

**Synthesis of Bis(indenyl)zirconium Dihydrides and Subsequent  
Rearrangement to  $\eta^5$ ,  $\eta^3$ -4,5-Dihydroindendiyl Ligands: Evidence for  
Intermediates During the Hydrogenation to Tetrahydroindenyl  
Derivatives.**

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- *Supporting Information* -

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**General Considerations.** All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.<sup>1</sup> Benzene-  $d_6$  and toluene-  $d_8$  for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves or sodium metal. Solutions of 4.0 M HCl and 4.0 M DCl in dioxane were purchased from Aldrich and degassed before use. 1.6 M Solutions of *n*-BuLi in hexanes and MeLi in ether were purchased from Acros and were used as received. Carbon monoxide was purchased from Aldrich. The carbon monoxide was passed through a liquid nitrogen cooled trap before use. Argon, dihydrogen and dideuterium gases were passed through drying columns with MnO and 4 Å molecular sieves prior to admission to the high vacuum line. **1-Cl<sub>2</sub>**, **2-Cl<sub>2</sub>**, **5-Cl<sub>2</sub>**, **1**, **2**, **5**, **8** and **1-THF** were prepared according to literature procedures.<sup>2,3</sup> All calibrated gas bulb experiments were conducted using a 100.1 mL bulb unless noted otherwise.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Inova 400 Spectrometer operating at 399.779 MHz (<sup>1</sup>H) and 110.524 MHz (<sup>13</sup>C). All chemical shifts are reported relative to SiMe<sub>4</sub> using <sup>1</sup>H (residual) or <sup>13</sup>C NMR chemical shifts of the solvent as a secondary standard. <sup>2</sup>H NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 76.740 MHz and the spectra were referenced using an internal benzene- $d_6$  standard.

Gradient selected COSY spectra were acquired with a sweep width of 5.4 kHz. A total of 128 points were collected in the indirectly detected dimension with 4 scans and

2k points per increment. The resulting matrix was zero filled to 1k x 1k complex data points and squared sinusoidal window functions were applied in both dimensions prior to Fourier transform. Gradient selected HSQC spectra were acquired with sweep widths of 5.6 kHz and 21.4 kHz in  $^1\text{H}$  and  $^{13}\text{C}$  dimensions respectively. A total of 200 complex points were collected in the indirectly detected dimension with 12 scans and 2k points per increment. The resulting matrix was zero filled to 1k x 1k complex data points and Gaussian line broadening window functions were applied in both dimensions prior to Fourier transform.

NOESY spectra were acquired with a sweep width of 1.8 kHz and a mixing time of 200 ms in phase-sensitive mode. A total of 64 complex points were collected in the indirectly detected dimension with 16 scans and 1k points per increment. The resulting matrix was zero filled to 2k x 2k complex data points and 90 shifted squared sinusoidal window functions were applied in both dimensions prior to Fourier transform. All 2D spectra were acquired at 23 °C unless otherwise noted.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and were then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with a molybdenum X-ray tube ( $\lambda = 0.71073 \text{ \AA}$ ). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Infrared spectroscopy was conducted on a Mattson RS-

10500 Research Series FT-IR spectrometer calibrated with a polystyrene standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

**Preparation of  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2\text{Zr(CH}_3)_2$  (**1-Me**<sub>2</sub>)).** A 100 mL round-bottomed flask was charged with 0.350 g (0.514 mmol) of **1-Cl**<sub>2</sub> and approximately 15 mL of toluene was added. The resulting yellow solution was chilled in a liquid nitrogen cooled cold well for 20 minutes and 0.71 mL (1.1 mmol) of 1.6 M MeLi was added to the solution over the course of five minutes. The resulting reaction mixture was then evacuated for ten minutes to remove any residual diethyl ether introduced from the MeLi solution. After this procedure, the reaction mixture was stirred overnight. Filtration through Celite followed by solvent removal in vacuo and recrystallization from pentane at -35 °C yields 0.24 g (73%) of an off-white solid identified as **1-Me**<sub>2</sub>. Anal. Calcd. for C<sub>32</sub>H<sub>52</sub>Si<sub>4</sub>Zr: C, 60.02; H, 8.19. Found: C, 59.81; H, 8.54. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  = -0.89 (s, 6H, Zr-CH<sub>3</sub>), 0.35 (s, 36H, SiMe<sub>3</sub>), 6.49 (s, 2H, Cp), 7.05 (m, 4H, Benzo), 7.65 (m, 4H, Benzo). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>):  $\delta$  = 1.95 (SiMe<sub>3</sub>), 42.59 (ZrCH<sub>3</sub>), 114.69, 125.22, 127.14, 128.04, 136.43 (Cp/Benzo).

**Preparation of  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(CMe}_2\text{H)}_2\text{Zr(CH}_3)_2$  (**5-Me**<sub>2</sub>)).** This compound was prepared in a similar manner as **1-Me**<sub>2</sub> using 0.150 g (0.270 mmol) of **5-Cl**<sub>2</sub> and 0.37 mL (mmol) of 1.6 M MeLi yielding 0.120 g (84%) of an off-white solid identified as **5-Me**<sub>2</sub>. Anal. Calcd. for C<sub>32</sub>H<sub>44</sub>Zr: C, 73.92; H, 8.53. Found: C, 74.13; H, 8.81. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  = -0.13 (s, 6H, Zr-CH<sub>3</sub>), 1.07 (d, 8Hz, 12H, CHMe<sub>2</sub>), 1.12 (d, 8Hz, 12H,

CHMe<sub>2</sub>), 2.82 (m, 4H, CHMe<sub>2</sub>), 6.46 (s, 2H, Cp), 6.91 (m, 4H, Benzo), 7.15 (m, 4H, Benzo). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): δ = 21.43 (CHMe<sub>2</sub>), 25.66 (CHMe<sub>2</sub>), 26.00 (CHMe<sub>2</sub>), 36.61 (Zr-CH<sub>3</sub>), 117.24, 120.97, 121.71, 123.21, 125.04 (Cp/Benzo).

**Observation of (η<sup>5</sup>-C<sub>9</sub>H<sub>5</sub>-1,3-(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub>ZrH<sub>2</sub> (1-H<sub>2</sub>).** A J. Young NMR tube was charged with 0.02 g (0.033 mmol) of **1** and dissolved in approximately 0.5 mL of benzene-*d*<sub>6</sub>. On a high vacuum line, the tube was submerged in liquid nitrogen and degassed prior to addition of one atmosphere of dihydrogen. The tube was thawed and shaken until a color change from burgundy to yellow was observed. Observation of the product was conducted in the absence of excess dihydrogen. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 0.29 (s, 36H, SiMe<sub>3</sub>), 6.49 (br s, 2H, Zr-*H*), 6.74 (m, 4H, Benzo), 7.14 (m, 4H, Benzo), 7.83 (s, 2H, Cp).

**Observation of (η<sup>5</sup>-C<sub>9</sub>H<sub>5</sub>-1,3-(SiMe<sub>2</sub>Ph)<sub>2</sub>)<sub>2</sub>ZrH<sub>2</sub> (2-H<sub>2</sub>).** This compound was observed in a similar manner as **1-H<sub>2</sub>** using 0.018 g (0.042 mmol) of **2** and <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 0.30 (s, 12H, SiMe<sub>2</sub>Ph), 0.34 (s, 12H, SiMe<sub>2</sub>Ph), 6.99 (m, 4H, Benzo), 7.14 (br, 8H, Ph), 7.18 (br, 4H, Ph), 7.21 (m, 4H, Benzo), 7.23 (br, 8H, Ph), 7.93 (s, 1H, Cp).

**Observation of (η<sup>5</sup>-C<sub>9</sub>H<sub>5</sub>-1,3-(SiMe<sub>3</sub>)<sub>2</sub>)(η<sup>5</sup>-C<sub>9</sub>H<sub>5</sub>-1,3-(CMe<sub>2</sub>H)<sub>2</sub>)ZrH<sub>2</sub> (8-H<sub>2</sub>).** This compound was observed in a similar manner to **1-H<sub>2</sub>** using 0.015 g (0.03 mmol) of **8** dissolved in 0.5 mL of benzene-*d*<sub>6</sub>. Solvent was removed from the sample and recrystallization in pentane afforded solid suitable for elemental analysis. Anal. Calcd. for C<sub>30</sub>H<sub>44</sub>Si<sub>2</sub>Zr: C, 65.27; H, 8.03. Found: C, 65.37; H, 8.13. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ =

0.29 (s, 18H,  $\text{SiMe}_3$ ), 1.15 (d, 8 Hz, 12H,  $\text{CHMe}_2$ ), 2.81 (m, 1H,  $\text{CHMe}_2$ ), 6.61 (br s, 2H, Zr-H), 6.74 (m, 2H, Benzo), 6.83 (m, 2H, Benzo), 7.04 (m, 2H, Benzo), 7.21 (m, 2H, Benzo), 7.70 (s, 1H, Cp), 7.80 (s, 1H, Cp).

**Preparation of  $(\eta^5\text{-C}_9\text{H}_9\text{-1,3-(CHMe}_2)_2)_2\text{ZrH}_2$  (**5-THI-H<sub>2</sub>**).** This compound was prepared in a similar manner as **1-THI-H<sub>2</sub>**, using 0.105 g (0.21 mmol) of **5**. Recrystallization of the resulting foam in pentane at  $-35\text{ }^\circ\text{C}$  yields 0.042 g (39%) of **5-THI-H<sub>2</sub>** as an off-white solid. Anal. Calcd. for  $\text{C}_{30}\text{H}_{48}\text{Zr}$ : C, 72.07; H, 9.68. Found: C, 71.85; H, 9.64.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  = 1.10 (d, 7Hz, 12H,  $\text{CHMe}_2$ ), 1.18 (d, 7Hz, 12H,  $\text{CHMe}_2$ ), 1.76 (br, 4H, THI), 2.14 (br, 4H, THI), 2.78 (br, 4H, THI), 2.83 (br, 4H, THI), 2.97 (m, 4H,  $\text{CHMe}_2$ ), 5.43 (s, 2H, Cp), 7.07 (s, 2H, Zr-H).  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  = 23.67, 24.51, 25.53, 26.52, 28.67 ( $\text{CHMe}_2/\text{THI}$ ), 97.86, 125.70, 129.34 (Cp).

**Preparation of  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)(\eta^5, \eta^3\text{-C}_9\text{H}_6\text{-1,3-(SiMe}_3)_2)\text{ZrH}$  (**1-syn-DHID-H**).**

A J. Young NMR tube containing 0.025 mmol of **1-H<sub>2</sub>** in benzene- $d_6$  was allowed to stand at  $23\text{ }^\circ\text{C}$  for approximately 1 hour.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  = 0.24 (s, 9H,  $\text{SiMe}_3$ ), 0.27 (s, 9H,  $\text{SiMe}_3$ ), 0.31 (s, 9H,  $\text{SiMe}_3$ ), 0.41 (s, 9H,  $\text{SiMe}_3$ ), 1.25 (s, 1H, Zr-H), 1.93 (d, 1H, 13Hz,  $\text{CH}_2$ ), 2.47 (m, 1H,  $\text{CH}_2$ ), 3.20 (br, 1H, allyl CH), 4.77 (br, 1H, allyl CH), 5.21 (br, 1H, allyl CH), 5.87 (s, 1H, Cp), 6.86 (m, 2H, Benzo), 7.15 (s, 1H, Cp), 7.43 (m, 1H, Benzo), 7.48 (m, 1H, Benzo).  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  = 1.16, 1.50, 1.99, 2.73 ( $\text{SiMe}_3$ ), 22.81, 41.51, 97.91, 101.55, 105.18, 105.57, 106.09, 109.24, 111.22, 118.82, 123.19, 123.57, 126.02, 126.16, 126.27, 131.11, 131.11 (Cp/Benzo). One Cp/Benzo resonance not located.

**Preparation of  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)(\eta^5, \eta^3\text{-C}_9\text{H}_6\text{-1,3-(SiMe}_3)_2)\text{ZrH}$  (1-*anti*-DHID-H).** A J. Young NMR tube was charged with 0.018 g (0.029 mmol) of **1** and 100  $\mu\text{L}$  (> 50 equivalents) of THF. The contents of the tube were frozen in liquid nitrogen, degassed and one atmosphere of dihydrogen added. After thawing the benzene solution, the tube was vigorously shaken for approximately two minutes during which time the solution changed color from blood red to light yellow orange. The observation of the product was conducted in the absence of excess dihydrogen.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  = 0.23 (s, 9H, SiMe<sub>3</sub>), 0.25 (s, 9H, SiMe<sub>3</sub>), 0.34 (s, 9H, SiMe<sub>3</sub>), 0.41 (s, 9H, SiMe<sub>3</sub>), 1.49 (br, 1H, allyl CH), 2.55 (d, 12Hz, 1H, CH<sub>2</sub>), 3.04 (m, 1H, CH<sub>2</sub>), 4.78 (br, 1H, allyl CH), 5.24 (s, 1H, Cp), 6.44 (d, 7Hz, 1H, allyl CH), 6.76 (s, 1H, Cp), 6.88 (m, 2H, Benzo), 7.60 (br, 2H, Benzo).  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  = 1.30, 1.56, 1.97, 2.13 (SiMe<sub>3</sub>), 21.43, 34.92, 96.11, 99.28, 104.08, 105.67, 107.47, 108.94, 114.77, 122.39, 123.28, 123.63, 126.17, 126.29, 126.97, 129.86, 131.94, 145.77 (Cp/Benzo).

**Preparation of  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_2\text{Ph})_2)(\eta^5, \eta^3\text{-C}_9\text{H}_6\text{-1,3-(SiMe}_2\text{Ph})_2)\text{ZrH}$  (2-*syn*-DHID-H).** This compound was observed in a similar manner as **1-syn-DHID-H** using 0.016 mmol of **2-H<sub>2</sub>**. Solvent removal and recrystallization in pentane affords material suitable for elemental analysis when **2-H<sub>2</sub>** is generated on larger scales. Anal. Calcd. for C<sub>50</sub>H<sub>56</sub>Si<sub>4</sub>Zr: C, 69.78; H, 6.56. Found: C, 69.42; H, 6.45.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  = 0.40 (s, 3H, SiMe<sub>2</sub>Ph), 0.47 (s, 3H, SiMe<sub>2</sub>Ph), 0.59 (s, 6H, 2SiMe<sub>2</sub>Ph), 0.61 (s, 3H, SiMe<sub>2</sub>Ph), 0.68 (s, 6H, SiMe<sub>2</sub>Ph), 0.84 (s, 3H, SiMe<sub>2</sub>Ph), 1.53 (s, 1H, Zr-H), 1.78 (d, 1H, 12Hz, CH<sub>2</sub>), 2.46 (m, 1H, allyl CH), 3.22 (br, 1H, allyl CH), 4.65 (br, 1H, allyl CH), 5.01



(br, 1H, allyl *CH*), 6.01 (s, 1H, Cp), 6.73 (m, 2H, Benzo/Ph), 7.09 (m, 6H, Benzo/Ph), 7.18 (m, 8H, Benzo/Ph), 7.27 (m, 2H, Benzo/Ph), 7.32 (m, 2H, Benzo/Ph), 7.38 (m, 2H, Benzo/Ph), 7.57 (m, 2H, Benzo/Ph).  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  = -0.66, -0.34, -0.32, -0.30, 0.10, 0.61, 1.08, 2.29 ( $\text{SiMe}_2\text{Ph}$ ), 22.57, 41.41, 98.35, 102.96, 103.29, 104.13, 105.91, 107.38, 109.32, 120.86, 123.32, 123.67, 123.71, 123.93, 124.30, 125.74, 125.94, 126.58, 129.39, 129.51, 129.63, 129.67, 129.72, 129.96, 130.97, 137.59, 139.88, 140.18, 140.66, 142.13, 147.89, 148.28 (Cp/Benzo/Ph). Two Cp/Benzo/Ph resonances not located.

**Observation of 2-*anti*-DHID-H.** This molecule was prepared in a similar manner as **1-*anti*-DHID-H** using a 0.025 mmol sample of **5**. Conversion to **2-*anti*-DHID-H** occurs over the course of minutes.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  = 0.15 (s, 3H,  $\text{SiMe}_2\text{Ph}$ ), 0.44 (s, 3H,  $\text{SiMe}_2\text{Ph}$ ), 0.46 (s, 3H,  $\text{SiMe}_2\text{Ph}$ ), 0.51 (s, 3H,  $\text{SiMe}_2\text{Ph}$ ), 0.53 (s, 3H,  $\text{SiMe}_2\text{Ph}$ ), 0.60 (s, 3H,  $\text{SiMe}_2\text{Ph}$ ), 0.63 (s, 3H,  $\text{SiMe}_2\text{Ph}$ ), 0.70 (s, 1H, Zr-*H*), 0.80 (s, 3H,  $\text{SiMe}_2\text{Ph}$ ), 2.35 (d, 11Hz, 1H,  $\text{CH}_2$ ), 2.95 (m, 1H,  $\text{CH}_2$ ), 4.54 (m, 1H, allyl *CH*), 5.24 (s, 1H, Cp), 6.22 (d, 7Hz, 1H, allyl *CH*), 6.23 (s, 1H, Cp), 6.76 (m, 1H, Benzo), 7.00 (m, 1H, Benzo), 7.11 (m, 6H, Ph), 7.18 (m, 7H, Ph), 7.26 (m, 2H, Ph), 7.29 (m, 2H, Ph), 7.32 (d, 7Hz, 1H, Ph), 7.50 (m, 2H, Ph), 7.60 (d, 7Hz, 2H, Benzo). One allyl *CH* not found.

**Preparation of  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(CHMe}_2)_2)(\eta^5, \eta^3\text{-C}_9\text{H}_6\text{-1,3-(CMe}_2\text{H)}_2)\text{ZrH}$  (**5-*anti*-DHID-H**).** This molecule was prepared in a similar manner as **1-*anti*-DHID-H** using a 0.027 mmol sample of **5**. Conversion to **5-*anti*-DHID-H** occurs over the course of an hour. Solvent removal and recrystallization in pentane affords material suitable for

elemental analysis and X-ray diffraction studies when **5-anti-DHID-H** is generated on larger scales. Anal. Calcd. for  $C_{30}H_{40}Zr$ : C, 73.26; H, 8.20. Found: C, 72.84; H, 8.27.  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  = 1.02 (d, 7Hz, 6H,  $CHMe_2$ ), 1.13 (m, 12H,  $CHMe_2$ ), 1.35 (m, 6H,  $CHMe_2$ ), 1.78 (d, 7Hz, 1H,  $CH_2$ ), 2.05 (m, 1H,  $CHMe_2$ ), 2.48 (m, 1H,  $CHMe_2$ ), 2.60 (m, 1H, allyl  $CH$ ), 2.99 (m, 1H,  $CHMe_2$ ), 3.41 (m, 1H,  $CHMe_2$ ), 4.56 (t, 7Hz, 1H, allyl  $CH$ ), 5.04 (s, 1H, Cp), 6.72 (s, 1H, Cp), 6.80 (d, 7Hz, 1H, allyl  $CH$ ), 6.86 (m, 1H, Benzo), 6.99 (m, 1H, Benzo), 7.33 (m, 2H, Benzo).  $^{13}C$  NMR (benzene- $d_6$ ):  $\delta$  = 19.53, 21.09, 22.17, 23.32, 23.11, 24.11, 26.09, 26.62, 28.12, 28.71, 29.79, 37.31 ( $CHMe_2$ ), 49.66, 97.57, 99.15, 107.93, 111.87, 113.91, 113.97, 114.09, 116.47, 120.88, 120.96, 121.50, 121.82, 125.07, 125.30, 125.55, 127.20 (Cp/Benzo). One Cp/Benzo resonance not located.

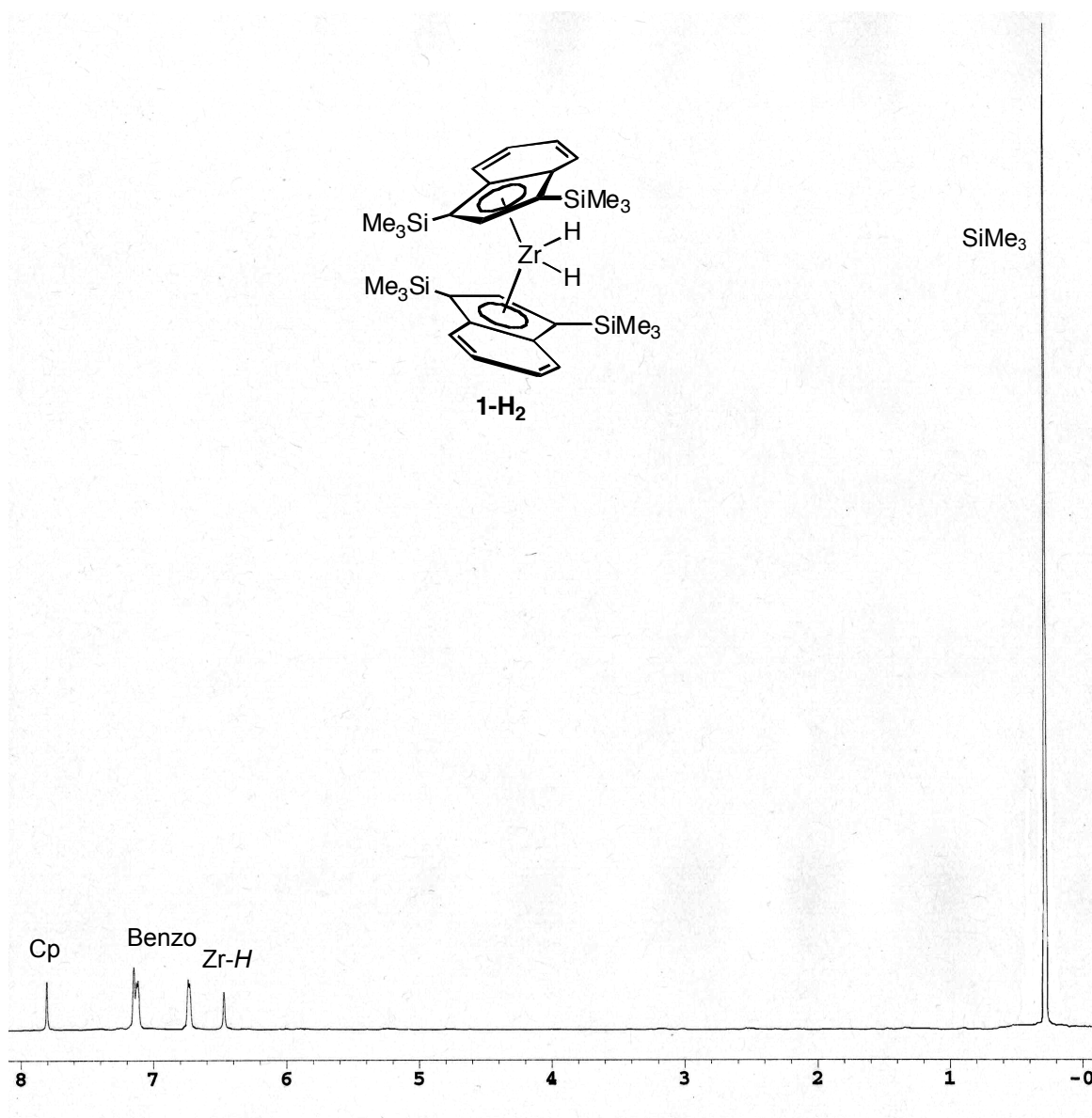
**Preparation of  $(\eta^5-C_9H_5-1,3-(SiMe_3)_2)(\eta^5, \eta^3-C_9H_6-1,3-(CMe_2H)_2)ZrH$  (8-syn-DHID-**

**H)**. This compound was prepared in a similar manner as **1-syn-DHID-H** using 0.020 mmol of **8**. By  $^1H$  NMR spectroscopy, a 5:1 preference of two isomers exists.  $^1H$  NMR (benzene- $d_6$ ): (major)  $\delta$  = 0.30 (s, 9H,  $SiMe_3$ ), 0.37 (s, 9H,  $SiMe_3$ ), 1.01 (d, 8Hz, 3H,  $CHMe_2$ ), 1.09 (d, 8Hz, 3H,  $CHMe_2$ ), 1.25 (d, 8Hz, 3H,  $CHMe_2$ ), 1.44 (d, 8Hz, 3H,  $CHMe_2$ ), 2.04 (d, 12Hz, 1H,  $CH_2$ ), 2.10 (m, 1H,  $CHMe_2$ ), 2.59 (m, 1H,  $CH_2$ ), 3.13 (m, 1H,  $CHMe_2$ ), 3.27 (br, 1H,  $CH$ ), 4.81 (br, 1H,  $CH$ ), 5.12 (d, 7Hz, 1H,  $CH$ ), 5.42 (s, 1H, Cp), 6.79 (s, 1H, Cp), 6.91 (m, 1H, Benzo), 7.34 (d, 10Hz, 1H, Benzo), 7.45 (d, 10Hz, 1H, Benzo). One Benzo resonance and the Zr-H were not located. (minor) 0.36 (s, 9H,  $SiMe_3$ ), 0.41 (s, 9H,  $SiMe_3$ ), 1.14 (br, 6H,  $CHMe_2$ ), 1.34 ((d, 8Hz, 3H,  $CHMe_2$ ), 1.62 (br, 1H,  $CH_2$ ), 2.81 (m, 1H,  $CH_2$ ), 4.59 (br, 1H,  $CH$ ), 5.15 (s, 1H, Cp), 6.72 (m, 1H, Benzo), 7.04 (br, 1H, Benzo), 7.12 (br, 2H, Benzo). One  $CHMe_2$ , one Zr-H, two allyl, and one

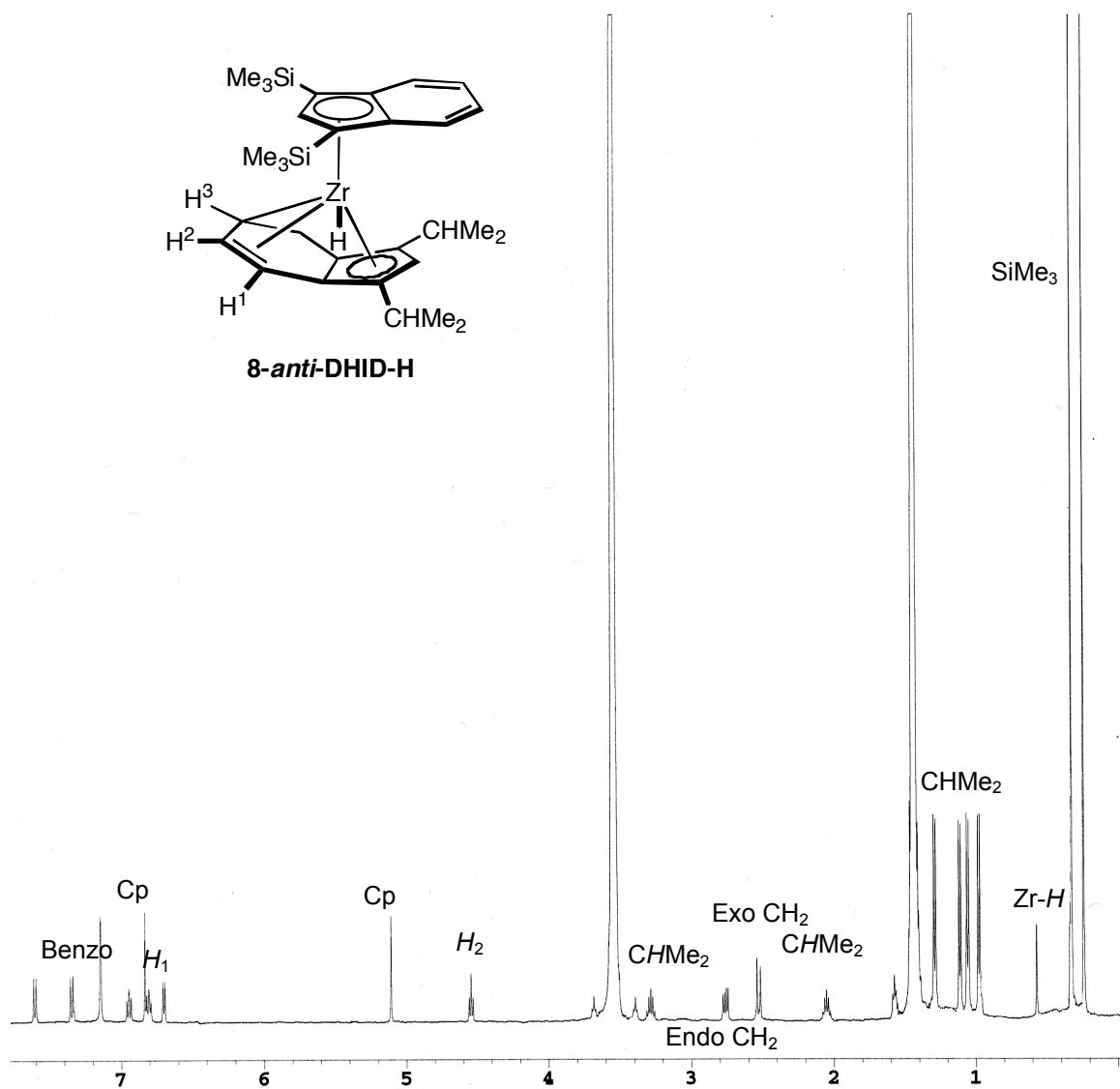
Benzo resonance of minor isomer not located.  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  = (major) 1.18, 1.48 ( $\text{SiMe}_3$ ), 20.64, 22.16, 24.08, 25.01, 27.65, 28.17, 28.26 ( $\text{CHMe}_2/\text{CH}_2$ ), 43.53, 89.66, 98.27, 102.27, 106.41, 107.87, 116.21, 117.50, 122.51, 122.99, 124.15, 124.53, 125.15, 125.51, 125.82, 127.63, 130.81 (Cp/Benzo). (minor) 1.26, 1.42 ( $\text{SiMe}_3$ ), 21.28, 21.71, 23.70, 24.68, 24.89, 27.29, 28.50 ( $\text{CHMe}_2/\text{CH}_2$ ), 86.40, 93.40, 95.49, 98.22, 98.44, 104.43, 105.02, 109.88, 120.77, 122.21, 122.81, 126.61, 127.05, 127.56 (Cp/Benzo). Three Cp/Benzo resonances not located.

**Observation of  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)(\eta^5, \eta^3\text{-C}_9\text{H}_6\text{-1,3-(CMe}_2\text{H})_2\text{)ZrH}$  (**8-anti-DHID-H**).** This molecule was prepared in a similar manner as **1-anti-DHID-H** using a 0.022 mmol sample of **8**. Conversion to two isomers of **8-anti-DHID-H** in an approximate 5:1 ratio occurs over the course of minutes.  $^1\text{H}$  NMR (benzene- $d_6$ ): (major)  $\delta$  = 0.28 (s, 9H,  $\text{SiMe}_3$ ), 0.36 (s, 9H,  $\text{SiMe}_3$ ), 0.66 (s, 1H, Zr- $H$ ), 1.01 (d, 7Hz, 3H,  $\text{CHMe}_2$ ), 1.11 (d, 7Hz, 3H,  $\text{CHMe}_2$ ), 1.14 (d, 7Hz, 3H,  $\text{CHMe}_2$ ), 1.34 (d, 7Hz, 3H,  $\text{CHMe}_2$ ), 2.10 (d, 7Hz, 1H,  $\text{CHMe}_2$ ), 2.61 (d, 12Hz, 1H,  $\text{CH}_2$ ), 2.81 (m, 1H,  $\text{CH}_2$ ), 3.35 (m, 1H,  $\text{CHMe}_2$ ), 4.60 (m, 1H, allyl  $\text{CH}$ ), 5.16 (s, 1H, Cp), 6.77 (d, 7Hz, 1H, allyl  $\text{CH}$ ), 6.81 (m, 1H, Benzo), 6.95 (m, 1H, Benzo), 7.37 (d, 8Hz, 1H, Benzo), 7.64 (d, 8Hz, 1H, Benzo). (minor)  $\delta$  = 0.38 (s, 9H,  $\text{SiMe}_3$ ), 0.40 (s, 9H,  $\text{SiMe}_3$ ), 0.55 (s, 1H, Zr- $H$ ), 1.09 (d, 8Hz, 3H,  $\text{CHMe}_2$ ), 1.21 (d, 8Hz, 3H,  $\text{CHMe}_2$ ), 1.25 (d, 8Hz, 3H,  $\text{CHMe}_2$ ), 1.31 (d, 8Hz, 3H,  $\text{CHMe}_2$ ), 2.56 (d, 12Hz, 1H,  $\text{CH}_2$ ), 3.07 (m, 1H,  $\text{CH}_2$ ), 3.27 (m, 1H,  $\text{CHMe}_2$ ), 4.42 (m, 1H, allyl  $\text{CH}$ ), 5.08 (s, 1H, Cp), 6.40 (d, 7Hz, 1H, allyl  $\text{CH}$ ), 6.76 (m, 1H, Benzo), 7.27 (d, 8Hz, 1H, Benzo), 7.34 (d, 8Hz, 1H, Benzo). One  $\text{CHMe}_2$ , one allyl  $\text{CH}$ , and one Benzo resonance not located.  $^{13}\text{C}$  NMR (benzene- $d_6$ ): (major)  $\delta$  = 1.17 (2  $\text{SiMe}_3$ ), 19.87 ( $\text{CH}_2$ ), 21.66, 23.65,

24.67, 27.23, 28.43, 29.76 (CHMe<sub>2</sub>), 36.36 (allyl CH), 86.33, 98.15, 98.44, 103.58,  
104.97, 109.85, 114.56, 116.19, 122.21, 122.83, 124.14, 126.51, 127.10, 127.55, 130.75  
(Benzo/DHID), 131.69 (Cp).

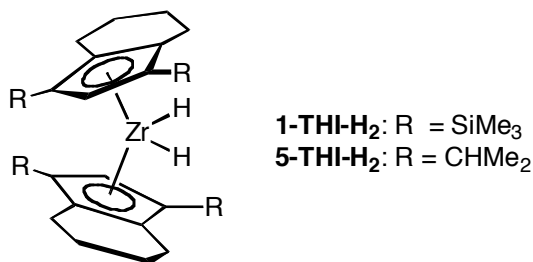


**Figure S1.**  $^1\text{H}$  NMR spectrum of  $\mathbf{1-H_2}$  in benzene- $d_6$ .



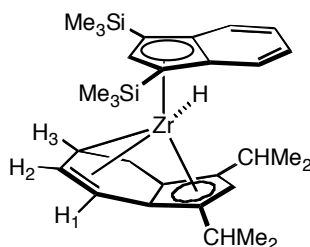
**Figure S2.** <sup>1</sup>H NMR spectrum of the major isomer of **8-anti-DHID-H** with excess THF present in benzene-*d*<sub>6</sub>.

**Assignment of the  $^1\text{H}$  NMR Spectrum of 1-THI- $\text{H}_2$  by 2-D NMR Spectroscopy.**



The *endo* hydrogens on the tetrahydroindenyl ligands of **1-THI- $\text{H}_2$**  were assigned from a NOESY NMR experiment conducted at 23 °C with a mixing time of 200 ms. Intense crosspeaks are observed between the zirconium hydride at 6.61 ppm and two tetrahydroindenyl protons centered at 2.09 and 2.68 ppm, indicating that these two protons are *endo* with respect to the metal center. An additional *g*-HSQC experiment at 23 °C allows assignment of the *exo* tetrahydroindenyl hydrogens and their position relative to the *endo* hydrogens. Based on correlations of the methylene hydrogens to the identical carbons, the resonance at 2.79 ppm is assigned as the *exo* hydrogen on the same carbon as the 2.68 ppm *endo* hydrogen and the THI resonance at 1.75 ppm is assigned as the *exo* hydrogen on the same carbon as the 2.09 ppm *endo* hydrogen.

Full  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignment of the major isomer of **8-syn-DHID-H**.



Hydrogen assignment	Major isomer $^1\text{H}$ shift ppm	Major isomer $^{13}\text{C}$ shift ppm
DHID- $\text{H}_1$	5.12	98.27
DHID- $\text{H}_2$	4.81	107.97
DHID- $\text{H}_3$	3.27	43.53
Endo-DHID- $\text{CH}_2$	2.59	20.64
Exo-DHID- $\text{CH}_2$	2.04	20.64
Cp-DHID	5.42	102.27
Cp-Indenyl	6.79	125.51
Benzo (proximal)	7.34	124.15
Benzo (proximal)	7.45	125.82
Benzo (distal)	6.79	122.99
Benzo (distal)	6.91	124.53
Zr-H	Not located	--

$^{13}\text{C}$  shifts assigned directly from a g-HSQC spectrum

Carbon Assignment	Major isomer $^{13}\text{C}$ shift ppm
Benzo bridgehead 1	106.41
Benzo bridgehead 2	125.15
Quaternary Cp carbon 1	127.63
Quaternary Cp carbon 2	130.81
DHID bridgehead 1	89.66
DHID bridgehead 2	117.50
Quaternary DHID Cp carbon 1	116.21
Quaternary DHID Cp carbon 2	122.51

$^{13}\text{C}$  shifts assigned directly from a g-HMBC spectrum

From 2D NOESY (23 °C, 250 ms mixing time):

**Endo  $sp^3$  hybridized hydrogen:**

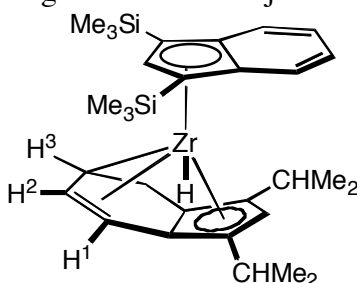
Shows NOE enhancement to one isopropyl methine and no enhancement to the trimethylsilyl resonances

**Proximal alkene hydrogen ( $\text{H}_1$ ):**

Shows NOE enhancement to  $\text{H}_2$  and the complimentary isopropyl methine.



Full  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignment of the major isomer of **8-*anti*-DHID-H**.



Hydrogen assignment	Major isomer $^1\text{H}$ shift ppm	Major isomer $^{13}\text{C}$ shift ppm
DHID- $\text{H}_1$	6.77	98.44
DHID- $\text{H}_2$	4.60	109.85
DHID- $\text{H}_3$	1.62	36.36
<i>Endo</i> -DHID- $\text{CH}_2$	2.81	19.87
<i>Exo</i> -DHID- $\text{CH}_2$	2.61	19.87
Cp-DHID	5.15	98.15
Cp-Indenyl	6.84	127.10
Benzo (proximal)	7.37	127.55
Benzo (proximal)	7.64	124.14
Benzo (distal)	6.81	122.21
Benzo (distal)	6.95	122.83
Zr-H	0.66	--

$^{13}\text{C}$  shifts assigned directly from a *g*-HSQC spectrum

Carbon Assignment	Major isomer $^{13}\text{C}$ shift ppm
Benzo bridgehead 1	103.58
Benzo bridgehead 2	126.51
Quaternary Cp carbon 1	130.32
Quaternary Cp carbon 2	131.37
DHID bridgehead 1	86.33
DHID bridgehead 2	116.19
Quaternary DHID Cp carbon 1	104.97
Quaternary DHID Cp carbon 2	114.56

$^{13}\text{C}$  shifts assigned directly from a *g*-HMBC spectrum

From 2D NOESY (23 °C, 250 ms mixing time):

**Zirconium Hydride:**

Shows NOE enhancement to one isopropyl methine and no enhancement to the *endo* methylene hydrogen.

***Endo*  $\text{sp}^3$  hybridized hydrogen:**

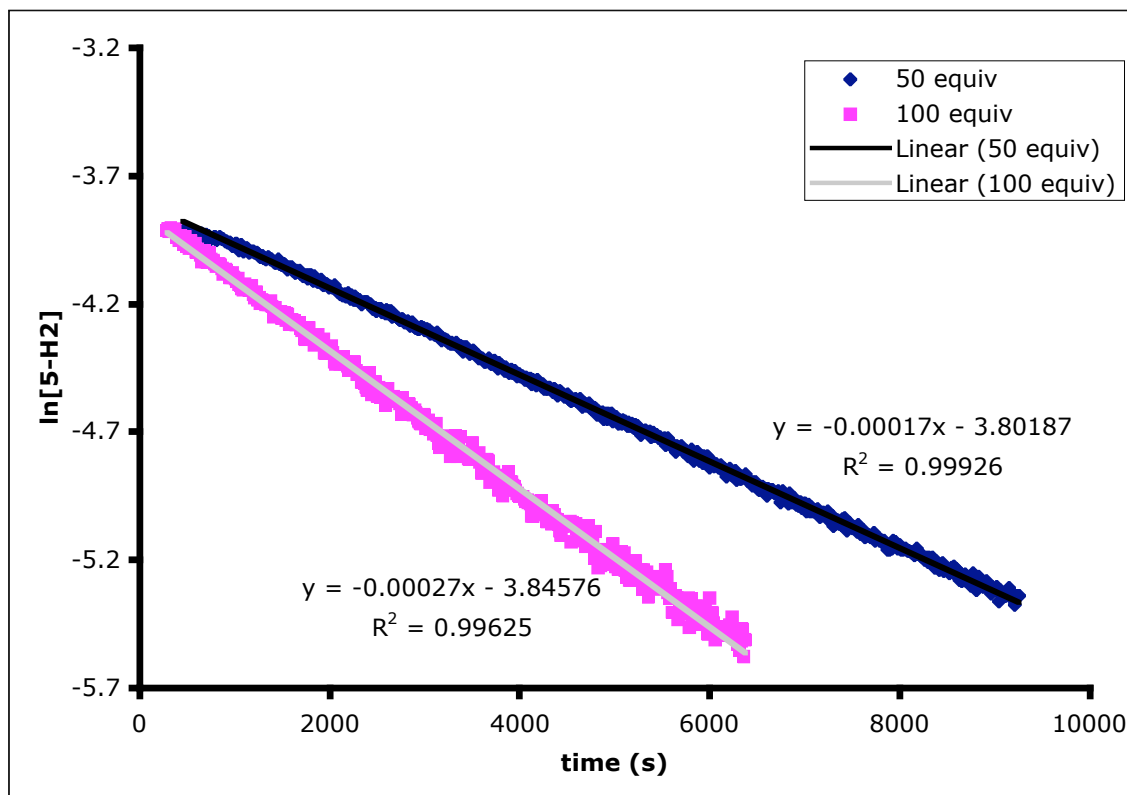
Shows NOE enhancement to the complimentary isopropyl methine.

**Proximal alkene hydrogen ( $\text{H}_1$ ):**

Shows NOE enhancement to the same isopropyl methine as the zirconium hydride.

Kinetic data for **5-anti-DHID-H** formation as a function of THF concentration

All kinetic runs were performed using 0.4 mL of 0.02M solutions of **5-H<sub>2</sub>**. The appropriate amount of THF was added by calibrated gas bulb on a vacuum line and the conversion to **5-anti-DHID-H** was monitored in an NMR probe at 23°C by a <sup>1</sup>H NMR arrayed experiment. Single scans were collected every 15 seconds and integration of the disappearance of the Zr-H resonances were used to extract the appropriate rate constants. Examining appearance of **5-anti-DHID-H** also gave comparable rates. Representative plots for the 50 and 100 equivalent runs are shown in a graph below.



## References.

<sup>1</sup> Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

<sup>2</sup> Bradley, C.A.; Lobkovsky, E.; Chirik, P.J. *J. Am. Chem. Soc.* **2003**, *125*, 8110.

<sup>3</sup> Bradley, C.A.; Flores-Torres, S.; Lobkovsky, E.; Abruña, H.D.; Chirik, P.J. *Organometallics* **2004**, *23*, 5332.