	-2(1)	4(1)	2(1)
C(6)	20(1)	22(1)	13(1)	2(1)	-3(1)	-3(1)
C(7)	30(1)	23(1)	17(1)	3(1)	-1(1)	-4(1)
C(8)	20(1)	36(1)	21(1)	2(1)	-5(1)	-4(1)
C(9)	27(1)	23(1)	16(1)	-1(1)	-3(1)	-4(1)
C(10)	20(1)	17(1)	13(1)	0(1)	3(1)	-3(1)
C(11)	11(1)	24(1)	15(1)	0(1)	-1(1)	3(1)
C(12)	17(1)	27(1)	13(1)	1(1)	-1(1)	8(1)
C(13)	20(1)	38(1)	14(1)	-5(1)	-4(1)	8(1)
C(14)	17(1)	30(1)	28(1)	-12(1)	-4(1)	-1(1)
C(15)	12(1)	26(1)	24(1)	-5(1)	1(1)	-2(1)
C(16)	34(1)	20(1)	31(1)	5(1)	12(1)	-2(1)
C(17)	28(1)	24(1)	29(1)	5(1)	2(1)	3(1)
C(18)	44(1)	15(1)	32(1)	-4(1)	13(1)	-3(1)
C(19)	37(1)	23(1)	27(1)	-6(1)	5(1)	3(1)
C(20)	55(1)	28(1)	25(1)	-3(1)	11(1)	1(1)
C(21)	27(1)	22(1)	20(1)	2(1)	10(1)	0(1)
C(22)	18(1)	32(1)	34(1)	0(1)	3(1)	-6(1)
C(23)	36(1)	20(1)	23(1)	1(1)	4(1)	-6(1)
C(24)	24(1)	22(1)	25(1)	6(1)	4(1)	0(1)
C(25)	20(1)	18(1)	15(1)	-3(1)	4(1)	1(1)
C(26)	24(1)	22(1)	20(1)	-2(1)	3(1)	1(1)
C(27)	34(1)	22(1)	20(1)	1(1)	8(1)	-4(1)
C(28)	23(1)	30(1)	23(1)	-7(1)	8(1)	-8(1)
C(29)	20(1)	32(1)	22(1)	-3(1)	0(1)	-2(1)
C(30)	21(1)	26(1)	15(1)	0(1)	1(1)	-2(1)
N(1)	26(1)	26(1)	31(1)	10(1)	-5(1)	-4(1)
N(2)	15(1)	18(1)	13(1)	2(1)	-1(1)	-2(1)
N(3)	23(1)	17(1)	21(1)	3(1)	5(1)	1(1)
N(4)	18(1)	18(1)	21(1)	0(1)	3(1)	-4(1)
O(1)	46(1)	24(1)	38(1)	10(1)	-21(1)	-12(1)
O(2)	27(1)	25(1)	13(1)	-4(1)	0(1)	3(1)
O(3)	23(1)	15(1)	19(1)	0(1)	7(1)	0(1)

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $\{PhB(\eta^5\text{-}C_5H_4)(Ox^{Me2})_2\}Zr(NMe_2)_2THF$ (**4**).

	x	y	z	U(eq)
H(2A)	2731	5211	6688	63
H(2B)	3493	5867	7174	63
H(2C)	2900	5282	7867	63
H(3A)	5265	4470	6267	51
H(3B)	4906	5358	6155	51
H(3C)	4149	4680	5719	51
H(4A)	5630	5093	7906	39
H(4B)	4687	5244	8615	39

H(7A)	5558	1403	10868	35
H(7B)	6740	1286	11323	35
H(7C)	6373	907	10276	35
H(8A)	8027	1657	9742	39
H(8B)	8166	2119	10768	39
H(8C)	7995	2587	9748	39
H(9A)	6158	2717	11411	27
H(9B)	6711	3260	10628	27
H(12)	5133	2783	6387	23
H(13)	5274	1476	5492	29
H(14)	4471	417	6566	30
H(15)	3851	1082	8123	25
H(16A)	5888	-663	8332	42
H(16B)	4987	-39	8499	42
H(16C)	5790	-288	9404	42
H(17A)	7581	154	9458	41
H(17B)	7975	635	8543	41
H(17C)	7681	-265	8413	41
H(18A)	6160	-142	6272	36
H(18B)	7259	-381	6847	36
H(19A)	6959	-642	4978	34
H(19B)	8116	-404	5437	34
H(20A)	7776	579	4280	43
H(20B)	6554	629	4516	43
H(21A)	8326	1193	5715	27
H(21B)	7217	1626	5481	27
H(22A)	8907	2254	6939	43
H(22B)	8725	1427	7442	43
H(22C)	9074	2160	8115	43
H(23A)	7891	3212	8270	40
H(23B)	6717	3162	7774	40
H(23C)	7683	3274	7093	40
H(26)	3609	1786	9948	26
H(27)	1952	1414	10394	30
H(28)	440	1958	9602	30
H(29)	615	2876	8344	30
H(30)	2268	3230	7882	25