

Formation of Trivalent Zirconocene Complexes from *ansa*-Zirconocene-Based Olefin-Polymerization Precatalysts - an EPR- and NMR-Spectroscopic Study.

Taylor N. Lenton,<sup>H</sup> John E. Bercaw,<sup>\*,H</sup> Valentina N. Panchenko,<sup>1</sup> Vladimir A. Zakharov,<sup>1</sup> Dmitrii E. Babushkin,<sup>\*,1</sup> Igor E. Soshnikov,<sup>1</sup> Evgenii P. Talsi,<sup>1</sup> Hans H. Brintzinger<sup>\*,§</sup>

<sup>H</sup> Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, USA.

<sup>1</sup> Boreskov Institute of Catalysis, Russian Academy of Science, Siberian Branch, Pr. Lavrentieva 5, 630090 Novosibirsk, Russian Federation,

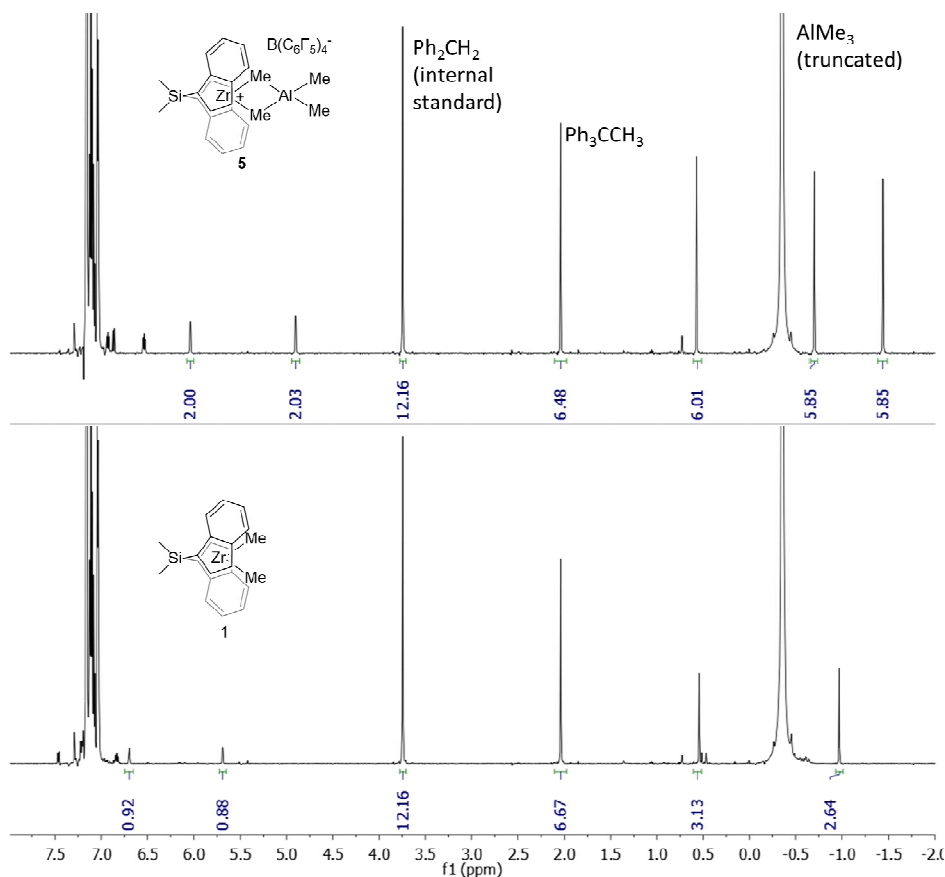
<sup>§</sup> Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany.

e-mail: Bercaw@caltech.edu; Dimi@catalysis.ru, hans.brintzinger@uni-konstanz.de

Supporting Information.

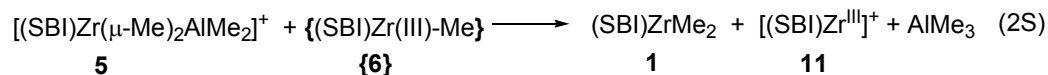
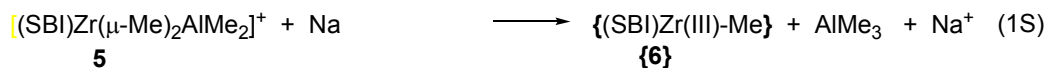
- S2 <sup>1</sup>H NMR spectra, formation of (SBI)ZrMe<sub>2</sub> by reduction of [(SBI)Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> with NaHg
- S3 Modeling of the EPR signal assigned to (SBI)Zr<sup>III</sup>(μ-H)<sub>2</sub>AlR<sub>2</sub>
- S4 Modeling of the EPR signal assigned to (SBI)Zr<sup>III</sup>-<sup>i</sup>Bu
- S5 EPR spectra, reaction of (SBI)Zr<sup>III</sup>-<sup>i</sup>Bu with PMe<sub>2</sub>Ph
- S6 EPR spectra, conversion of (SBI)Zr<sup>III</sup>-(μ-H)<sub>2</sub>AlR<sub>2</sub> to (SB)IZr<sup>III</sup>-<sup>i</sup>Bu and *vice versa*
- S7 EPR spectra, reaction of (SBI)Zr<sup>III</sup>(μ-Cl)<sub>2</sub>AlR<sub>2</sub> with AlMe<sub>3</sub>
- S8 EPR spectra, reaction of (SBI)Zr<sup>III</sup>-(μ-Cl)<sub>2</sub>AlR<sub>2</sub> with HAl<sup>i</sup>Bu<sub>2</sub>
- S9 Preparation of crystalline (SBI)Zr<sup>III</sup>(μ-Cl)<sub>2</sub>AlR<sub>2</sub> and structure determination
- S10 EPR spectra, conversion of [(SBI)Zr<sup>III</sup>]<sup>+</sup> to (SBI)Zr<sup>III</sup>-(μ-H)<sub>2</sub>AlR<sub>2</sub>
- S11 EPR spectra, reaction of (SBI)ZrMe<sub>2</sub> with HAlMe<sub>2</sub> and AlMe<sub>3</sub>
- S12 <sup>1</sup>H NMR spectra, intermediates in the reaction of (SBI)ZrMe<sub>2</sub> with HAl<sup>i</sup>Bu<sub>2</sub>
- S13 Paramagnetic <sup>1</sup>H NMR signals of (SBI)Zr<sup>III</sup>-(μ-Cl)<sub>2</sub>AlMe<sub>2</sub>
- S14 Time course of isobutane evolution
- S15 Experimental Details

Formation of (SBI)ZrMe<sub>2</sub> during reduction of [(SBI)Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> with NaHg

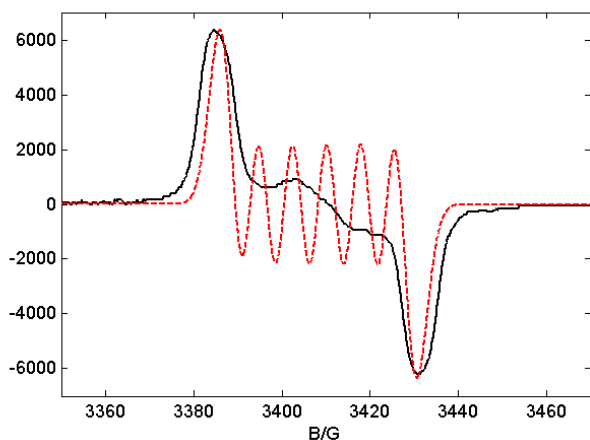


**Figure S1.** <sup>1</sup>H NMR spectra of a 3.5 mM solution of [(SBI)Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> in C<sub>6</sub>D<sub>6</sub>, prepared by reaction of (SBI)ZrMe<sub>2</sub> with 1 equiv. of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> in the presence of excess AlMe<sub>3</sub> (top) and of the same solution after shaking with ca. 100 mg of 1%-NaHg for 1 h (bottom). The signal of diphenylmethane (Ph<sub>2</sub>CH<sub>2</sub>) at 3.7 ppm was used as internal standard for quantitation of the amounts of (SBI)ZrMe<sub>2</sub> formed in relation to that of [(SBI)Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> reduced.

Formation of ½ equiv of (SBI)ZrMe<sub>2</sub> upon reduction of the cation [(SBI)Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> is explained in the main text by equations 12 and 13. An alternative explanation for these observations would be the intermediary formation of (SBI)Zr(III)-Me (**{6}**, equations 1S and 2S).

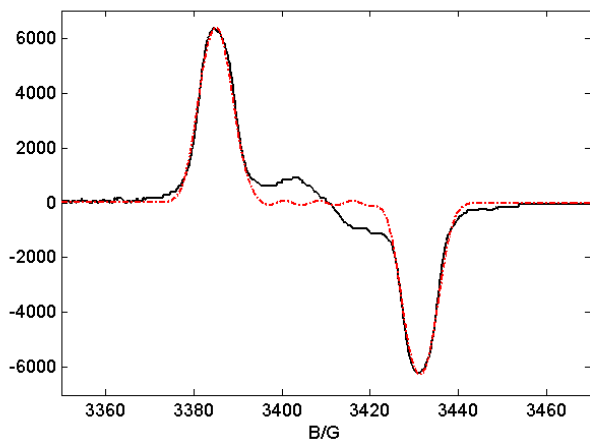


Modeling of the EPR signal assigned to  $(\text{SBI})\text{Zr}^{\text{III}}(\mu\text{-H})_2\text{AlR}_2$



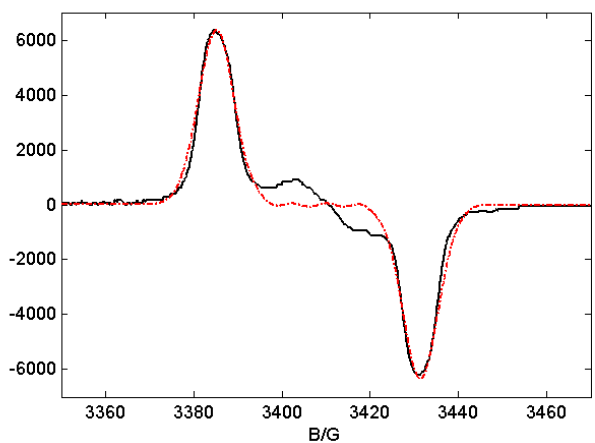
g2=1.9716;  
A2Al=21.3; (in MHz)  
lw2=.7; (in mT)  
Sys2.Nucs='27Al';  
Sys2.A=[A2Al A2Al A2Al]; (in MHz)

**Figure S2.** Hyperfine interaction with one  $^{27}\text{Al}$  nucleus with  $a(^{27}\text{Al}) = 7.6 \text{ G}$  (21.3 MHz) and line width  $lw2 = 7 \text{ G}$  gives a 6-line signal.



g2=1.9716;  
A2Al=21.3; (in MHz)  
lw2= 1.1; (in mT)  
Sys2.Nucs='27Al';  
Sys2.A=[A2Al A2Al A2Al]; (in MHz)

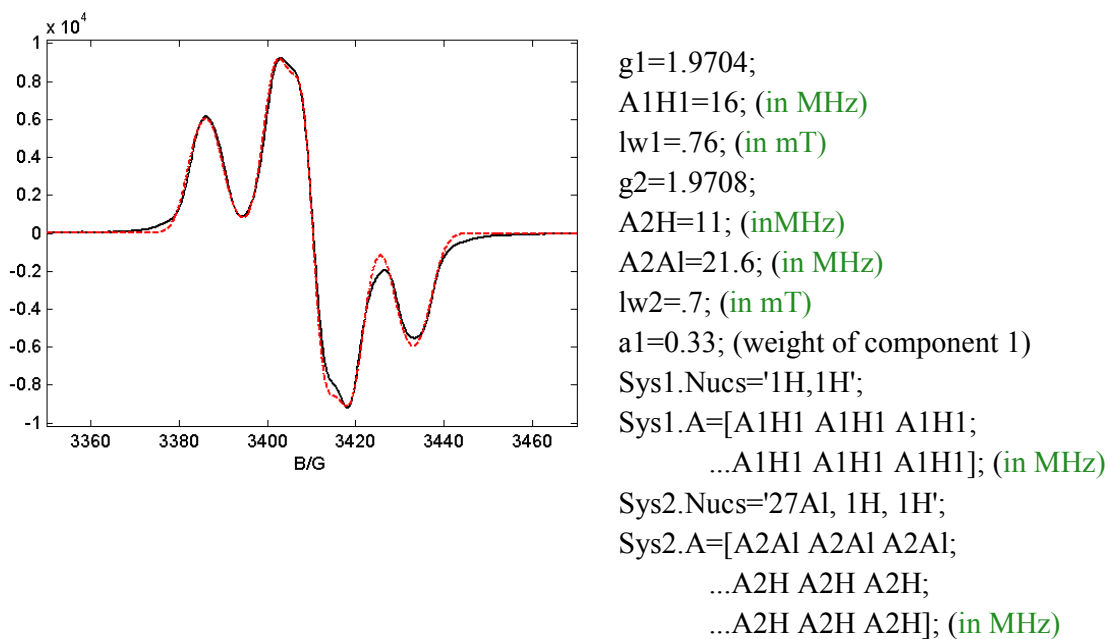
**Figure S3.** The mid-section of the signal is evened out by a larger line width of  $lw2 = 11 \text{ G}$ .



g2=1.9716;  
A2H=11; (in MHz)  
A2Al=21.3; (in MHz)  
lw2=.7; (in mT)  
Sys2.Nucs='27Al, 1H, 1H';  
Sys2.A=[A2Al A2Al A2Al;  
...A2H A2H A2H;  
... A2H A2H A2H]; (in MHz)

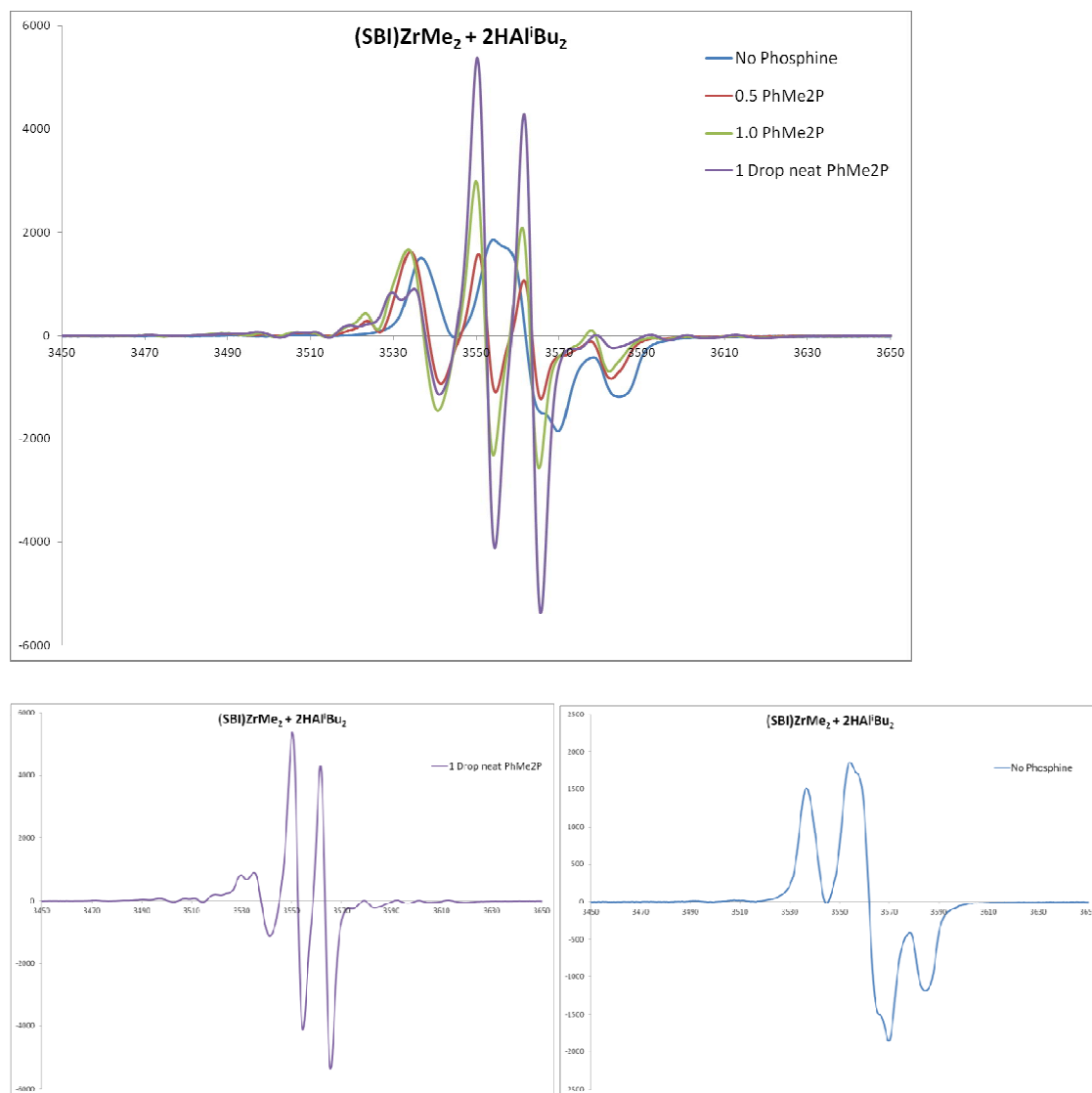
**Figure S4.** The same effect is brought about, at line width  $lw2 = 7 \text{ G}$ , by interaction with two  $^1\text{H}$  nuclei, each with  $a(^1\text{H}) = 3.9 \text{ G}$  (11 MHz).

## Modeling of the EPR signal assigned to (SBI)Zr<sup>III</sup>-<sup>i</sup>Bu



**Figure S5.** The “inner” signal in Figure 5 (black) is reproduced through hyperfine splitting by two <sup>1</sup>H nuclei (red) with  $a(^1\text{H}) = 5.7 \text{ G}$  (16 MHz) at a line width of 7.6 G, as expected for (SBI)Zr<sup>III</sup>-CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> (component 1, weight 33% of total intensity). The superimposed “outer-wings” signal due to (SBI)Zr<sup>III</sup>(μ-H)<sub>2</sub>AlR<sub>2</sub> is modeled using the same parameters as described in S-2 above.

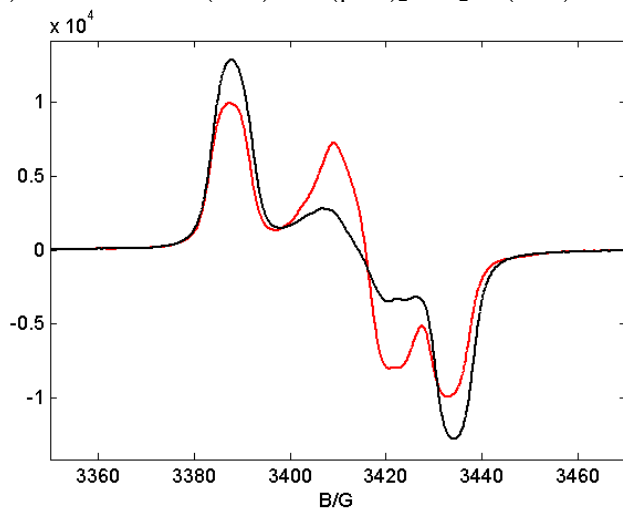
EPR spectra, reaction of  $(\text{SBI})\text{Zr}^{\text{III}}-i\text{Bu}$  with  $\text{PMe}_2\text{Ph}$



**Figure S6.** EPR spectra (X band, 25°C) of a 3.5 mM solution of  $(\text{SBI})\text{ZrMe}_2$ , which had reacted with 2 equiv. of  $\text{HAi}^i\text{Bu}_2$  for one day, before and after addition of increasing amounts of  $\text{PMe}_2\text{Ph}$ .

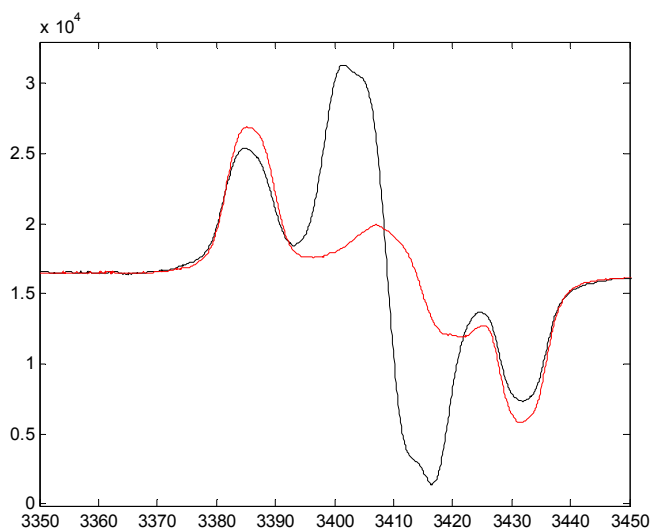
EPR spectra, conversion of  $(\text{SBI})\text{Zr}^{\text{III}}-(\mu\text{-H})_2\text{AlR}_2$  to  $(\text{SBI})\text{Zr}^{\text{III}}-i\text{Bu}$  and *vice versa*

a) Conversion of  $(\text{SBI})\text{Zr}^{\text{III}}-(\mu\text{-H})_2\text{AlR}_2$  to  $(\text{SBI})\text{Zr}^{\text{III}}-i\text{Bu}$



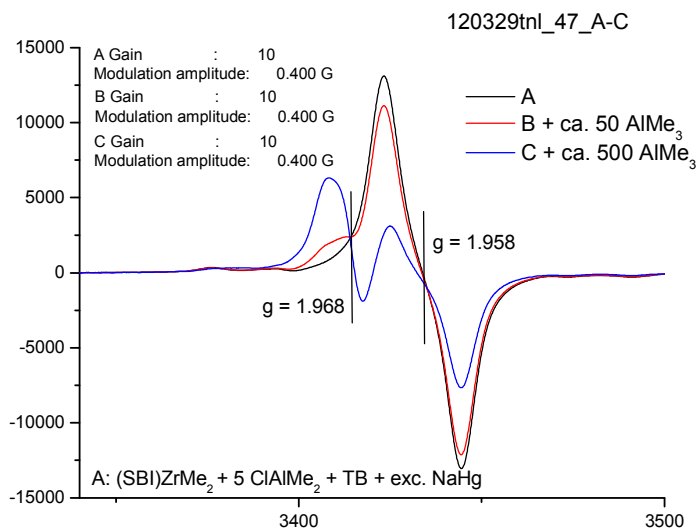
**Figure S7.** Black: EPR spectra (X band, 25°C) of a 3.5 mM solution of  $(\text{SBI})\text{ZrMe}_2$ , which had reacted with 4 equiv. of  $\text{HAl}^i\text{Bu}_2$  for one day. Red: After addition of 3.5 equivalents of triisobutylaluminum.

b) Conversion of  $(\text{SBI})\text{Zr}^{\text{III}}-i\text{Bu}$  to  $(\text{SBI})\text{Zr}^{\text{III}}-(\mu\text{-H})_2\text{AlR}_2$



**Figure S8.** Black: EPR spectra (X band, 25°C) of a 3.5 mM solution of  $(\text{SBI})\text{ZrMe}_2$ , which had reacted with 2 equiv. of  $\text{HAl}^i\text{Bu}_2$  for one day. Red: After addition of another two equivalents of  $\text{HAl}^i\text{Bu}_2$ .

EPR spectra, reaction of  $(\text{SBI})\text{Zr}^{\text{III}}(\mu\text{-Cl})_2\text{AlR}_2$  with  $\text{AlMe}_3$

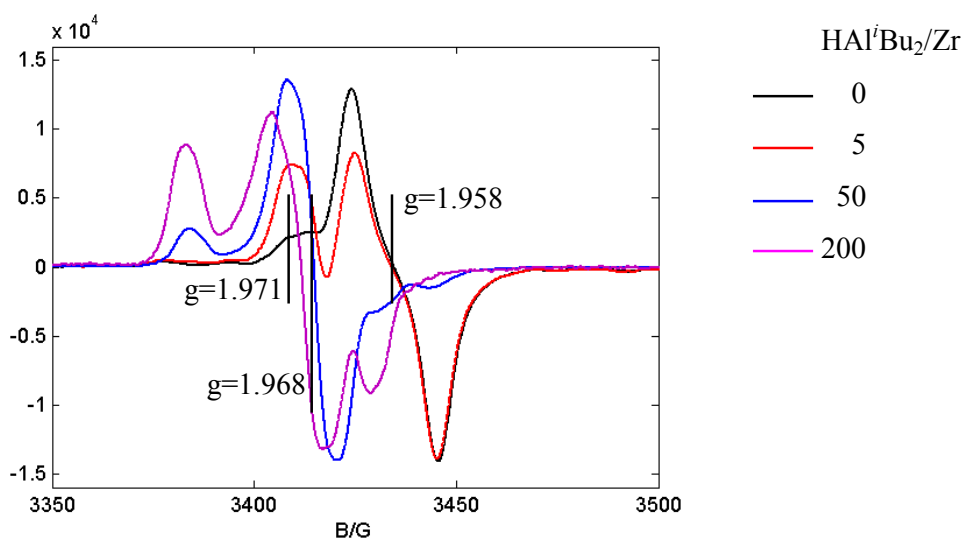


**Figure S9.** Black: EPR spectrum (X band, 25°C) of a 3.5 mM solution of  $(\text{SBI})\text{Zr}^{\text{III}}(\mu\text{-Cl})_2\text{AlR}_2$ , obtained by reaction of a 3.5 mM solution of **1** with 5 equiv. of  $\text{ClAlMe}_2$  and 1 equiv. of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_3]$  and excess  $\text{NaHg}$  (1% w/w).

Red: EPR spectrum of the same solution after addition of 50 equiv. of  $\text{AlMe}_3$

Blue: EPR spectrum of the same solution after addition of 500 equiv. of  $\text{AlMe}_3$

EPR spectra, reaction of  $(\text{SBI})\text{Zr}^{\text{III}}(\mu\text{-Cl})_2\text{AlR}_2$  with  $\text{HAl}^i\text{Bu}_2$



**Figure S10.** EPR spectra of a 1 mM solution of  $(\text{SBI})\text{ZrMe}_2$  in toluene, which had reacted, in this order, with 5 equiv. of  $\text{AlMe}_3$ , 1 equiv. of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  and ca. 20 equiv. of  $\text{AlCl}_3$  to give a green solution of  $[(\text{SBI})\text{Zr}(\mu\text{-Cl})_2\text{AlR}_2]^+$ , after shaking with excess (3 drops) of 1-% w/w sodium amalgam (black) and of the same solution after addition of 5 (red), 50 (blue) and 200 (magenta) equiv. of  $\text{HAl}^i\text{Bu}_2$ .

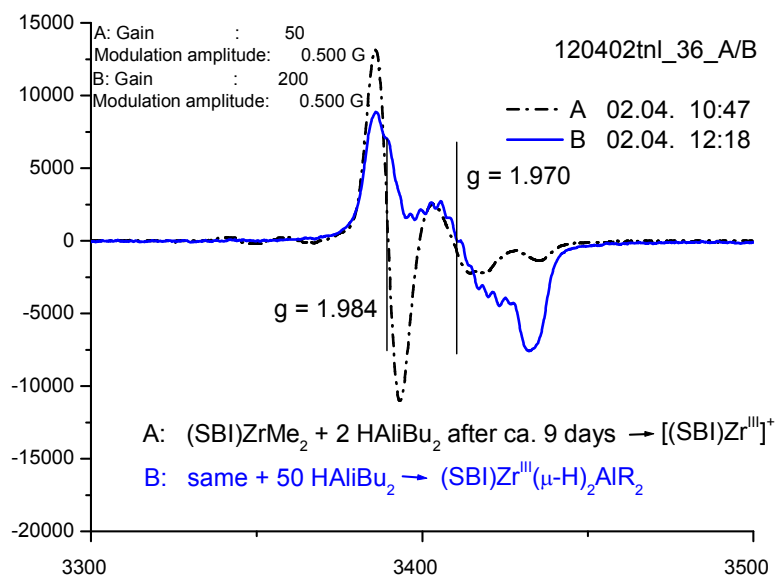
Addition of increasing amounts of  $\text{HAl}^i\text{Bu}_2$  converts  $(\text{SBI})\text{Zr}^{\text{III}}(\mu\text{-Cl})_2\text{AlR}_2$  ( $g = 1.958$ ) first to  $(\text{SBI})\text{Zr}^{\text{III}}\text{Cl}$  ( $g = 1.968$ ) and then mostly to  $(\text{SBI})\text{Zr}^{\text{III}}(\mu\text{-H})_2\text{AlR}_2$  ( $g = 1.971$ );  $\text{R} = \text{Me}, ^i\text{Bu}$ .



Preparation of crystalline (SBI)Zr<sup>III</sup>( $\mu$ -Cl)<sub>2</sub>AlR<sub>2</sub> and structure determination.

To 8 mg (0.020 mmol) of (SBI)ZrMe<sub>2</sub> was added 1.4 mL HAlBu<sub>2</sub> (28 mM) in pentane, 0.04 mmol). The mixture was allowed to sit overnight after which it was filtered and 1 mL ClAlMe<sub>2</sub> was added (~1 M in pentane, 1 mmol). The solution was cooled to -10 °C overnight in a glass vial and then further to -25 °C after which several crystals formed directly above the solvent line. Crystals were removed from the cooled glass vial to a microscope slide coated with Fluorolube®. Samples were selected and mounted using a cryoloop that was also coated with Fluorolube®. Data collection was carried out on a BrukerKAPPA APEXII diffractometer with a 0.71073 Å MoKR source.

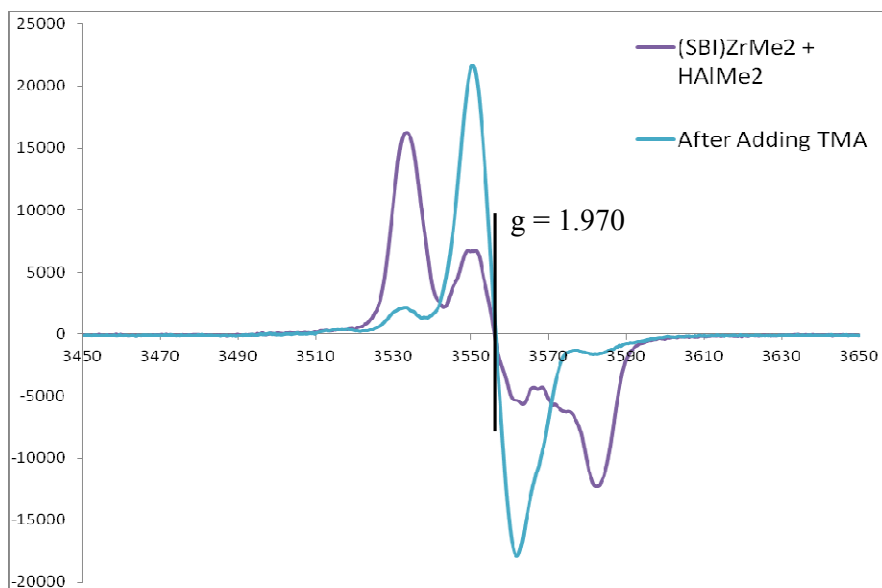
EPR spectra, conversion of  $[(\text{SBI})\text{Zr}^{\text{III}}]^+$  to  $(\text{SBI})\text{Zr}^{\text{III}}-(\mu\text{-H})_2\text{AlR}_2$  by  $\text{HAl}^i\text{Bu}_2$



**Figure S11.** EPR spectra (X band, 25°C) of a 3.5 mM solution of  $(\text{SBI})\text{ZrMe}_2$  in toluene, which had reacted with 2 equiv. of  $\text{HAl}^i\text{Bu}_2$  for 9 days (cf. Figure 6 of main text, black broken line) and of the same solution 5 min after addition of 50 equiv. of  $\text{HAl}^i\text{Bu}_2$  (blue solid line)

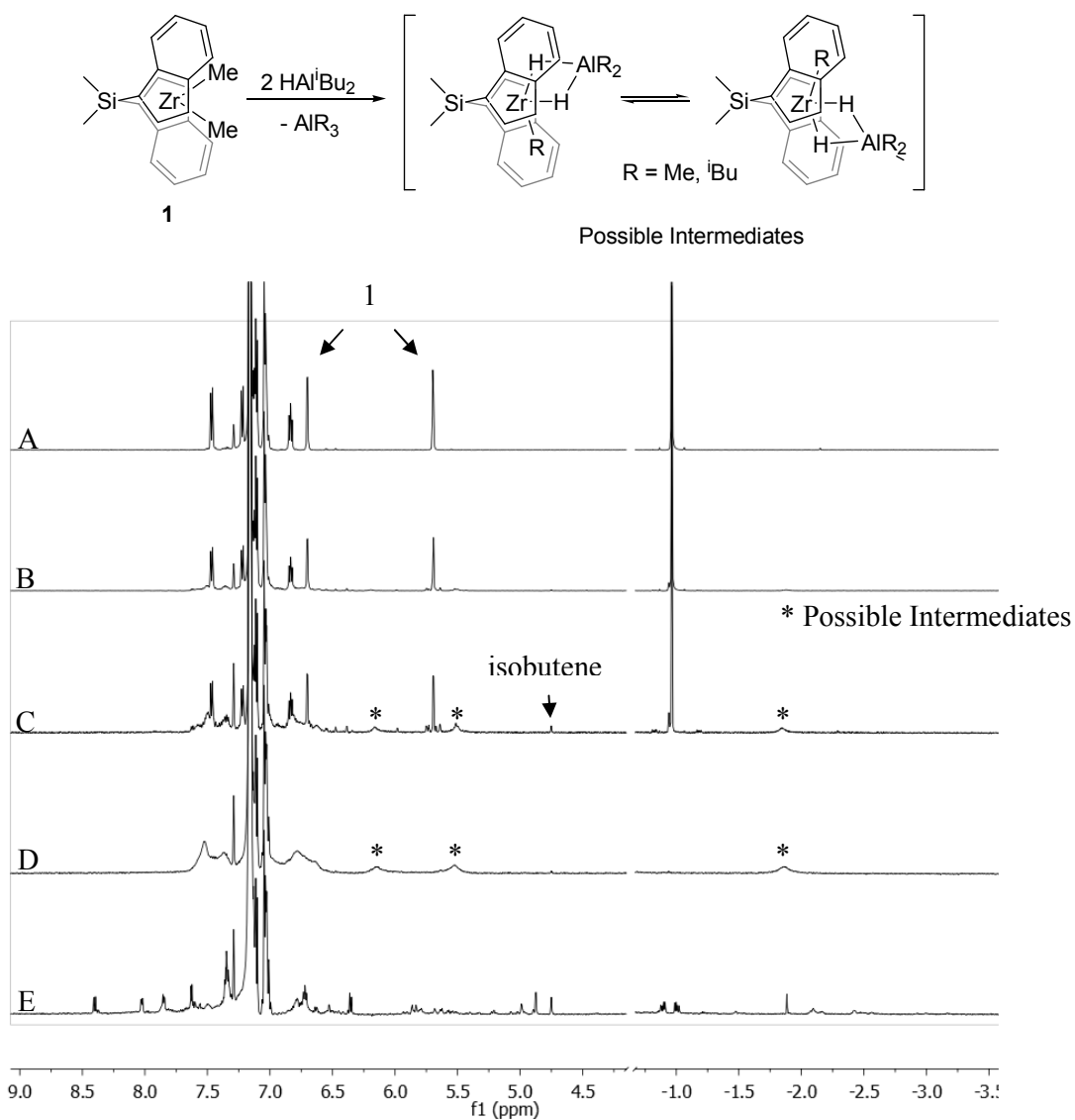
Addition of excess  $\text{HAl}^i\text{Bu}_2$  converts  $[(\text{SBI})\text{Zr}^{\text{III}}]^+$  ( $g=1.984$ ) to  $(\text{SBI})\text{Zr}^{\text{III}}-(\mu\text{-H})_2\text{AlR}_2$  ( $g=1.970$ ).

EPR spectra, reaction of  $(\text{SBI})\text{ZrMe}_2$  with  $\text{HAlMe}_2$  and  $\text{AlMe}_3$



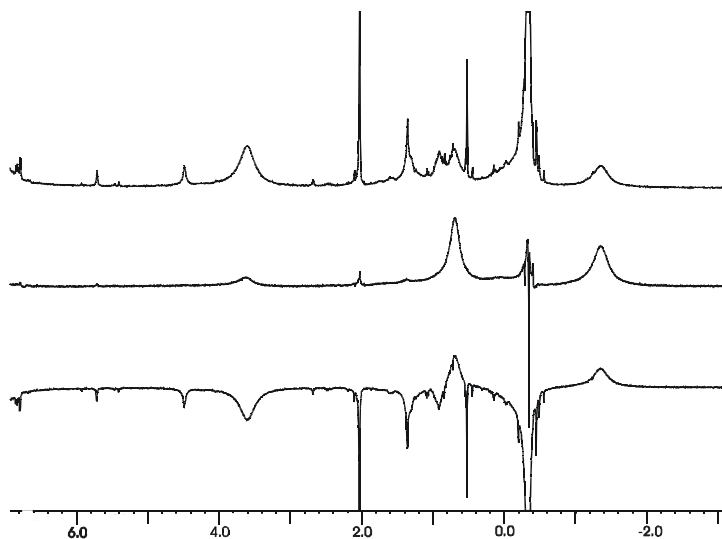
**Figure S12.** EPR spectra (X band, 25°C) of a 3.5 mM solution of  $(\text{SBI})\text{ZrMe}_2$  in toluene after reaction with ca. 10 equiv. of  $\text{HAlMe}_2$  for ca. 22 h (violet) and of the same solution after addition of 10 equiv. of  $\text{AlMe}_3$  (blue).

$^1\text{H}$  NMR spectra, intermediates in the reaction of  $(\text{SBI})\text{ZrMe}_2$  with  $\text{HAl}^i\text{Bu}_2$



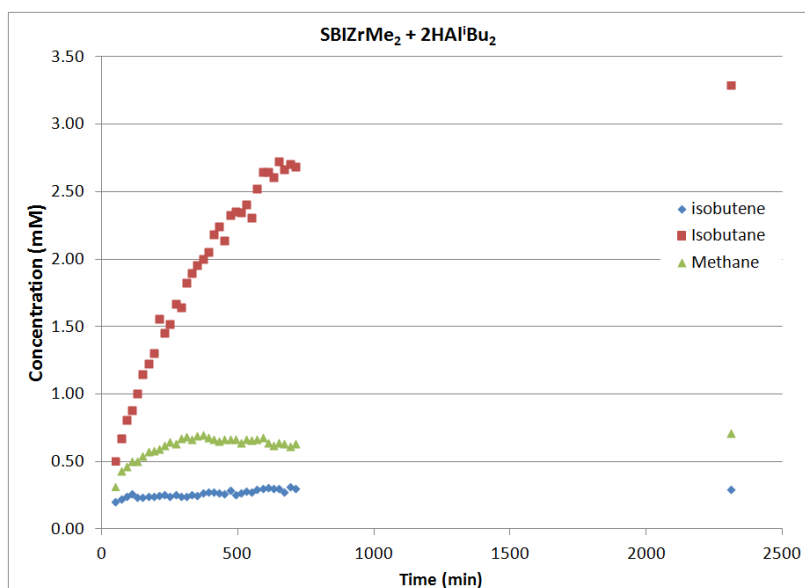
**Figure S13.**  $^1\text{H}$  NMR spectra (600 MHz, 25°C) of 3.5 mM solutions in benzene- $d_6$  of  
 A)  $(\text{SBI})\text{ZrMe}_2$  (**1**)  
 B)  $(\text{SBI})\text{ZrMe}_2$  10 min after addition of 1 equiv. of  $\text{HAl}^i\text{Bu}_2$   
 C)  $(\text{SBI})\text{ZrMe}_2$  10 min after addition of 2 equiv. of  $\text{HAl}^i\text{Bu}_2$   
 D)  $(\text{SBI})\text{ZrMe}_2$  10 min after addition of 4 equiv. of  $\text{HAl}^i\text{Bu}_2$   
 E) the same solution as seen in spectrum D after 12 hours.

Paramagnetic  $^1\text{H}$  NMR signals of  $(\text{SBI})\text{Zr}^{\text{III}}-(\mu\text{-Cl})_2\text{AlMe}_2$

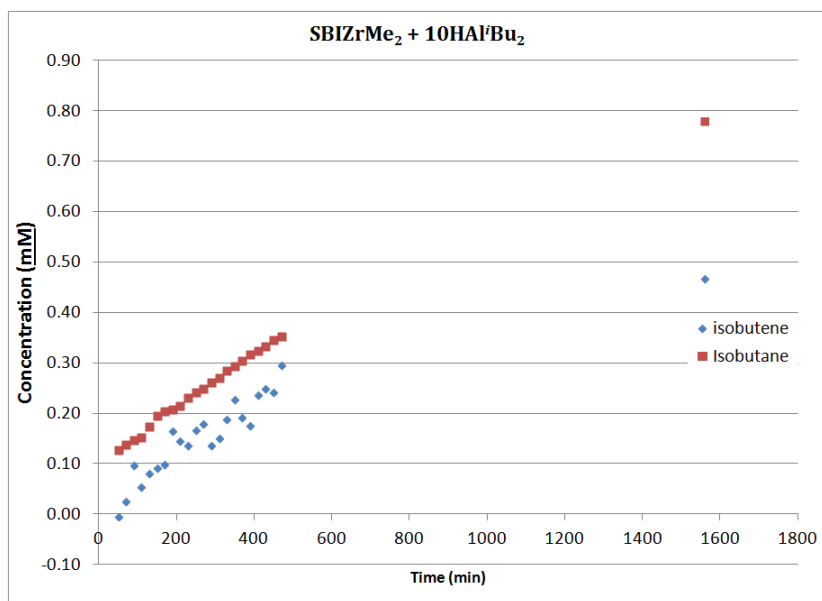


**Figure S14.**  $^1\text{H}$  NMR spectra of the products obtained by reduction of  $[(\text{SBI})\text{Zr}^{\text{IV}}(\mu\text{-Cl})_2\text{AlMe}_2]^+$  (1 mM in  $\text{C}_6\text{D}_6$ ) with 1 equiv. of  $\text{Cp}_2\text{Co}$ : normal one-pulse acquisition (top trace); inversion-recovery experiment with 25 ms delay between  $180^\circ$  and  $90^\circ$  pulses, scaled by an empirical factor of 1.1 (bottom trace), and summation of these two spectra (middle trace). Signals of all diamagnetic species are inverted in the bottom spectrum, due to their slow relaxation, while the fast-relaxing paramagnetic signals at 0.69 ppm and  $-1.35$  ppm recover almost completely. Addition of this and the conventional  $^1\text{H}$  NMR spectrum thus cancels the diamagnetic signals almost entirely, while leaving the paramagnetic signals at 97.4% and 86.1% of their theoretical intensity (calculated based on measured  $T_1$  times and a delay of 25 ms). The integral ratio of the paramagnetic signals at 0.69 ppm and  $-1.35$  ppm is slightly distorted (by 6.4%) in the middle trace. Thus, an apparent ratio (1.02) corresponds to 0.96 when corrected for this distortion.

### Time course of isobutane evolution



**Figure S15.** Isobutane, isobutene, and methane concentration derived from <sup>1</sup>H NMR spectra of a 3.5 mM solution of (SBI)ZrMe<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>, at increasing times after addition of 2 equiv. of HA<sup>i</sup>Bu<sub>2</sub>.



**Figure S16.** Isobutane, and isobutene concentrations derived from <sup>1</sup>H NMR spectra of a 3.5 mM solution of (SBI)ZrMe<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>, before and at increasing times after addition of 10 equiv. of HA<sup>i</sup>Bu<sub>2</sub>.

## Experimental Details

**Solutions of AlMe<sub>2</sub>Cl.** Solutions of ClAlMe<sub>2</sub> were prepared at 280 mM and 28 mM concentrations by dissolving 0.2 mL (0.934 mmol) of trimethyl aluminum in 4.8 mL of toluene, adding 62.3 mg (0.467 mmol) of aluminum chloride to the solution and stirring until the solid had dissolved. From this 280 mM solution, a 28 mM toluene solution of ClAlMe<sub>2</sub> was formed by adding 0.2 mL to 1.8 mL of toluene. These solutions were used as stock ClAlMe<sub>2</sub> solutions in the experiments described below.

**Solutions of [(SBI)Zr(μ-Cl)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>.** To a solution of 2.3 mg (5.6 μmol) (SBI)ZrMe<sub>2</sub> in 0.8 mL toluene was added 0.1 mL of the 280 mM ClAlMe<sub>2</sub> solution prepared above. The solution was diluted with toluene to a total volume of 1.6 mL and transferred to a vial containing 5.16 mg (5.6 μmol) of solid [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Complete dissolution of the trityl salt yielded a dark blue, 3.5 mM solution of [(SBI)Zr(μ-Cl)<sub>2</sub>AlMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in toluene. Analogously prepared benzene-d<sub>6</sub> and toluene-d<sub>8</sub> solution of [(SBI)Zr(μ-Cl)<sub>2</sub>AlMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] gave rise to <sup>1</sup>H NMR signals at 6.26, 5.23 and 0.68 ppm (25 °C, 600 MHz) and to a characteristic UV/vis absorbance band at 614 nm, in close agreement to values of 6.26, 5.17 and 0.71 ppm and 614 nm, reported for the homologous cation [(SBI)Zr(μ-Cl)<sub>2</sub>Al<sup>t</sup>Bu<sub>2</sub>]<sup>+</sup> in C<sub>6</sub>D<sub>6</sub> solution (Baldwin, S. M.; Bercaw, J. E.; Henling, L. M.; Day, M. W.; Brintzinger, H. H. *J. Am. Chem. Soc.* **2011**, *133*, 1805-1813).

**Solutions of [(SBI)Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>.** To a solution of 4.0 mg (9.8 μmol) of (SBI)ZrMe<sub>2</sub> in 2.8 mL of either toluene or benzene-d<sub>6</sub> was added 3 drops (22.5 mg, 0.3 mmol) of trimethylaluminum. The solution was transferred to a vial containing 9.0 mg (9.8 μmol) of solid [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Complete dissolution of the trityl salt yielded an orange-red, 3.5 mM solution of [(SBI)Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

**Solutions of [(SBI)Zr(μ-H)<sub>3</sub>AlR<sub>2</sub>]<sup>+</sup>.** To a solution of 4.0 mg (9.8 μmol) of (SBI)ZrMe<sub>2</sub> in 1.4 mL of toluene or benzene-d<sub>6</sub> was added 1.4 mL (28 mM, 39.2 μmol) of diisobutylaluminum hydride in toluene or benzene-d<sub>6</sub> via microliter syringe. The solution was transferred to a vial containing 9.0 mg (9.8 μmol) of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Complete dissolution of the trityl salt yielded a yellow, 3.5 mM solution of [(SBI)Zr(μ-H)<sub>3</sub>AlR<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in toluene.

**Reductions with sodium amalgam.** A 1-mL syringe with 16-gauge needle was used to add three drops (ca. 50 mg) of sodium amalgam (1% wt/wt) to a vial containing 0.8 mL of a 3.5 mM solution of the respective Zr(IV) compound. The vial was capped and placed in a wrist-action shaker for one hour. Excess sodium amalgam was allowed to settle to the bottom of the vial and the solution was transferred with a pipette into a 5 mm OD glass tube for EPR and NMR spectroscopy.

**Reduction of (SBI)ZrMe<sub>2</sub> with 10 equivalents of HAl<sup>i</sup>Bu<sub>2</sub>.** To a solution of 4.0 mg (9.8 μmol) of (SBI)ZrMe<sub>2</sub> in 1.4 mL of toluene or benzene-d<sub>6</sub> was added 0.35 mL (280 mM, 98.0 μmol) of diisobutylaluminum hydride in toluene or benzene-d<sub>6</sub> via microliter syringe. The solution was diluted with toluene or benzene-d<sub>6</sub> to a total volume of 2.8 mL (3.5 mM Zr). From this solution, 0.8 mL was transferred to a 5 mm OD glass tube to monitor the reaction by EPR and/or NMR spectroscopy (cf. Figures 4 and SI-7).

**Reduction of (SBI)ZrMe<sub>2</sub> with 4 equivalents of HAl<sup>i</sup>Bu<sub>2</sub>.** To a solution of 4.0 mg (9.8 μmol) of (SBI)ZrMe<sub>2</sub> in 1.4 mL of toluene or benzene-d<sub>6</sub> was added 1.4 mL (28 mM, 19.6 μmol) of diisobutylaluminum hydride in toluene or benzene-d<sub>6</sub> via microliter syringe.

Addition of Al<sup>i</sup>Bu<sub>3</sub>. To an NMR tube containing 0.8 mL of the zirconium solution described above, was added 0.01 mL of a 1 M solution of triisobutylaluminum in toluene.

**Reduction of (SBI)ZrMe<sub>2</sub> with 2 equivalents of HAl<sup>i</sup>Bu<sub>2</sub>.** To a solution of 4.0 mg (9.8 μmol) of (SBI)ZrMe<sub>2</sub> in 1.4 mL of toluene or benzene-d<sub>6</sub> was added 0.7 mL (28 mM, 19.6 μmol) of diisobutylaluminum hydride in toluene or benzene-d<sub>6</sub> via microliter syringe. The solution was diluted with toluene or benzene-d<sub>6</sub> to a total volume of 2.8 mL and allowed to sit overnight before further use.

Addition of HAl<sup>i</sup>Bu<sub>2</sub>. To an NMR tube containing 0.8 mL of the zirconocene solution described above, was added 0.1 mL of diisobutylaluminum hydride (280 mM in benzene-d<sub>6</sub>, 2 equiv)

Addition of Dimethylphenylphosphine. From the zirconocene solution described above, 0.2 mL (3.5 mM, 7 μmol) was transferred to a 4 mm OD quartz EPR tube and 10 μL of dimethylphenylphosphine (0.35 μmol, 0.5 equiv.) was added. After obtaining an EPR spectrum, the tube was returned to the glove box, where an additional 10 μL dimethylphenylphosphine (0.35 μmol, 1 equiv.) was added. After obtaining EPR spectra and returning the tube to the glove box, 1 drop of neat dimethylphenylphosphine was added before obtaining a final spectrum.



Conversion to (SBI)Zr( $\mu$ -Cl)<sub>2</sub>AlR<sub>2</sub>. Two NMR tubes were prepared with 0.8 mL each of the (SBI)ZrMe<sub>2</sub>/diisobutylaluminum reaction mixture described above. To the first tube, one equivalent of ClAlMe<sub>2</sub> in toluene (0.1 mL, 28 mM) was added via syringe. After obtaining an EPR spectrum, the tube was returned to the box and a second equivalent of ClAlMe<sub>2</sub> was added in the same manner. This was continued sequentially until 9 equivalents had been added. Similarly, ClAlMe<sub>2</sub> was added in 10-equivalent steps to the second tube by adding 0.1 mL aliquots of a 280 mM solution of ClAlMe<sub>2</sub> in toluene, EPR spectra being obtained before and after each addition.

**Reduction of (SBI)ZrMe<sub>2</sub> with 1 equivalent of HAl<sup>i</sup>Bu<sub>2</sub>,** To a solution of 4.0 mg (9.8  $\mu$ mol) of (SBI)ZrMe<sub>2</sub> in 1.4 mL of benzene-d<sub>6</sub> was added (0.35 mL) (28 mM, 9.8  $\mu$ mol) of diisobutylaluminum hydride in benzene-d<sub>6</sub> via microliter syringe. The solution was diluted with toluene or benzene-d<sub>6</sub> to a total volume of 2.8 mL. A portion of this solution (0.8 mL, 3.5 mM) was transferred to a 5 mm OD NMR tube and monitored by EPR and NMR spectroscopy for 6 days, after which full formation of the EPR signal assigned to [(SBI)Zr<sup>III</sup>]<sup>+</sup> was observed.

Reaction with HAl<sup>i</sup>Bu<sub>2</sub>. To an NMR tube containing 0.8 mL of the zirconocene solution described above was added 0.1 mL (280 mM, 2 equiv) of diisobutylaluminum hydride in benzene-d<sub>6</sub>.