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Synthesis, Structural Characterization, and Quantitative Basicity Studies of Lithium Zirconimidate Complexes

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General Procedures. All air- and moisture-sensitive compounds were manipulated using standard Schlenk techniques or in a glovebox under an inert atmosphere (N_2). Glassware was dried overnight at 180 °C or flame dried under vacuum immediately prior to use. Sealed NMR tubes were prepared by attaching the NMR tube directly to a Kontes high-vacuum stopcock via a Cajon Ultra-Torr reducing union and then flame-sealing on a vacuum line with the tube cooled to -196 °C. Glass reaction vessels fitted with ground glass joints and Teflon stopcocks are referred to as bombs. All NMR spectra were obtained at ambient temperature using Bruker AVB-400, AVQ-400, DRX-500, or AV-500 spectrometers. Unless otherwise stated, all NMR data are reported in C_6D_6 solvent. The ^1H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield from TMS and are referenced relative to residual protiated solvent. In cases where assignment of ^1H resonances was ambiguous, 2D NMR experiments (^1H-^1H NOESY or ^1H-^1H COSY) were performed as necessary.

The $^{13}C\{^1H\}$ NMR chemical shifts (δ) are reported in ppm relative to the carbon resonance of the deuterated solvent. Where assignment of ^{13}C resonances was ambiguous, assignments were made by analysis of spectra from standard DEPT 135° pulse sequences and additional 2D NMR experiments (^1H-^{13}C HSQC, ^1H-^{13}C HMBC, etc) as necessary. All ^6Li and ^7Li NMR chemical shifts (δ) are reported in ppm relative to external 1M LiCl in D_2O. Elemental analyses were performed at the University of California, Berkeley Microanalytical facility. Purification and full characterization of complexes **2b**-**e** and complex **2g** was difficult due to extreme thermal instability. In these cases, ^1H and ^{13}C NMR spectra are provided in lieu of elemental analyses. X-ray structures were obtained at the UC Berkeley CHEXRAY facility and the structures were solved by Dr. Fred Hollander and Dr. Allen Oliver.

Materials. Pentane, benzene, and THF (Fisher) were passed through a column of activated Alumina (type A2, size 12 x 32, UOP LLC) under nitrogen pressure and sparged with N_2 prior to use. All solvents were stored over 3Å molecular sieves in a glovebox at room temperature and filtered through a plug of basic alumina immediately prior to use. $[D_8]$THF (Cambridge Isotope Laboratories) was vacuum transferred from sodium-benzophenone and C_6D_6 was vacuum transferred from calcium hydride. The deuterated solvents were then de-gassed by three freeze-pump-thaw cycles, and stored over 3 Å molecular sieves in a glovebox at room temperature. Prior to use, deuterated solvents were filtered through a plug of basic alumina. 12-crown-4 was distilled from calcium hydride and stored in the glovebox. [*rac*-(ebthi)Zr(Me)(Cl)] (**1e**),[1] [*rac*-(ebthi)Zr(NH^{t}Bu)(Me)] (**2e**),[1] [$Cp^*_2ZrMe_2$],[2] [$Cp^*\{\eta^5\text{-}C_5HMe_4\}ZrMe_2$],[3] [$\{\eta^5\text{-}C_5HMe_4\}_2ZrMe_2$],[3] ^{t}BuNHLi,[4] [$Ph_3C$][Li(THF)$_4$],[5] and Ph_3CD[6] were prepared according to reported literature procedures. Alkyllithium reagents were titrated with salicylaldehyde phenylhydrazone immediately prior to use.[7] NH_4Cl, $Me_3N{\cdot}HCl$, and triphenylmethane were purchased from Aldrich and stored in the glovebox. Bis(indenyl)$ZrCl_2$ was purchased from Strem and used as received.

Experimental Details for X-ray Structure Determinations. A fragment of a crystal was mounted onto a Kapton loop using Paratone N hydrocarbon oil. All measurements were made on a SMART[8a] (**3b**) or a Bruker APEX[8b] (**3d**) CCD area detector with graphite monochromated Mo-Kα radiation. The crystal was centered in the beam and cooled to a temperature of -143 ± 1 (**3b**) or -100 ± 1 °C (**3d**). Cell constants and an orientation matrix were obtained from a least-squares refinement using the measured positions of **3b**: 2605 or **3d**: 2105 centered reflections [with **3b**: $I > 10\sigma(I)$] in the range **3b**: $4.98 < 2\theta < 47.91^{o}$ or **3d**: $5.00 < 2\theta < 38.00^{o}$. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3°. The raw data were integrated by the program SAINT **3b**: v.5.04[9a] or **3d**: v.6.40[9b] to a maximum 2θ value of 49.4° (**3b**) and 52.8° (**3d**). The data were corrected for Lorentz and polarization effects and were analyzed for agreement and possible absorption using XPREP.[10] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS[11] (Tmax = 1.00, Tmin = 0.39 (**3b**) or 0.88 (**3d**). Of the 13069 reflections that were collected for complex **3b**, 2565 were unique ($R_{int} = 0.051$); equivalent reflections were merged. No decay correction was applied. Both structures were solved by direct methods[12] and expanded using Fourier techniques.[13] All non-hydrogen atoms were refined anisotropically except for the lithium atoms, which were refined isotropically. Hydrogen atoms were included but not refined for **3b**. The final cycle of full-matrix least-squares refinement was based on 2807 (**3b**) or 4015 (**3d**) reflections (all data) and 293 (**3b**) or 284 (**3d**) variable parameters and converged (largest parameter shift was 0.00 (**3b** and **3d**) times its esd) with conventional unweighted and weighted agreement factors of: $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.046$ (**3b**) or 0.039 (**3d**); $\omega R_2 = [(\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2)]^{1/2} = 0.046$ (**3b**) or $\omega R_2 = [(\Sigma\omega(|F_o|- |F_c|)^2/\Sigma\omega F_o^{2})]^{1/2} = 0.046$ (**3d**). The standard deviation of an observation of unit weight[14] was 1.46 (**3b**) or 1.29 (**3d**). The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Neutral atom scattering factors were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in F_{calc};[16] the values for Δf' and Δf'' were those of Creagh and McAuley.[17] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[18] Calculations were performed using the teXsan[19] crystallographic software package of Molecular Structure Corporation. ORTEP diagrams were created using the ORTEP-3 software package[20] and rendered using the POV-ray graphics program.[21]

$[\mathrm{Cp^*_2Zr(Me)(Cl)}]$ (1b). A solution of $[\mathrm{Cp^*_2ZrMe_2}]$[2] (0.852 g, 2.17 mmol) in THF (40 mL) was added to a glass vessel equipped with a vacuum stopcock that had been previously charged with solid $\mathrm{Me_3N{\cdot}HCl}$ (0.203 g, 2.13 mmol, Aldrich). The reaction mixture was heated to 45 °C and stirred overnight under an atmosphere of N_2. In the glovebox, the solution was filtered and the volatile materials were removed under vacuum. The remaining solid was washed with pentane (5 mL) to yield complex **1b** as an analytically pure, colorless solid (0.602 g, 67%). The NMR data reported here are consistent with those previously reported for **1b**.[22] ^{1}H NMR (400 MHz, δ): 1.79 (s, 30H, Cp*), -0.02 (s, 3H, Me) ppm. ^{13}C{^{1}H} NMR (100 MHz): δ 119.8 ($\{\eta^5\text{-}C_5\mathrm{Me}_5\}$), 38.5 (Zr*Me*), 11.7 ($\{\eta^5\text{-}\mathrm{C}_5 Me_5\}$) ppm. Anal. Calcd for $\mathrm{C_{21}H_{33}ClZr}$: C, 61.20; H, 8.07. Found: C, 61.41; H, 8.01.

$[\mathrm{Cp^*\{\eta^5\text{-}C_5HMe_4\}Zr(Me)(Cl)}]$ (1c). Complex **1c** was prepared under conditions identical to those used for **1b** using $[\mathrm{Cp^*Cp^{Me4}ZrMe_2}]$[3] (0.613 g, 1.67 mmol) and solid $\mathrm{Me_3N{\cdot}HCl}$ (0.144 g, 1.50 mmol) in THF (30 mL). After recrystallization from THF, the analytically pure product was obtained as a pale yellow, crystalline solid (0.451g, 70%). The NMR data reported here are consistent with that previously reported for **1c**.[22] ^{1}H NMR (400 MHz, [D$_8$]THF, δ): 5.16 (s, 1H, $\{\eta^5\text{-}\mathrm{C}_5 H\mathrm{Me}_4\}$), 1.95 (s, 3H, $\{\eta^5\text{-}\mathrm{C}_5\mathrm{H} Me_4\}$), 1.94 (s, 3H, $\{\eta^5\text{-}\mathrm{C}_5\mathrm{H} Me_4\}$), 1.93 (s, 15H, $\{\eta^5\text{-}\mathrm{C}_5 Me_5\}$), 1.85 (s, 3H, $\{\eta^5\text{-}\mathrm{C}_5\mathrm{H} Me_4\}$), 1.66 (s, 3H, $\{\eta^5\text{-}\mathrm{C}_5\mathrm{H} Me_4\}$), -0.42 (s, 3H, Zr*Me*) ppm. ^{13}C{^{1}H} NMR (125 MHz, [D$_8$]THF, δ): 125.0 ($\{\eta^5\text{-}C_5\mathrm{HMe}_4\}_q$), 124.5 ($\{\eta^5\text{-}C_5\mathrm{Me}_5$), 117.6 ($\{\eta^5\text{-}C_5\mathrm{HMe}_4\}_q$), 115.8 ($\{\eta^5\text{-}C_5\mathrm{HMe}_4\}_q$), 115.0 ($\{\eta^5\text{-}C_5\mathrm{HMe}_4\}_q$), 105.6 ($\{\eta^5\text{-}C_5\mathrm{HMe}_4\}_t$), 34.8 (Zr*Me*), 10.2 ($\{\eta^5\text{-}C_5\mathrm{H}Me_4\}$), 10.1 ($\{\eta^5\text{-}C_5\mathrm{H}Me_4\}$), 9.8

($\{\eta^5\text{-}C_5\mathit{Me}_5\}$), 9.7 ($\{\eta^5\text{-}\mathit{C}_5H\mathit{Me}_4\}$), 9.4 ($\{\eta^5\text{-}\mathit{C}_5H\mathit{Me}_4\}$) ppm. Anal. Calcd for $C_{19}H_{31}ClZr$: C, 60.33; H, 7.85. Found: C, 60.12; H, 7.97.

[$\{\eta^5\text{-}C_5HMe_4\}_2Zr(Me)(Cl)$] (1d). Compound **1d** was prepared under conditions identical to those used for **1b** using $\{\eta^5\text{-}C_5HMe_4\}_2ZrMe_2$[3] (0.613 g, 1.67 mmol) and solid $Me_3N{\cdot}HCl$ (0.144 g, 1.50 mmol) in THF (30 mL). The crude product was recrystallized from THF to yield clear, colorless blocks (0.539 g, 84%). ^1H NMR (400 MHz, δ): 4.91 (s, 2H, $\{\eta^5\text{-}C_5\mathit{H}Me_4\}$), 2.06 (s, 3H, $\{\eta^5\text{-}C_5H\mathit{Me}_4\}$), 1.91(s, 3H, $\{\eta^5\text{-}C_5H\mathit{Me}_4\}$), 1.79 (s, 3H, $\{\eta^5\text{-}C_5H\mathit{Me}_4\}$), 1.56 (s, 3H, $\{\eta^5\text{-}C_5H\mathit{Me}_4\}$), -0.03 (s, 3H, Zr*Me*). ^{13}C NMR(100 MHz, δ): 125.0 ($\{\eta^5\text{-}\mathit{C}_5HMe_4\}_q$), 124.3 ($\{\eta^5\text{-}\mathit{C}_5HMe_4\}_q$), 117.7 ($\{\eta^5\text{-}\mathit{C}_5HMe_4\}_q$), 117.4 ($\{\eta^5\text{-}\mathit{C}_5HMe_4\}_q$), 107.1 ($\{\eta^5\text{-}\mathit{C}_5HMe_4\}_t$), 37.2 (Zr*Me*), 13.4 ($\{\eta^5\text{-}C_5H\mathit{Me}_4\}$), 12.9 ($\{\eta^5\text{-}C_5H\mathit{Me}_4\}$), 11.8 ($\{\eta^5\text{-}C_5H\mathit{Me}_4\}$), 11.2 ($\{\eta^5\text{-}C_5H\mathit{Me}_4\}$). Anal. Calcd for $C_{19}H_{29}ClZr$: C, 59.41; H, 7.61. Found: C, 59.32; H, 7.84.

[$Cp^*_2Zr(N^tBu)[Li(THF)](Me)$] (3b), Method A. In the glovebox, a solution of $Cp^*_2Zr(Me)(Cl)$ (**1b**) (0.077 g, 0.19 mmol) and ^tBuNHLi (0.029 g, 0.37 mmol, 2 equiv) in THF (7 mL) was stirred at room temperature for 12 h. The volatile materials were removed under vacuum and the resulting solid residue was extracted into pentane (15 mL). The pentane solution was filtered away from solid LiCl to give analytically pure, colorless crystalline blocks of **3b** after cooling the concentrated pentane solution to -30 °C (0.074 g, 74%). Complex **3b** was found to be stable when stored in the solid state in a -30 °C freezer in the glovebox, but slowly decomposed over the course of one week in a sealed NMR tube in C_6D_6. ^1H NMR (400 MHz, δ): 3.3-3.2 (m, 4H, THF), 2.11 (s, 30H, $\{\eta^5\text{-}C_5\mathit{Me}_5\}$), 1.36 (s, 9H, C*Me*$_3$), 1.1-1.0 (m, 4H, THF), -0.75 (s (br), 3H, Zr*Me*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, δ): 114.2 ($\{\eta^5\text{-}\mathit{C}_5Me_5\}$), 68.7 (THF), 60.8 (*C*Me$_3$), 37.4 (C*Me*$_3$), 25.2 (THF), 12.9 ($\{\eta^5\text{-}C_5\mathit{Me}_5\}$), 9.5 (br, Zr*Me*) ppm. A non-decoupled 2D $^{13}C\text{-}^1H$ HMQC NMR experiment yielded the $^1H\text{-}^{13}C$ coupling constant for the Zr-*Me* group: $^1J_{C\text{-}H}$ = 107 Hz. ^6Li NMR (59 MHz, δ): 1.6 ppm. ^7Li NMR (194 MHz, δ): 1.6 ppm. A non-decoupled 1D $^6Li\text{-}^1H$ HMQC NMR experiment yielded the $^1H\text{-}^6Li$

coupling constant for the ZrMeLi fragment (400 MHz, δ): -0.8 (d, $^{2}J_{6\text{Li-1H}}$ = 2.3 Hz, Zr*Me*Li) ppm. A ^{1}H-decoupled, non-^{13}C-decoupled 1D ^{7}Li-^{13}C HMQC NMR experiment yielded the ^{7}Li-^{13}C coupling constant for the ZrMeLi fragment (194 MHz, δ): 1.6 (d, $^{1}J_{7\text{Li-13C}}$ = 12 Hz, ZrMe*Li*) ppm. Anal. Calcd for $C_{29}H_{50}$LiNOZr: C, 66.61; H, 9.57; N, 2.66. Found: C, 65.94; H, 9.29; N, 2.66.

Method B. A Schlenk flask equipped with a magnetic stir bar was charged with a solution of [Cp*$_2$Zr(N^{t}Bu)(THF)] (**4b**) (0.100 g, 0.198 mmol) in Et$_2$O (20 mL). After the solution was cooled to -78 °C, MeLi (0.100 mL, 0.198 mmol, 2.0 M in Et$_2$O) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 10 h. The solvent was removed in vacuo, yielding a colorless powder (0.078 g, 75%); the NMR spectra of this product were consistent with those obtained using product isolated via Method A.

[Cp*{η^5-C$_5$HMe$_4$}Zr(N^{t}Bu)[Li(THF)](Me)] (3c). Complex **3c** was prepared under conditions similar to those used for **3b** using a solution of Cp*{η^5-C$_5$HMe$_4$}Zr(Me)(Cl) (**1c**) (0.100 g, 0.26 mmol) and ^{t}BuNHLi (0.245 g, 3.10 mmol) in THF (20 mL), which was stirred at room temperature for 8 h. The crude product was recrystallized from THF to yield pale yellow blocks (0.112 g, 86%). Complex **3b** was stable for two weeks when stored as a solid at -30 °C, and decomposed at room temperature within 2 h. Solutions of complex **3b** in benzene or THF decomposed slowly over 4 days. An analytically pure sample of **3b** has not been obtained. ^{1}H NMR (500 MHz, [D$_8$]THF, δ): 4.96 (s, 1H, {η^5-C$_5$*H*Me$_4$}), 3.6-3.7 (m, 4H, THF), 2.25 (s, 3H, {η^5-C$_5$H*Me$_4$*}), 1.94 (s, 3H, {η^5-C$_5$H*Me$_4$*}), 1.89 (s, 15H, {η^5-C$_5$*Me$_5$*}), 1.7-1.8 (m, 4H, THF), 1.68 (s, 3H, {η^5-C$_5$H*Me$_4$*}), 1.60 (s, 3H, {η^5-C$_5$H*Me$_4$*}), 1.08 (s, 9H, C*Me$_3$*), -1.00 (s, 3H, Zr*Me*) ppm. ^{13}C NMR (125 MHz, [D$_8$]THF, 10 °C, δ): 116.3 ({η^5-*C$_5$*HMe$_4$}$_q$), 116.1 ({η^5-*C$_5$*HMe$_4$}$_q$), 112.4 ({η^5-*C$_5$*Me$_5$}), 112.2 ({η^5-*C$_5$*HMe$_4$}$_q$), 107.4 ({η^5-*C$_5$*HMe$_4$}$_q$), 103.5 ({η^5-*C$_5$*HMe$_4$}$_t$), 67.2 (THF), 59.5 (*C*Me$_3$), 35.7 (C*Me$_3$*), 25.4 (THF), 13.5 ({η^5-C$_5$H*Me$_4$*}), 12.8 ({η^5-C$_5$H*Me$_4$*}), 12.1 ({η^5-C$_5$*Me$_5$*}), 11.9 ({η^5-C$_5$H*Me$_4$*}), 11.0 ({η^5-C$_5$H*Me$_4$*}), 9.6 (br, Zr*Me*) ppm.

$[\{\eta^5\text{-}\mathrm{C_5HMe_4}\}_2\mathrm{Zr(N}^t\mathrm{Bu)[Li(THF)](Me)]}$ (3d). Complex **3d** was prepared under conditions similar to those used for **3b** using a solution of $\{\eta^5\text{-}\mathrm{C_5HMe_4}\}_2\mathrm{Zr(Me)(Cl)}$ (**1d**) (0.085 g, 0.22 mmol) and ^{t}BuNHLi (0.211 g, 2.66 mmol) in THF (12.0 mL), which was stirred at room temperature for 4 h. Complex **3d** was obtained as analytically pure, colorless crystalline blocks by crystallization from pentane at -30 ^{o}C (0.072 g, 64%). Complex **3d** was found to be stable when stored as a solid in a -30 ^{o}C freezer in the glovebox, but slowly decomposed over the course of one week in $\mathrm{C_6D_6}$ in a sealed NMR tube at room temperature. ^{1}H NMR (500 MHz, δ): 5.84 (s, 2H, $\{\eta^5\text{-}\mathrm{C_5}\mathit{H}\mathrm{Me_4}\}$), 3.3-3.2 (m, 4H, THF), 2.34 (s, 6H, $\{\eta^5\text{-}\mathrm{C_5H}\mathit{Me}_4\}$), 2.12 (s, 6H, $\{\eta^5\text{-}\mathrm{C_5H}\mathit{Me}_4\}$), 2.04 (s, 6H, $\{\eta^5\text{-}\mathrm{C_5H}\mathit{Me}_4\}$), 1.95 (s, 6H, $\{\eta^5\text{-}\mathrm{C_5H}\mathit{Me}_4\}$), 1.33 (s, 9H, $\mathrm{NC}\mathit{Me}_3$), 1.1-1.0 (m, 4H, THF), -0.81 (s (br), 3H, Zr*Me*) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125 MHz, δ): 118.6 ($\{\eta^5\text{-}\mathit{C}_5\mathrm{HMe_4}\}_\mathrm{q}$), 116.3 ($\{\eta^5\text{-}\mathit{C}_5\mathrm{HMe_4}\}_\mathrm{q}$), 111.8 ($\{\eta^5\text{-}\mathit{C}_5\mathrm{HMe_4}\}_\mathrm{q}$), 109.7 ($\{\eta^5\text{-}\mathit{C}_5\mathrm{HMe_4}\}_\mathrm{q}$), 108.2 (($\{\eta^5\text{-}\mathit{C}_5\mathrm{H}\mathit{Me}_4\}_\mathrm{t}$), 68.7 (THF), 60.7 ($\mathit{C}\mathrm{Me_3}$), 37.2 ($\mathrm{C}\mathit{Me}_3$), 25.1 (THF), 14.3 ($\{\eta^5\text{-}\mathrm{C_5H}\mathit{Me}_4\}$), 13.3 ($\{\eta^5\text{-}\mathrm{C_5H}\mathit{Me}_4\}$), 12.7 ($\{\eta^5\text{-}\mathrm{C_5H}\mathit{Me}_4\}$), 12.3 ($\{\eta^5\text{-}\mathrm{C_5H}\mathit{Me}_4\}$), 7.2 (br, Zr*Me*) ppm. A non-decoupled 2D ^{13}C-^{1}H HMQC NMR experiment yielded the ^{1}H -^{13}C coupling constant for the Zr-*Me* group: $^1J_{\mathrm{C\text{-}H}} = 107$ Hz. ^{6}Li NMR (59 MHz, δ): 1.6 ppm. ^{7}Li NMR (194 MHz, δ): 1.6 ppm. A non-decoupled 1D ^{6}Li-^{1}H HMQC NMR experiment yielded the ^{1}H-^{6}Li coupling constant for the ZrMeLi fragment (500 MHz, δ): -0.8 (d, $^2J_{\mathrm{6Li\text{-}1H}} = 1.3$ Hz, Zr*Me*Li) ppm. A non-decoupled 1D ^{7}Li-^{1}H HMQC NMR experiment yielded the ^{1}H-^{7}Li coupling constant for the ZrMeLi fragment (500 MHz, δ): -0.8 (d, $^2J_{\mathrm{7Li\text{-}1H}} = 2.3$ Hz, Zr*Me*Li) ppm. A ^{1}H-decoupled, non-^{13}C-decoupled 1D ^{7}Li-^{13}C HMQC NMR experiment yielded the ^{7}Li-^{13}C coupling constant for the ZrMeLi fragment (194 MHz, δ): 1.6 (d, $^1J_{\mathrm{7Li\text{-}13C}} = 10$ Hz, ZrMe*Li*) ppm. Anal. Calcd for $\mathrm{C_{27}H_{46}LiNOZr}$: C, 65.01; H, 9.29; N, 2.81. Found: C, 64.75; H, 9.33; N, 2.89.

[*rac*-(ebthi)Zr(N^{t}Bu)[Li(THF)$_2$](Me)] (3e), Method A. Complex **3e** was prepared under conditions similar to those used for **3b** using a solution of *rac*-(ebthi)Zr(Me)(Cl) (**1e**) (0.200 g, 0.49 mmol) and ^{t}BuNHLi (0.467 g, 5.90 mmol) in THF (40 mL), which was stirred at room temperature for

5 h. Analytically pure, clear, colorless crystalline blocks were obtained by crystallization from pentane at -30 °C (0.136 g, 53%). Complex **3e** was stable for one week when stored as a solid at -30 °C in the glovebox, but solutions of complex **3e** decomposed slowly at room temperature. ^{1}H NMR (400 MHz, [D$_8$]THF, δ): 5.92 (d, *J* = 2.8 Hz, 1H, Cp*H*), 5.42 (d, *J* = 3.0 Hz, 1H, Cp*H*), 5.14 (d, J = 3.0Hz, 1H, Cp*H*), 4.98 (d, J = 2.8 Hz, 1H, Cp*H*), 3.6-3.7 (m, 4H, THF), 3.1-3.2 (m, 1H), 2.89 (dt, *J* = 14.6 Hz, 5.8 Hz, 1H), 2.5-2.7 (m, 2H), 2.4-2.5 (m, 2H), 2.2-2.3 (m, 2H), 2.0-2.1 (m, 1H), 1.9-2.0 (m, 1H), 1.7-1.8 (m, 8H, THF), 1.4-1.6 (m, 2H), 1.11(s, 9H, C*Me*$_3$), -0.67 (s, 3H, Zr*Me*) ppm. ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, δ): 124.5 (ebthi$_q$), 122.8 (ebthi$_q$), 122.0 (ebthi$_q$), 119.0 (ebthi$_q$), 118.6 (ebthi$_q$), 112.7 (ebthi$_q$), 108.1 (ebthi$_t$), 106.1 (ebthi$_t$), 103.3 (ebthi$_t$), 98.4 (ebthi$_t$), 68.3 (THF), 60.6 (N*C*Me$_3$), 36.9 (NC*Me*$_3$), 27.4 (*C*H$_2$), 27.3 (*C*H$_2$), 25.8 (*C*H$_2$), 25.5 (THF), 25.5 (*C*H$_2$), 25.0 (*C*H$_2$), 24.7 (*C*H$_2$), 24.6 (*C*H$_2$), 24.2 (*C*H$_2$), 24.1 (*C*H$_2$), 24.0 (*C*H$_2$), 4.4 (Zr*Me*) ppm. Anal Calcd for $C_{33}H_{50}NO_2LiZr$: C, 67.07; H, 8.53; N, 2.37. Found: C, 66.94; H, 8.82; N, 2.70.

Method B. Complex **3e** was prepared under conditions identical to those used for **3b** (Method B) using [*rac*-(ebthi)Zr(N^{t}Bu)(THF)] (0.050 g, 0.100 mmol).[1] The product was obtained as a colorless powder (0.024 g, 45%); NMR spectra of this product were consistent with those obtained using product isolated via Method A.

[Cp*$_2$Zr(NH^{t}Bu)(Me)] (2b). In the glovebox, a solution of complex **3b** (0.135 g, 0.256 mmol) in THF (18 mL) and 12-crown-4 (0.044 mL, 0.273 mmol) was added to a vial previously charged with solid NH$_4$Cl (0.014 g, 0.26 mmol). The mixture was stirred at room temperature for 5 h. The volatile materials were removed under vacuum and the resulting solid residue was extracted into benzene (15 mL). After filtering the benzene solution away from solid LiCl and removing the volatile materials under vacuum, a colorless powder with spectroscopic properties consistent with **2b** was obtained (0.102 g, 89%, >85% pure by ^{1}H NMR spectroscopy). Complex **2b** was found to be stable when stored in the solid state in a -30 °C freezer in the glovebox, but the solid decomposed to several unidentified species within 4 hours at room temperature. A solution of complex **2b** in THF was stable for 4 days at room temperature, but also decomposed to several unidentified species over one week. An analytically pure sample of **2b** has not been obtained. ^{1}H NMR (400 MHz, δ): 3.49 (s, 1H, N*H*), 1.85 (s, 30H, Cp*), 1.18 (s, 9H, C*Me*$_3$), -0.19 (s, 3H, Zr*Me*) ppm. ^{13}C{^{1}H} NMR (100 MHz, δ): 117.0 ({η^5-*C*$_5$Me$_5$}$_q$), 56.3 (*C*Me$_3$), 35.0 (C*Me*$_3$), 27.6 (Zr*Me*), 12.1 ({η^5-C$_5$*Me*$_5$}) ppm.

[Cp*{η^5-C$_5$HMe$_4$}Zr(NH^{t}Bu)(Me)] (2c). Complex **2c** was prepared under conditions identical to those used for complex **2b** using a solution of [Cp*{η^5-C$_5$HMe$_4$}Zr(N^{t}Bu)(Li·THF)(Me)] (**3c**) (0.100 g, 0.20 mmol), 12-crown-4 (0.032 mL, 0.20 mmol) and NH$_4$Cl (0.014 g, 0.22 mmol) in THF (10 mL). A yellow powder with spectroscopic properties consistent with complex **2c** was isolated (0.060 g, 82%, >95% pure by ^{1}H NMR spectroscopy). Complex **2c** was stable for one week when stored at -30 °C, but slowly decomposed in solution at room temperature; an analytically pure sample has not been obtained. ^{1}H NMR (400 MHz, δ): 5.15 (s, 1H, {η^5-C$_5$*H*Me$_4$}), 3.80 (br s, 1H, N*H*), 1.95 (s, 3H, {η^5-C$_5$H*Me*$_4$}), 1.94 (s, 3H, {η^5-C$_5$H*Me*$_4$}), 1.86 (s, 3H, {η^5-C$_5$H*Me*$_4$}), 1.84 (s, 15H, {η^5-C$_5$*Me*$_5$}), 1.66 (s, 3H, {η^5-C$_5$H*Me*$_4$}), 1.16 (s, 9H, NC*Me*$_3$), -0.24 (s, 3H, Zr*Me*) ppm. ^{13}C NMR (100 MHz, δ): 122.3 ({η^5-*C*$_5$HMe$_4$}$_q$), 121.8 ({η^5-*C*$_5$HMe$_4$}$_q$), 116.3 ({η^5-*C*$_5$Me$_5$}), 113.4 ({η^5-*C*$_5$HMe$_4$}), 112.8 ({η^5-*C*$_5$HMe$_4$}$_q$), 107.6 ({η^5-*C*$_5$HMe$_4$}$_t$), 55.5 (N*C*Me$_3$), 34.5 (NC*Me*$_3$), 26.2 (Zr*Me*), 12.6 ({η^5-C$_5$H*Me*$_4$}), 12.4 ({η^5-C$_5$H*Me*$_4$}), 12.0 ({η^5-C$_5$*Me*$_5$}), 11.9 ({η^5-C$_5$H*Me*$_4$}), 11.4 ({η^5-C$_5$H*Me*$_4$}).

[{η^5-C$_5$HMe$_4$}$_2$Zr(NH^{t}Bu)(Me)] (2d). Complex **2d** was prepared under conditions identical to those used for complex **2b** using a solution of {η^5-C$_5$HMe$_4$}$_2$Zr(N^{t}Bu)[Li(THF)](Me) (**3d**) (0.050 g, 0.10 mmol), 12-crown-4 (0.016 mL, 0.10 mmol) and NH$_4$Cl (0.007 g, 0.11 mmol) in THF (4 mL). A colorless powder with spectroscopic properties consistent with complex **2d** was obtained (0.040 g, 94%, >90% pure by ^{1}H NMR spectroscopy). Complex **2d** was found to be somewhat stable when stored in the solid state in a -30 °C freezer, but slowly decomposed in solution at room temperature; an analytically pure sample has not been obtained. ^{1}H NMR (400 MHz, δ): 5.44 (s, 2H, {η^5-C$_5$*H*Me$_4$}), 4.37 (s, 1H, N*H*), 2.00 (s, 6H, {η^5-C_5H*Me*$_4$}), 1.85 (s, 6H, {η^5-C_5H*Me*$_4$}), 1.78 (s, 6H, {η^5-C_5H*Me*$_4$}), 1.68 (s, 6H, {η^5-C_5H*Me*$_4$}), 1.18 (s, 9H, NC*Me*$_3$), -0.31 (s, 3H, Zr*Me*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, δ): 121.0 ({η^5-*C*$_5$HMe$_4$}$_q$), 118.6 ({η^5-*C*$_5$HMe$_4$}$_q$), 117.0 ({η^5-*C*$_5$HMe$_4$}$_q$), 113.2 ({η^5-*C*$_5$HMe$_4$}$_q$), 106.8 ({η^5-*C*$_5$HMe$_4$}$_t$), 55.7 (N*C*Me$_3$), 34.7 (NC*Me*$_3$), 24.3 (Zr*Me*), 13.5 {η^5-C_5H*Me*$_4$}, 12.8 {η^5-C_5H*Me*$_4$}, 12.3 {η^5-C_5H*Me*$_4$}, 11.2 {η^5-C_5H*Me*$_4$} ppm.

[(THI)$_2$Zr(NH^{t}Bu)(Me)] (**2g**). Complex **2g** was prepared in 4 steps from commercially available bis(indenyl)$ZrCl_2$. Step 1: Bis(indenyl)$ZrCl_2$ was reduced to (THI)$_2ZrCl_2$ (bis(tetrahydroindenyl)$ZrCl_2$) using Adams' catalyst.[23] A Parr bomb equipped with a magnetic stir bar was charged with a slurry of bis(indenyl)$ZrCl_2$ (1.061 g, 2.55 mmol), PtO_2 (0.039 mg, 0.17 mmol), and dichloromethane (20 mL). The headspace of the Parr bomb was flushed three times with H_2 and charged to 1500 psi with H_2. The Parr bomb was sealed and the reaction mixture was stirred for 24 h at room temperature. After carefully venting the Parr bomb, the crude reaction mixture was filtered through a pad of Celite. The filter cake was washed with dichloromethane until the filtrate was colorless. The resultant greenish-yellow dichloromethane solution was concentrated in vacuo and the residue was re-dissolved in toluene. The toluene solution was warmed to 90 °C and filtered while still hot. The filtrate was allowed to stand overnight at -30 °C, yielding [(THI)$_2ZrCl_2$] as a pale green, flaky solid (0.912 g, 90%) that was used without further purification. The NMR data obtained with this material matched previously reported data.[24]

Step 2: A 100 mL, oven-dried Schlenk flask equipped with a magnetic stir bar was charged with a slurry of [(THI)$_2ZrCl_2$] (0.812 g, 1.60 mmol) in Et_2O (50 mL). A 2.04 M solution of MeLi (1.65 mL, 3.36 mmol) in diethyl ether was added dropwise. The resulting mixture was stirred at room temperature for 8 h, concentrated, taken into pentane, filtered, and concentrated to yield [(THI)$_2ZrMe_2$] as a brown oil, which was used without further purification (0.475 g, 83%). ^1H NMR (400 MHz, δ):

5.3-5.4 (m, 6H, Cp*H*), 2.4-2.6 (m, 8H), 1.4-1.6 (m, 8H), -0.19 (s, 6H, Zr*Me*) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, δ): 124.2 (THI$_{Cp,\ q}$), 107.4 (THI$_{Cp,\ t}$), 107.1 (THI$_{Cp,\ t}$), 34.6 (Zr*Me*), 24.7 (THI), 23.5 (THI).

Step 3: A THF solution (20 mL) of [$(THI)_2ZrMe_2$] (0.301 g, 0.84 mmol) was treated with $Me_3N{\cdot}HCl$ (0.078 g, 0.82 mmol) to yield [$(THI)_2Zr(Me)(Cl)$] in a procedure identical to that used to prepare complex **1b**. The crude product was recrystallized from THF to yield a colorless powder, which was used without further purification (0.276 g, 87%). ^1H NMR (400 MHz, [D_8]THF, δ): 5.8-5.9 (m, 2H, Cp*H*), 5.7-5.8 (m, 2H, Cp*H*), 5.6-5.7 (m, 2H, Cp*H*), 2.5-2.8 (m, 8H, THI), 1.8-1.9 (m, 4H, THI), 1.6-1.7 (m, 4H, THI), -0.02 (s, 3H, Zr*Me*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, [D_8]THF, δ): 125.4 (THI$_{Cp,\ q}$), 124.7 (THI$_{Cp,\ q}$), 109.0 (THI$_{Cp,\ t}$), 106.3 (THI$_{Cp,\ t}$), 103.2 (THI$_{Cp,\ t}$), 30.0 (Zr*Me*), 20.8 (THI), 20.7 (THI) ppm; two peaks not located (THI). Anal Calcd for $C_{19}H_{25}ClZr$: C, 60.04; H, 6.63. Found: C, 59.76; H, 6.57.

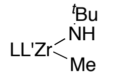
Step 4: In the glovebox, a 20 mL scintillation vial equipped with a stir bar was charged with a solution of [$(THI)_2Zr(Me)(Cl)$] (0.100 g, 0.26 mmol) in THF (4 mL). A solution of ^{t}BuNHLi (0.021 g, 0.26 mmol) in THF (2 mL) was added dropwise. The yellow reaction mixture was stirred for 10 min at ambient glovebox temperature. THF was then removed in vacuo, and the resulting residue was extracted with pentane. The combined pentane washes were filtered and concentrated to give a yellow oil (0.103 mg, 94%, >95% pure by ^1H NMR spectroscopy). Complex **2g** was somewhat stable in solution at room temperature but decomposed within 2 h upon removal of solvent; an analytically pure sample has not been obtained. ^1H NMR (400 MHz, [D_8]THF, δ): 5.8-5.9 (m, 2H, Cp*H*), 5.5-5.6 (m, 2H, Cp*H*), 5.3-5.4 (m, 2H, Cp*H*), 4.74 (br s, 1H, N*H*), 2.4-2.5 (m, 6H), 1.6-1.8 (m, 10H), 1.07 (s, 9H, C*Me*$_3$), -0.51 (s, 3H, Zr*Me*) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D_8]THF, δ): 123.1 (THI$_{Cp,\ q}$), 122.6 (THI$_{Cp,\ q}$), 105.8 (THI$_{Cp,\ t}$), 104.9 (THI$_{Cp,\ t}$), 103.9 (THI$_{Cp,\ t}$), 55.9 (N*C*Me_3), 33.6 (Zr*Me*), 24.1 (THI), 23.2 (THI), 23.1 (THI), 22.7 (THI) ppm; one peak not located (THI).

[$Cp^*_2Zr(N^tBu)(THF)$] (4b). In the glovebox, a bomb equipped with a magnetic stir bar was charged with a solution of [$Cp^*_2Zr(NH^tBu)(Me)$] (**2b**) (0.098 g, 0.217 mmol) in THF (10 mL). The bomb was sealed, brought out of the glovebox, and placed in a 45 °C oil bath for 48 h. Solvent was removed in vacuo to give a yellow, crystalline solid (0.101 g, 92%). ^{1}H NMR (400 MHz, δ): 3.7-3.8 (m, 4H, THF), 2.07 (s, 30H, {η^5-C_5*Me_5*}), 1.42 (s, 9H, NC*Me_3*), 1.2-1.3 (m, 4H, THF) ppm. ^{13}C{^{1}H} NMR (125 MHz, δ): 116.8 ({η^5-*C_5*Me_5}), 76.9-76.2 (THF), 62.8 (N*C*Me_3), 36.0 (NC*Me_3*), 26.1 (THF), 13.0 ({η^5-C_5*Me_5*}) ppm. Anal Calcd for $C_{28}H_{47}NOZr$: C, 66.61; H, 9.38; N, 2.77. Found: C, 66.33; H, 9.50; N, 2.83.

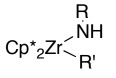
General Procedure for p*K*$_a$ Measurements. In the glovebox, a solution of lithium zirconacycle **3** (0.020 mmol), triphenylmethane (0.005 g, 0.020 mmol), and 12-crown-4 (10 μL, 0.67 M standard solution in [D_8]THF, 0.006 mmol) in [D_8]THF (0.600 mL), and a sealed capillary containing a 0.03 M solution of 1,3-dimethoxy-5-methylbenzene in C_6D_6 were placed in an NMR tube. The tube was then flame-sealed on a high vacuum line (*vide supra*). The reaction mixture became deep red within 24 hours, and was monitored by ^{1}H NMR once every 4 hours until no change in product distribution was observed for 12 consecutive hours. Each experiment was run three times using material from at least two different batches of lithium zirconacycle.

Procedure for Competition Experiment between 2d and 2e. In the glovebox, a solution of [*rac*-(ebthi)Zr(N^{t}Bu)[Li(THF)]$_2$(Me)] (**3e**) (0.015 g, 0.030 mmol), [{η^5-C_5HMe_4}$_2$Zr(NH^{t}Bu)(Me)] (**2d**) (0.012 g, 0.030 mmol), and 12-crown-4 (10 μL, 1.0 M standard solution in [D_8]THF) in [D_8]THF (0.600 mL) and a sealed capillary containing a 0.03 M solution of 1,3-dimethoxy-5-methylbenzene in C_6D_6 were placed in an NMR tube. The tube was then flame-sealed on a high vacuum line (*vide supra*). The reaction was monitored by ^{1}H NMR once every 8 hours for 72 hours, at which point no change in product distribution had been observed for 24 consecutive hours. This experiment was run three times using material from three different batches of **3e** and **2d**.

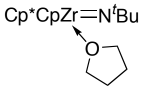
Attempted Isolation of Other Lithium Zirconimidate Complexes. No reaction was observed by ^{1}H NMR spectroscopy when methyl amide complexes **2a**,[25] **2f**,[26] or **2g** (0.020 mmol) were treated with a solution of ^{t}BuNHLi (0.019 g, 0.240 mmol) in [D$_8$]THF (0.600 mL) at room temperature. Decomposition was observed when solutions of methyl amide complexes **2a**, **2f**, or **2g** (0.020 mmol) in Et$_2$O (0.600 mL) were treated with MeLi or ^{n}BuLi (0.020 mmol) at -78 °C, and then allowed to warm to room temperature. Intractable product mixtures were obtained when a solution of complex **2h** (0.007 g, 0.014 mmol in 0.500 mL [D$_8$]THF) was treated with ^{t}BuNHLi (10 μL, 1.8 M solution in [D$_8$]THF).



2a: LL' = Cp*Cp
2f: LL' = Cp$_2$
2g: (tetrahydroindenyl)$_2$

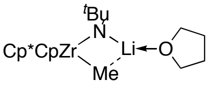


2h: R = Bz, R' = Me
2i: R = Me, R' = Me

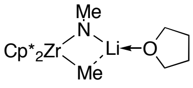


4a

When methyl amide complex **2i** (0.067 g, 0.165 mmol) was treated with a solution of ^{t}BuNHLi (0.013 g, 0.167 mmol) in THF (10 mL), a product with a ^{1}H NMR spectrum consistent with the corresponding lithium zirconimidate complex **3i** was isolated (see p. S-13). Upon treatment of **3i** with Brønsted acids, decomposition was observed.



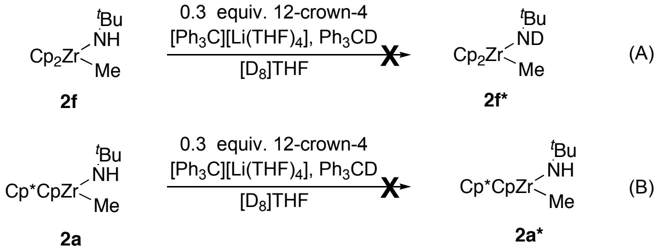
3a

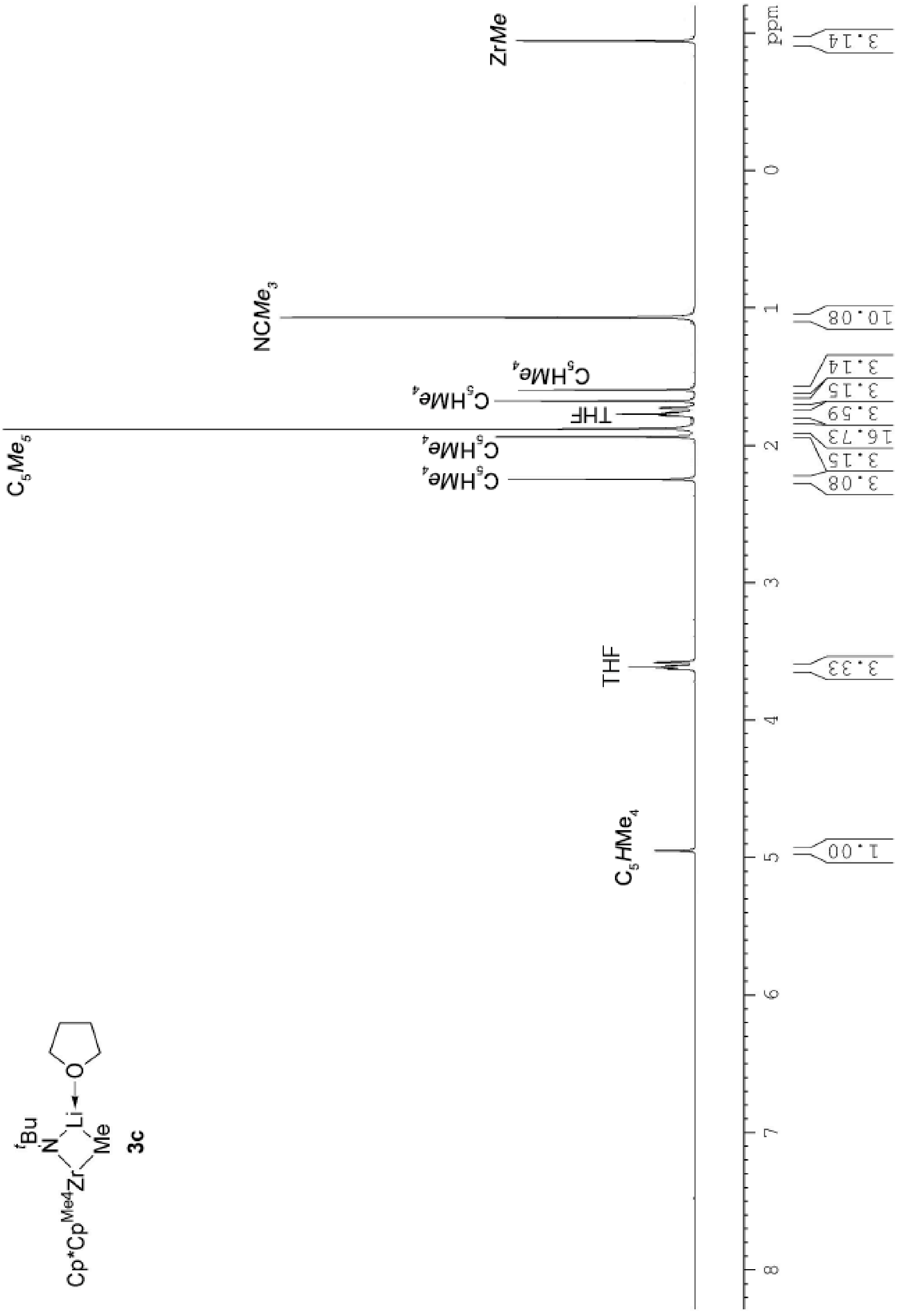


3i

A solution of imidozirconocene complex **4a**[25] (0.011 g, 0.024 mmol) in [D$_8$]THF (0.600 mL) was treated with methyllithium (0.016 mL, 1.6 M in Et$_2$O), resulting in the formation of a product that has a ^{1}H NMR spectrum consistent with zirconimidate complex **3a** (see p. S-14). However, this product decomposed upon concentration of the reaction mixture. When putative complex **3a** was generated in situ and subsequently treated with Brønsted acids, decomposition was observed.

Attempted Deuteration of Other Zirconium Methyl-Amide Complexes. When complexes **2a** and **2f** were treated with triphenylmethyllithium, deuterated triphenylmethane, and 12-crown-4 in [D$_8$]THF, no deuterium incorporation at the zirconium-amide N-H position was observed [Eqs. (A) and (B)]. These results indicate that the deprotonation reactions of complexes **2a** and **2f** have high kinetic barriers.

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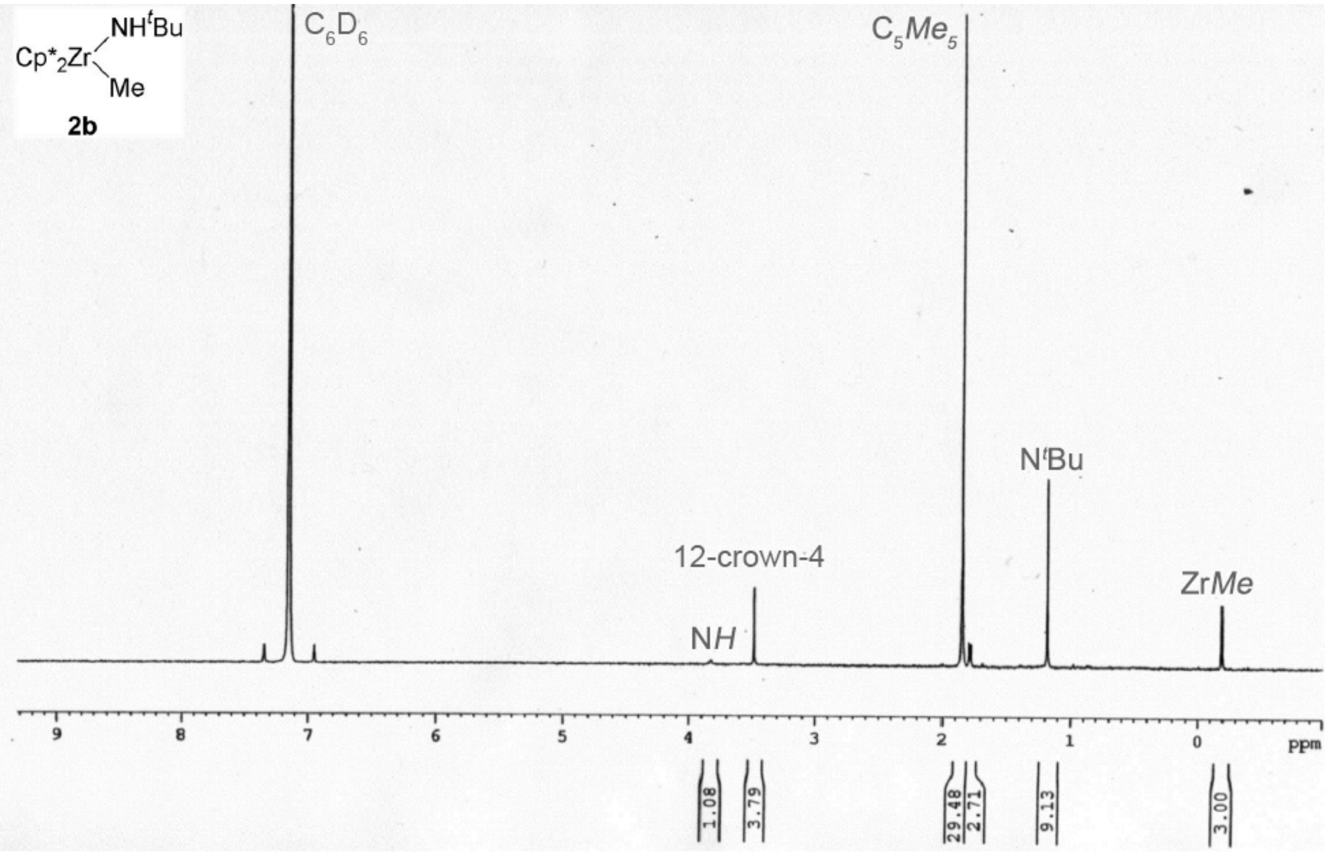
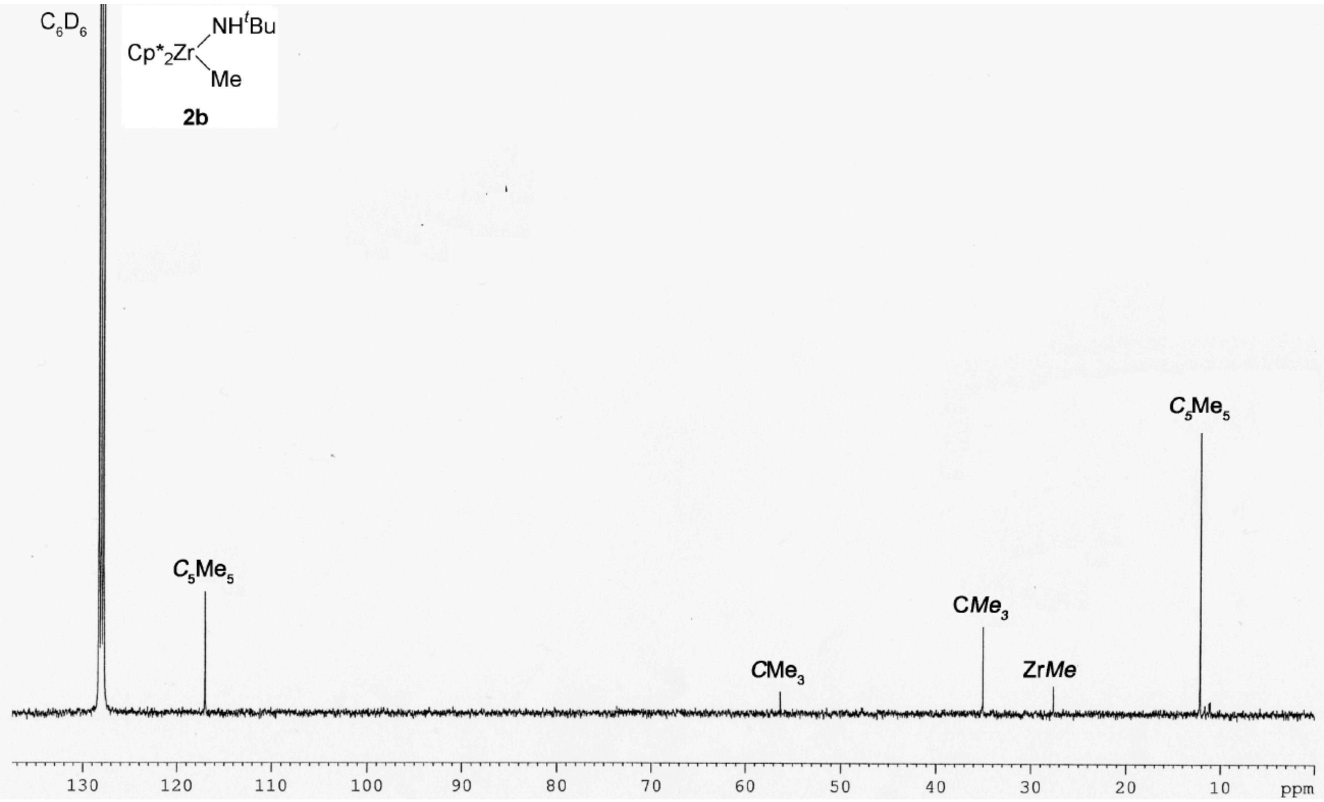
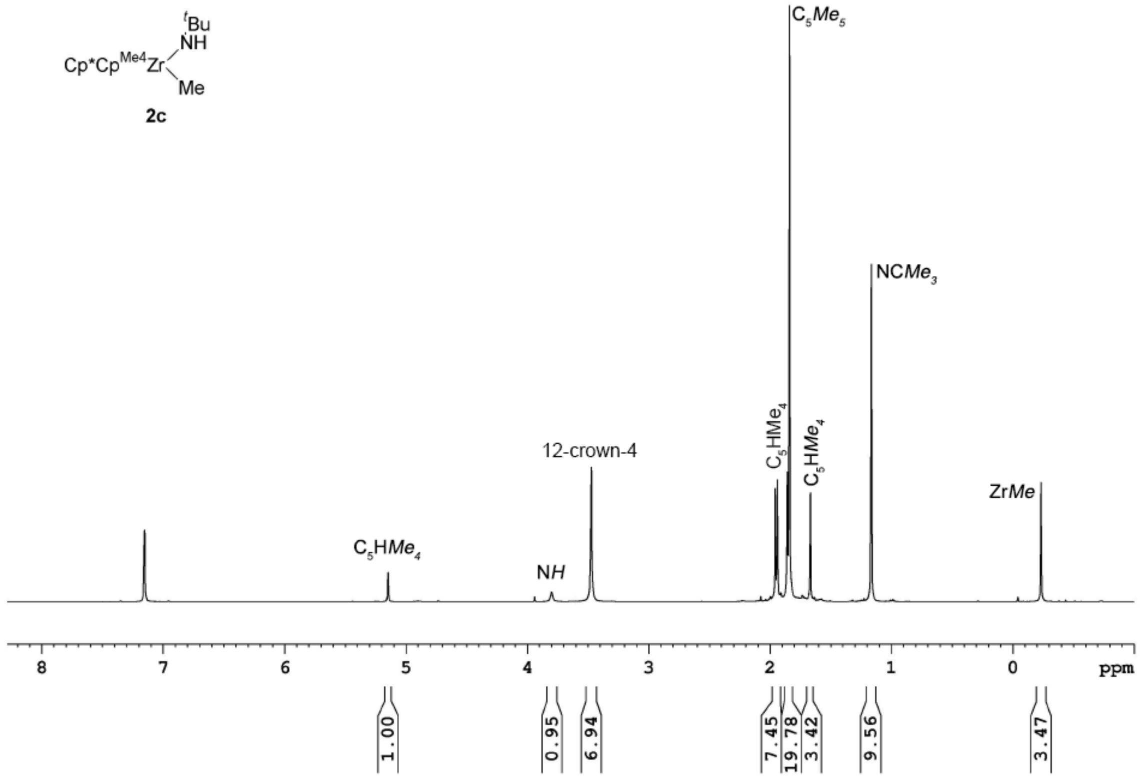
tBu
N
Li
O
Me
3c
ZrMe
NCMe3
C5HMe4
C5HMe4
THF
C5Me5
C5HMe4
C5HMe4
THF
C5HMe4
ppm
-1
0
1
2
3
4
5
6
7
8
3.14
10.08
3.14
3.15
3.59
16.73
3.15
3.08
3.33
1.00



NH^{t}Bu
Cp*$_2$Zr
Me
2b
C_6D_6
C_5Me_5
12-crown-4
NH
N^{t}Bu
ZrMe
9
8
7
6
5
4
3
2
1
0
ppm
1.08
3.79
29.48
2.71
9.13
3.00



C_6D_6
NH^{t}Bu
Cp*$_2$Zr
Me
2b
C_5Me$_5$
CMe$_3$
CMe$_3$
ZrMe
C$_5$Me$_5$
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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NH
Cp*CpMe4Zr
Me
2c
C5Me5
NCMe3
12-crown-4
C5HMe4
C5HMe4
C5HMe4
NH
ZrMe
8
7
6
5
4
3
2
1
0
ppm
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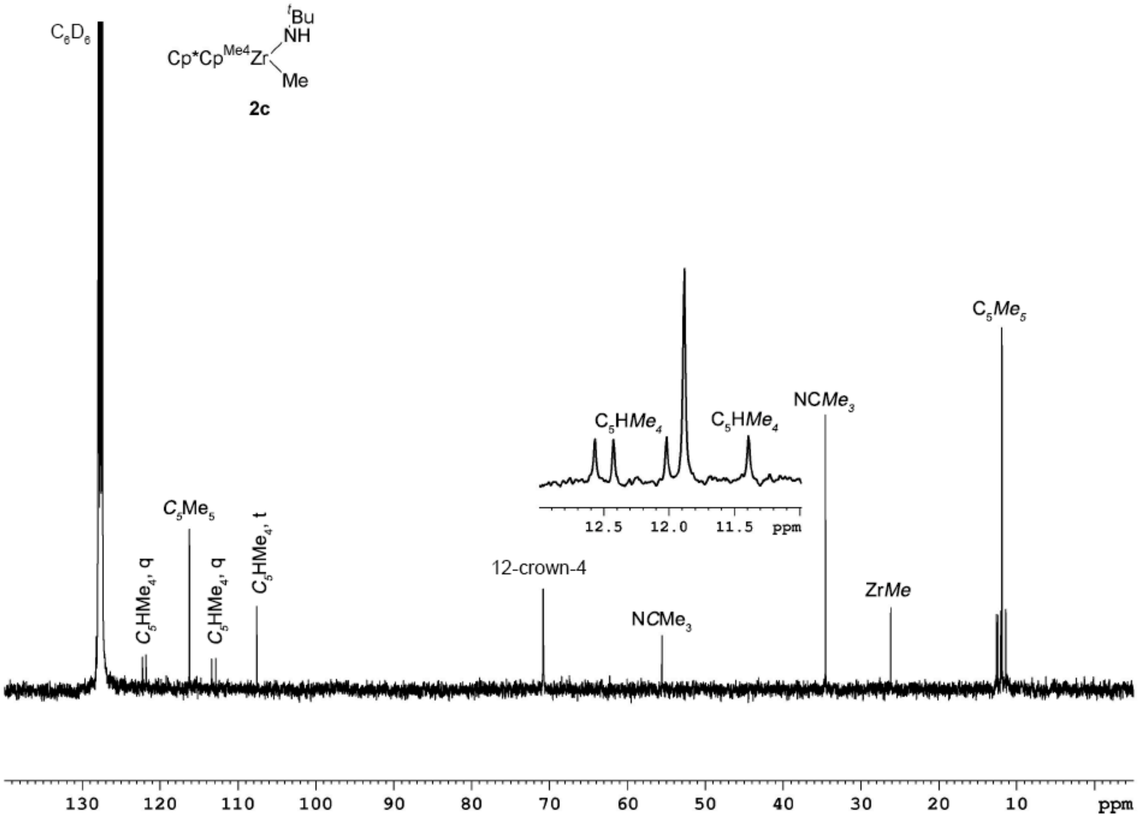
0.95
6.94
7.45
19.78
3.42
9.56
3.47


C6D6
tBu
NH
Cp*CpMe4Zr
Me
2c
C5Me5
C5HMe4
C5HMe4
12.5
12.0
11.5
ppm
NCMe3
C5Me5
C5HMe4, q
C5HMe4, q
C5HMe4, t
12-crown-4
NCMe3
ZrMe
130
120
110
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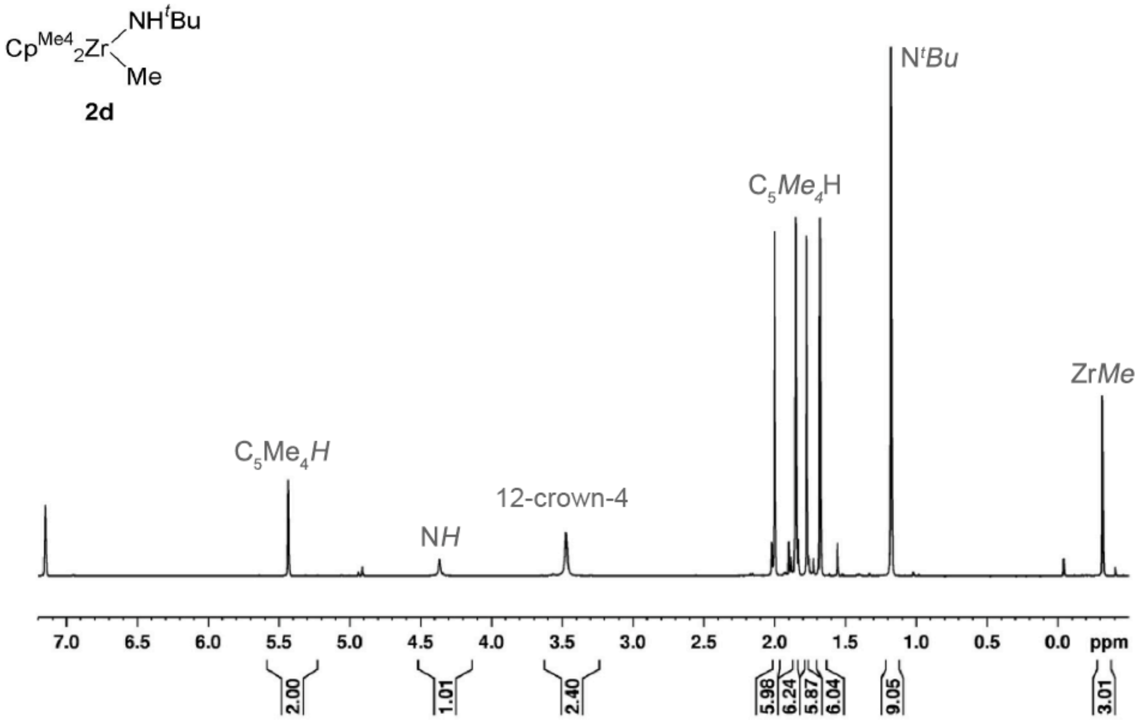
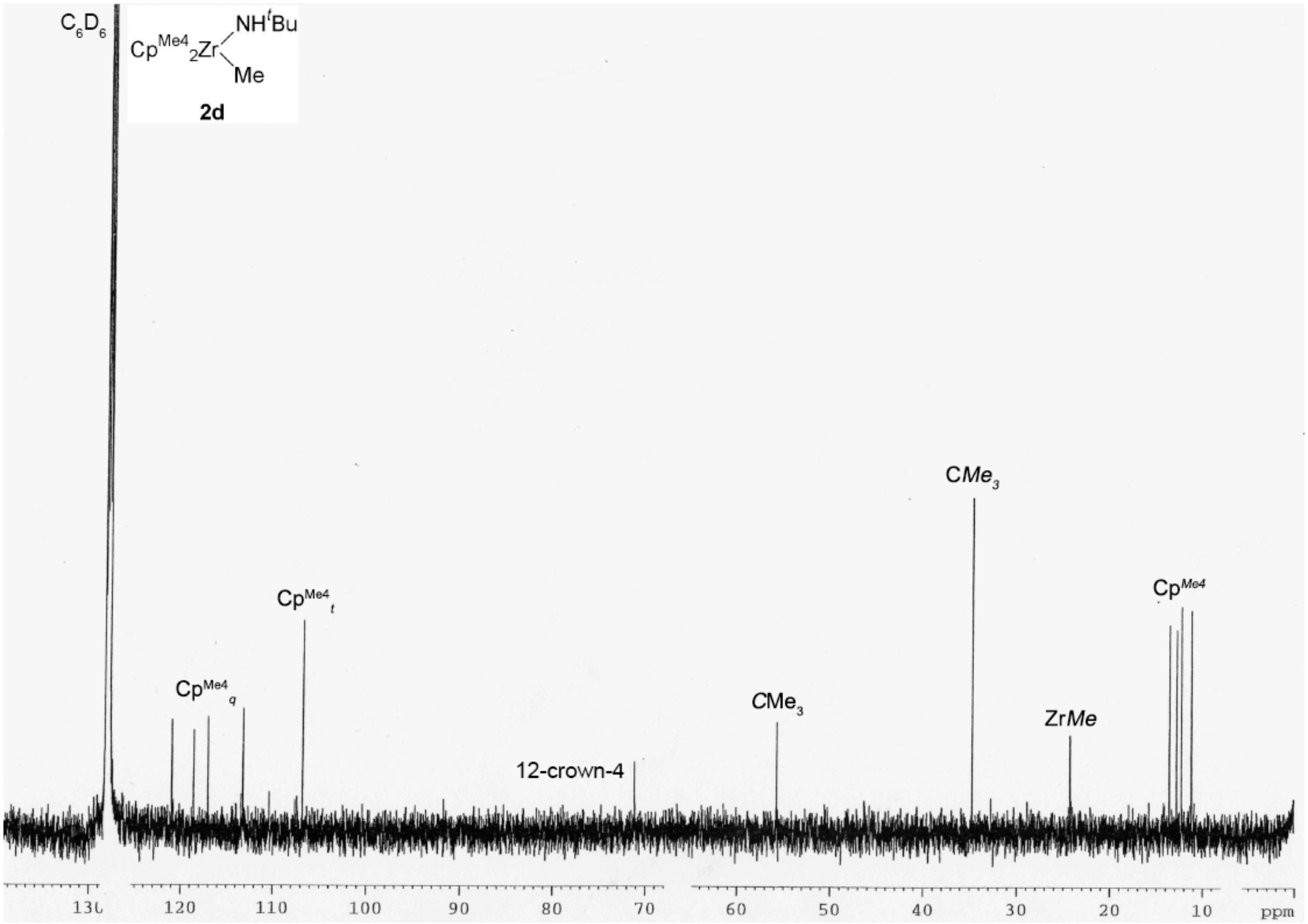
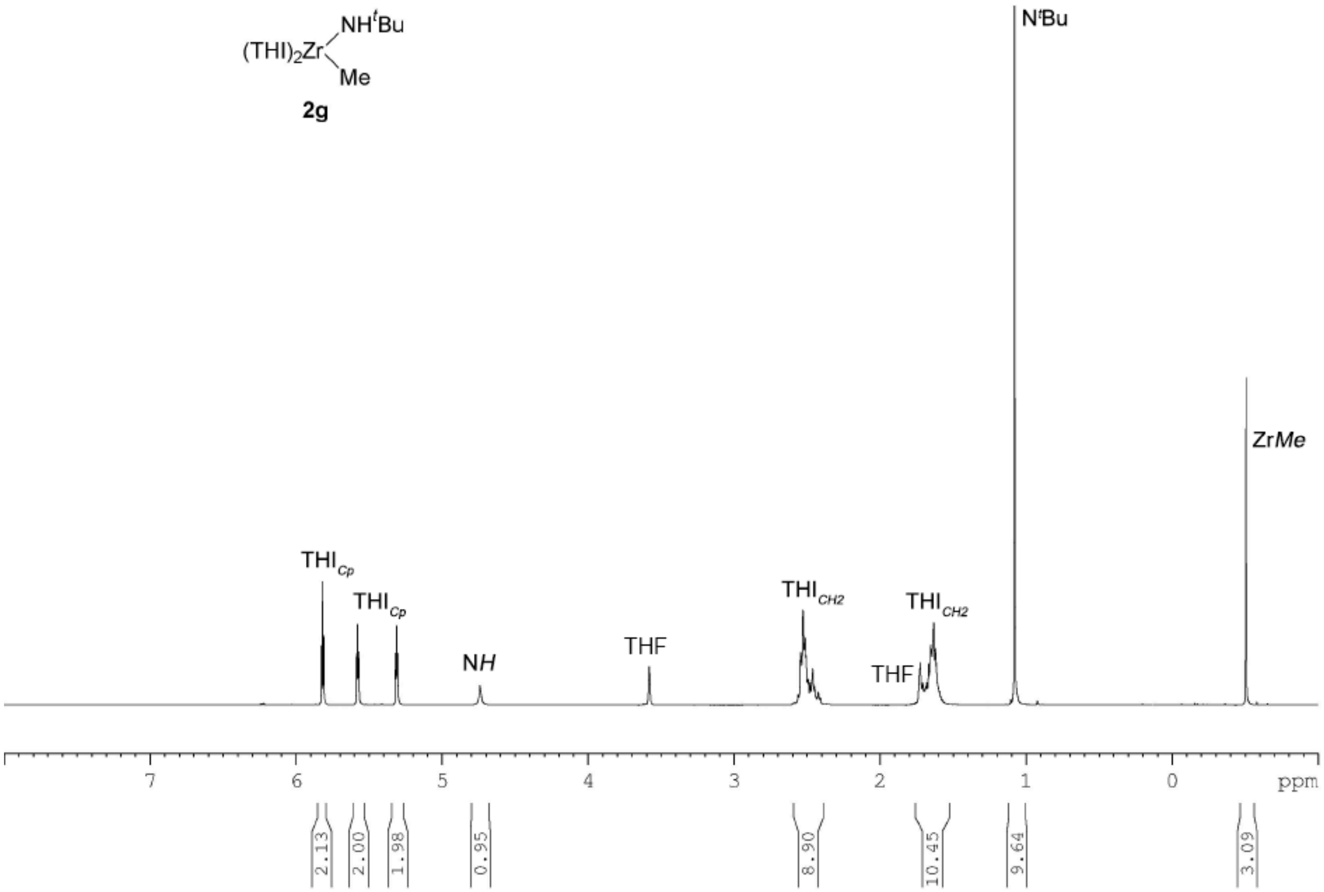
40
30
20
10
ppm

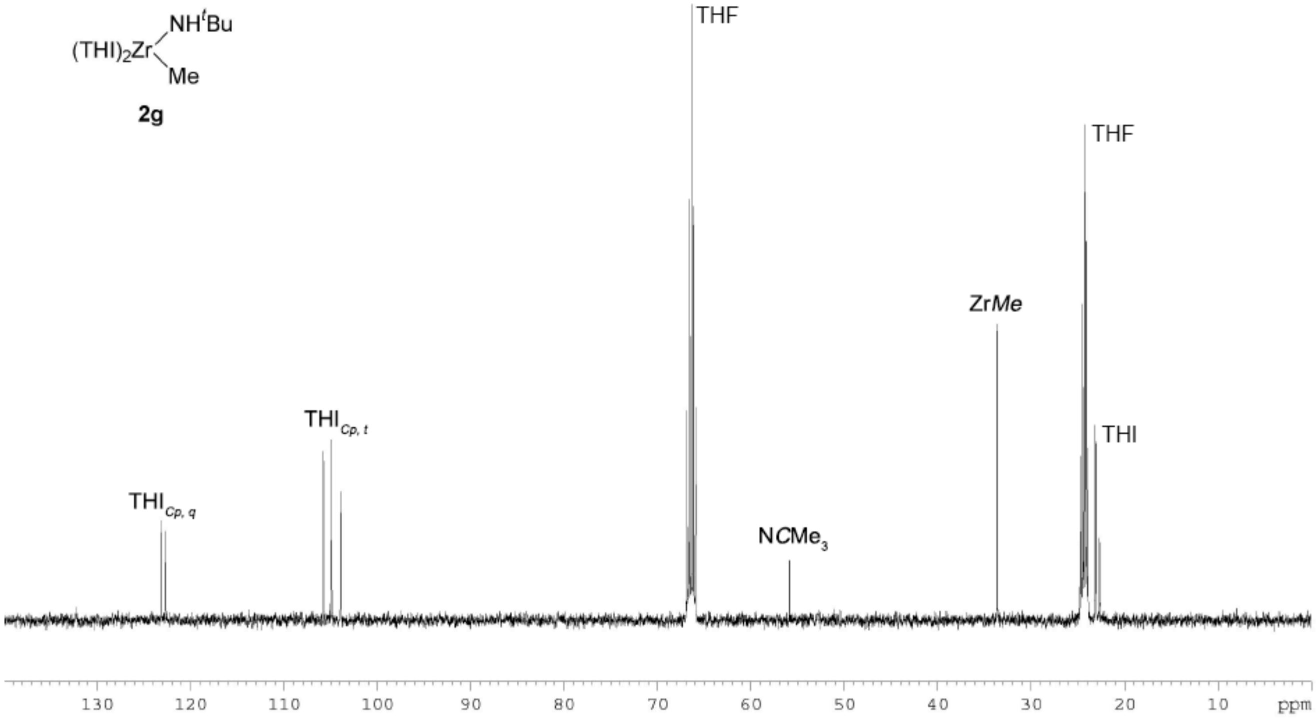


Cp^Me4 2Zr NH^tBu Me
2d
N^tBu
C5Me4H
ZrMe
C5Me4H
12-crown-4
NH
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.01
2.40
5.98
6.24
5.87
6.04
9.05
3.01



C6D6
Cp^Me4 2Zr NH^tBu Me
2d
CMe3
Cp^Me4
Cp^Me4 t
Cp^Me4 q
CMe3
ZrMe
12-crown-4
130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


(THI)2Zr NH^tBu Me
2g
N^tBu
ZrMe
THI_Cp
THI_Cp
NH
THF
THI_CH2
THF
THI_CH2
7
6
5
4
3
2
1
0
ppm
2.13
2.00
1.98
0.95
8.90
10.45
9.64
3.09


(THI)2Zr NH^tBu Me
2g
THF
THF
ZrMe
THI
THI_Cp, t
THI_Cp, q
NCMe3
130
120
110
100
90
80
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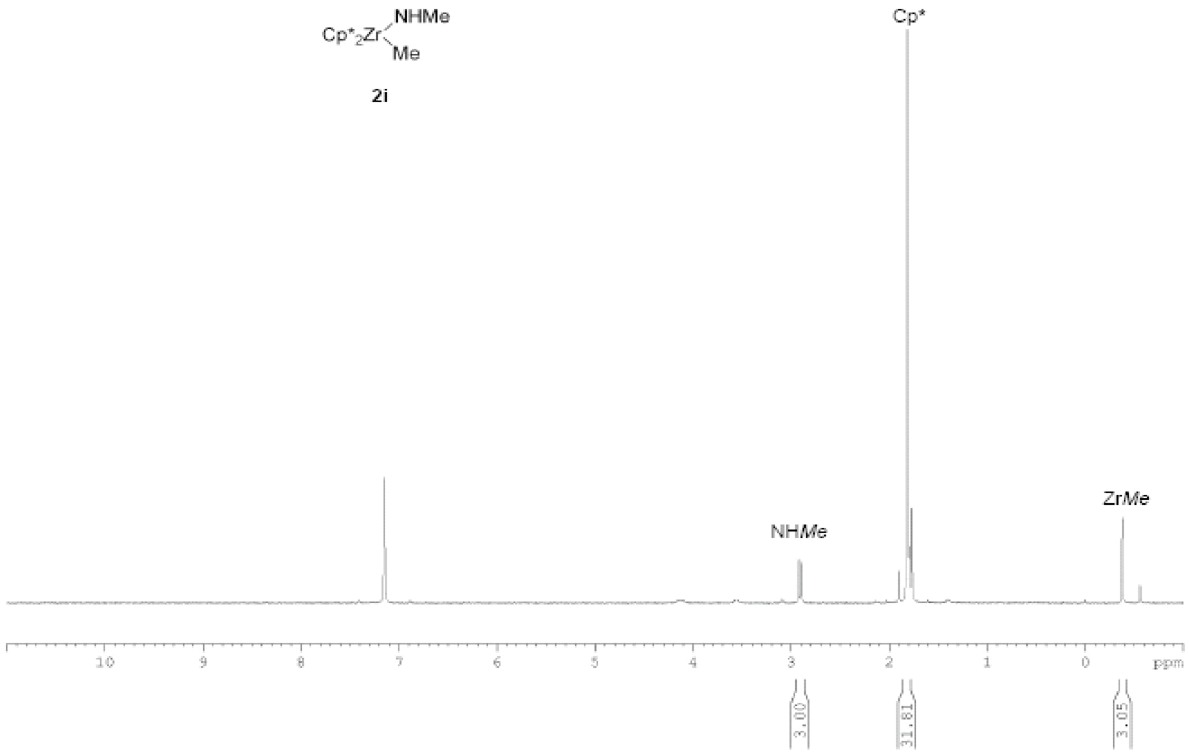
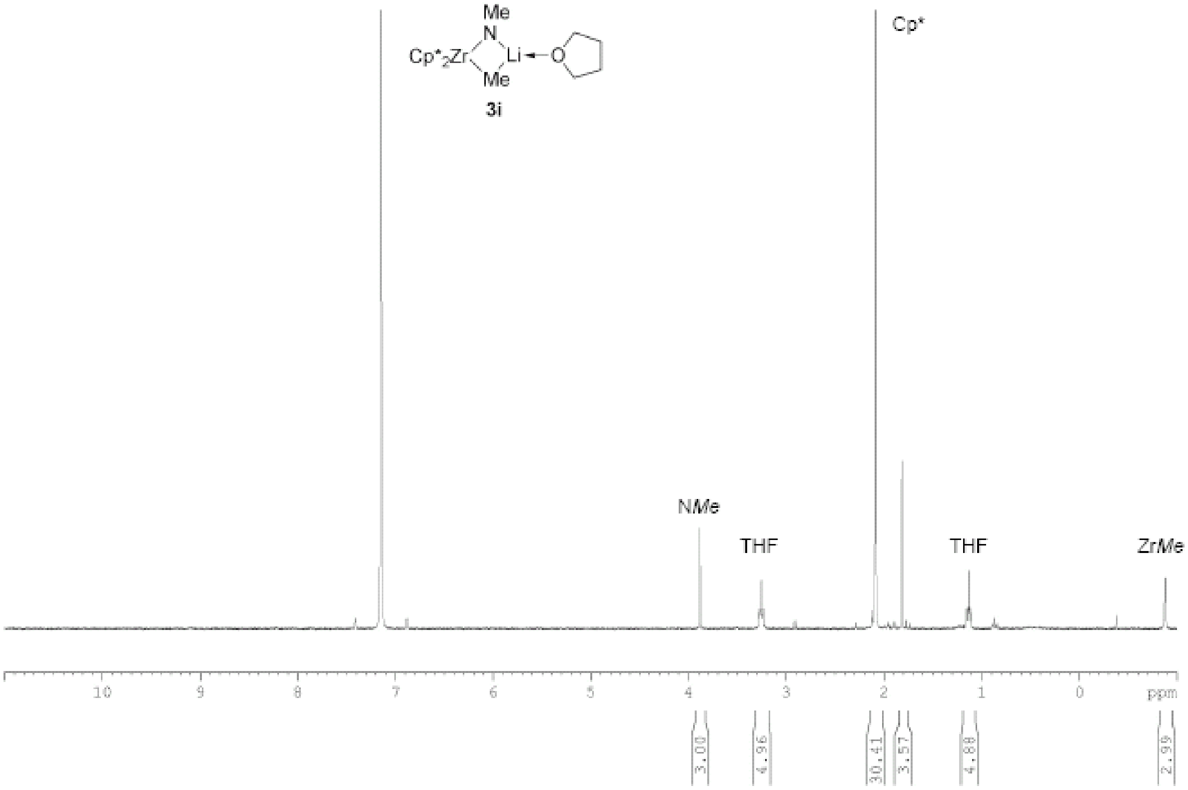
40
30
20
10
ppm



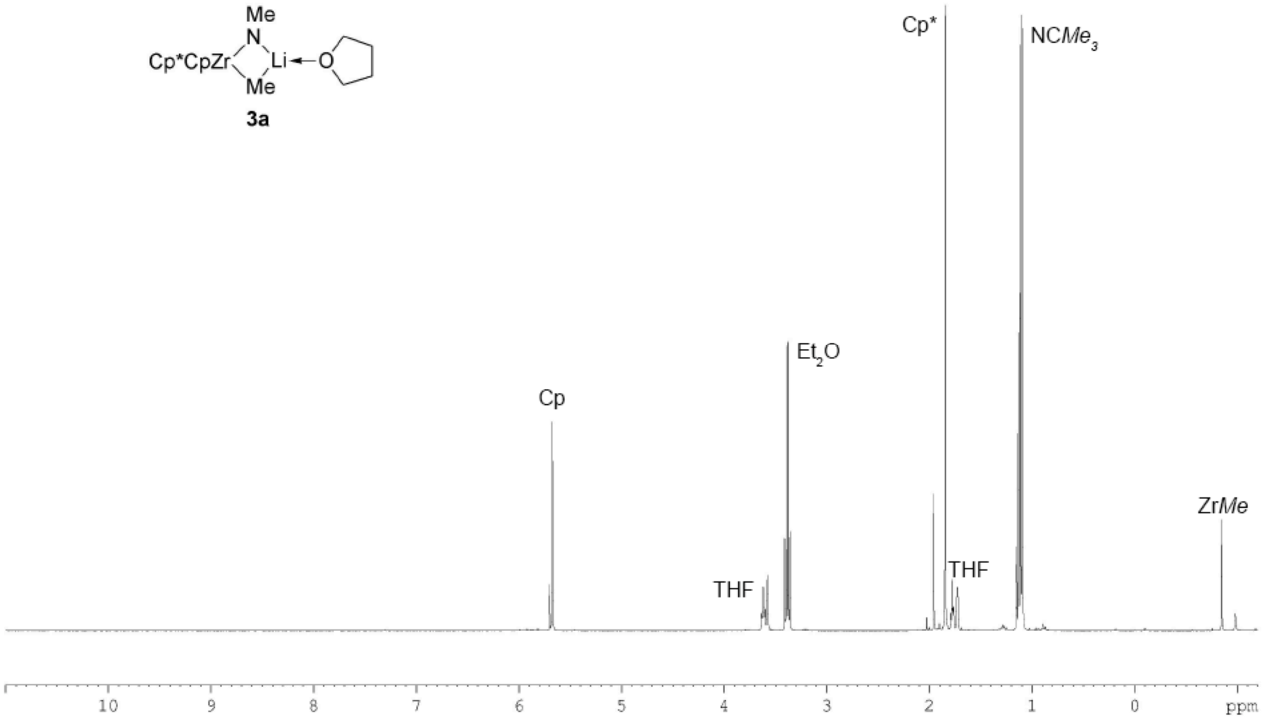
2i

Cp*2Zr NHMe Me
Cp*
NHMe
ZrMe
10
9
8
7
6
5
4
3
2
1
0
ppm
3.00
31.81
3.05



3i

Me
N
Cp*2Zr
Li
O
Me
Cp*
NMe
THF
THF
ZrMe
10
9
8
7
6
5
4
3
2
1
0
ppm
3.00
4.96
30.41
3.57
4.88
2.99



3a

Me
N
Cp*CpZr
Li
O
Me
Cp*
NCMe_3
Et$_2$O
Cp
THF
THF
Zr*Me*
10
9
8
7
6
5
4
3
2
1
0
ppm

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[14] Standard deviation of an observation of unit weight: $[\Sigma\omega(|F_o|^2 - |F_c|^2)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

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