## SUPPORTING INFORMATION

# Alkylaluminum-Complexed Zirconocene Hydrides - Identification of Hydride-Bridged Species by NMR-Spectroscopy. 

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Figure S1. ${ }^{1} \mathrm{H}$ spectrum of $\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{ZrH}_{2}(\mathbf{3})$ with 1 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ and 1 equiv. $\mathrm{ClAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S2. ${ }^{1} \mathrm{H}$ spectrum of $\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{ZrH}_{2}(3)$ with 1 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ and 2 equiv. $\mathrm{ClAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S3. ${ }^{1} \mathrm{H}$ spectrum of $\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Zr}(\mu-\mathrm{H})_{3}\left(\mathrm{Al}^{i} \mathrm{Bu}_{2}\right)_{3}(\mu-\mathrm{H})_{3}$ in toluene $-d_{8}$ at $-60^{\circ} \mathrm{C}$.


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Figure S8. ${ }^{1} \mathrm{H}$ spectrum of $(\mathrm{EBI}) \mathrm{ZrCl}_{2}(\mathbf{1 7})$ with 2 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S9. (EBTHI) $\mathrm{ZrCl}_{2}(\mathbf{1 8})$ with 2 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S10. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{Me}_{2} \mathrm{C}\left(\mathrm{C}_{5} \mathrm{H}_{4}\right)_{2} \mathrm{ZrCl}_{2}\left(\mathbf{1 9 )}\right.$ with excess $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S11. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{Me}_{2} \mathrm{Si}\left(\mathrm{C}_{5} \mathrm{H}_{4}\right)_{2} \mathrm{ZrCl}_{2}$ (19) with 6 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S12. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{Me}_{2} \mathrm{Si}\left(2,4-\mathrm{Me}_{2}-\mathrm{C}_{5} \mathrm{H}_{2}\right)_{2} \mathrm{ZrCl}_{2}$ (21) with excess $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S13. ${ }^{1} \mathrm{H}$ spectrum of $\left(\mathrm{Me}_{2} \mathrm{Si}_{2}\right)_{2}\left(\mathrm{C}_{5} \mathrm{H}_{3}\right)_{2} \mathrm{ZrCl}_{2}$ (22) with 2 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in toluene- $d_{8}$ at $-75^{\circ} \mathrm{C}$.


Figure S14. ${ }^{1} \mathrm{H}$ spectrum of $\left(\mathrm{Me}_{2} \mathrm{Si}_{2}\right)_{2}\left(2,4-{ }^{i} \mathrm{Pr}_{2}-\mathrm{C}_{5} \mathrm{H}_{3}\right)_{2} \mathrm{ZrCl}_{2}$ (23) with 2 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in toluene- $d_{8}$ at $-75^{\circ} \mathrm{C}$.


Figure S15. gCOSY of $(\mathrm{EBTHI}) \mathrm{ZrH}(\mu-\mathrm{H})_{2} \mathrm{Al}^{i} \mathrm{Bu}_{2}(\mathbf{2 5})$ in toluene- $d_{8}$ at $-75^{\circ} \mathrm{C}$.


Figure S16. ${ }^{1} \mathrm{H}$ spectrum of $((\mathrm{EBTHI}) \mathrm{ZrH}(\mu-\mathrm{H}))_{2}(24)$ with 4 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ and 2 equiv. $\mathrm{ClAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S17. ${ }^{1} \mathrm{H}$ spectrum of $((\mathrm{EBTHI}) \mathrm{ZrH}(\mu-\mathrm{H}))_{2}(24)$ with 4 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ and 4 equiv. $\mathrm{ClAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S18. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathrm{Me}_{2} \mathrm{C}(\text { indenyl })_{2} \mathrm{ZrCl}_{2}(27)$ with 2 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $\mathrm{d}_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S19. ${ }^{1} \mathrm{H}$ spectrum of meso- $\mathrm{Me}_{2} \mathrm{C}$ (indenyl) $)_{2} \mathrm{ZrCl}_{2}(\mathbf{2 8})$ with 2 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S20. gCOSY of $\mathrm{rac}-\mathrm{Me}_{2} \mathrm{Si}\left(\left(2-\mathrm{Me}_{3} \mathrm{Si}-4-\mathrm{Me}_{3} \mathrm{C}-\mathrm{C}_{5} \mathrm{H}_{2}\right) \mathrm{ZrH}(\mu-\mathrm{H})_{2} \mathrm{Al}^{i} \mathrm{Bu}_{2}\right.$ (32) in toluene- $d_{8}$ at $-75^{\circ} \mathrm{C}$


Figure S21. noedif of $\mathbf{3 2}$ in benzene $-d_{6}$ at $25^{\circ} \mathrm{C}$ irradiating the central hydride resonance $(\mathbf{A})$ and the terminal unbridged hydride resonance (B).
$A$



Figure S22. ${ }^{1} \mathrm{H}$ spectrum of meso- $\mathrm{Me}_{2} \mathrm{Si}\left(3-\mathrm{Me}_{3} \mathrm{C}-\mathrm{C}_{5} \mathrm{H}_{3}\right)_{2} \mathrm{ZrCl}_{2}$ (33) with 2 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in toluene- $d_{8}$ at $25^{\circ} \mathrm{C}$.


Figure S23. gCOSY of $\mathbf{3 3}$ with 2 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in toluene- $d_{8}$ at $25^{\circ} \mathrm{C}$.


Figure S24. noedif of $\mathbf{3 3}$ with 3 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S25. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{H}_{4} \mathrm{C}_{2}\left(\mathrm{C}_{5} \mathrm{H}_{4}\right)_{2} \mathrm{ZrCl}_{2}(\mathbf{3 5})$ with 4 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in toluene- $d_{8}$ at $0^{\circ} \mathrm{C}$.


Figure S26. NOESY1D of $\mathrm{Me}_{4} \mathrm{C}_{2}\left(\mathrm{C}_{5} \mathrm{H}_{4}\right)_{2} \mathrm{ZrCl}_{2}$ (36) with 4 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Figure S27. ${ }^{1} \mathrm{H}$ spectrum of (EBTHI) $\mathrm{ZrF}_{2}$ with 1 equiv. $\mathrm{HAl}^{i} \mathrm{Bu}_{2}$ in benzene- $d_{6}$ at $25^{\circ} \mathrm{C}$.


Appendix S-1. Analysis of changes in the chemical shift of the $\mathrm{ZrH}_{2}$ signal of ( SBI$) \mathrm{ZrCl}(\mu-$ $\mathrm{H})_{2} \mathrm{Al}^{i} \mathrm{Bu}_{2}$ upon addition of $\mathrm{Al}_{2} \mathrm{Me}_{6}$.

## 1) Adduct Formation:

Adduct formation of $(\mathrm{SBI}) \mathrm{ZrCl}(\mu-\mathrm{H})_{2} \mathrm{Al}^{i} \mathrm{Bu}_{2}$ with $\mathrm{Al}_{2} \mathrm{Me}_{6}$, is represented by Equ. 1, with $\mathbf{A}$ representing the starting complex, $\mathbf{X}_{2}$ the $\mathrm{AlMe}_{3}$ dimer and $\mathbf{A X}$ the adduct:

$$
\begin{equation*}
A+\frac{1}{2} X_{2} \leftrightarrow A X \tag{1}
\end{equation*}
$$

The equilibrium constant $K$ for this reaction is represented by Equ. 2:

$$
\begin{equation*}
K=\frac{[A X]}{[A] \sqrt{\left[X_{2}\right]}} \tag{2}
\end{equation*}
$$

Under conditions of rapid exchange between $\mathbf{A}$ and $\mathbf{A X}$ the chemical shift of the resulting signal, $\delta$, is the weighted average of the chemical shifts of $\mathbf{A}, \delta_{\mathrm{A}}$, and $\mathbf{A X}, \delta_{\mathrm{AX}}$ (Equ. 3).

$$
\begin{equation*}
\delta=\frac{[A]}{[A X]+[A]} \delta_{A}+\frac{[A X]}{[A X]+[A]} \delta_{A X} \tag{3}
\end{equation*}
$$

The difference in chemical shift, $\Delta \delta$, of the signal at any given concentration of added $\mathbf{X}, \delta$, and that of pure $\mathbf{A}$ is given by Equ. 4 .

$$
\begin{equation*}
\Delta \delta=\delta-\delta_{A} \tag{4}
\end{equation*}
$$

Combining Equ. 3 and Equ. 4 we get:

$$
\begin{equation*}
\Delta \delta=\left(\frac{[A]}{[A X]+[A]}-1\right) \delta_{A}+\frac{[A X]}{[A X]+[A]} \delta_{A X} \tag{5}
\end{equation*}
$$

Which simplifies to:

$$
\begin{equation*}
\Delta \delta=\frac{[A X]}{[A X]+[A]}\left(\delta_{A X}-\delta_{A}\right) \tag{6}
\end{equation*}
$$

With the maximum change in chemical shift represented as $\Delta \delta_{\text {max }}$, we get Equ. 7 .

$$
\begin{equation*}
\Delta \delta_{\max }=\delta_{A X}-\delta_{A} \tag{7}
\end{equation*}
$$

Taking the reciprocal of Equ. 6 and using Equ. 7 gives Equ. 8:

$$
\begin{equation*}
\frac{1}{\Delta \delta}=\frac{1}{\Delta \delta_{\max }}+\frac{1}{\Delta \delta_{\max }} \cdot \frac{[A]}{[A X]} \tag{8}
\end{equation*}
$$

Together with the equilibrium constant, Equ. 2, this yields a Benesi-Hildebrand type relation (Equ. 9):

$$
\begin{equation*}
\frac{1}{\Delta \delta}=\frac{1}{\Delta \delta_{\max }}+\frac{1}{\Delta \delta_{\max } K \sqrt{\left[X_{2}\right]}} \tag{9}
\end{equation*}
$$

Assuming that K is small, the amount of $\mathbf{X}_{\mathbf{2}}$ added is approximately equal to the amount of $\mathbf{X}_{\mathbf{2}}$ in solution. A plot of the reciprocal of the change in chemical shift against the reciprocal of the square root of the concentration of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ added should thus be linear, with a slope of $1 / \mathrm{K}$ and a $y$-axis intercept of $1 / \delta_{A X}$, neither of which should depend on $[\mathrm{Zr}]_{\text {Tот }}$.


The data plotted in Chart 1 according to Equation 9 approximate this requirement. Some curvature of the data in Chart 1 might originate from a partial dissociation of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ to $\mathrm{AlMe}_{3}$ in dilute solutions and/or from the fact that the most concentrated solutions of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ contain up to 20 volume percent $\mathrm{Al}_{2} \mathrm{Me}_{6}$, such that these solution can no longer be considered to be ideal solutions of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ in benzene. Nevertheless, the values of $1 / \delta_{\max }$ and of $1 / \mathrm{K}$ derived from the data for $[\mathrm{Zr}]=7 \mathrm{mM}$ and from those for $[\mathrm{Zr}]=28 \mathrm{mM}$ are indistinguishable within their error
margins. Our data are thus compatible with the view that the change in chemical shift of the $\mathrm{ZrH}_{2}$ signal upon addition of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ to a solution of $(\mathrm{SBI}) \mathrm{Zr}(\mathrm{Cl})(\mu-\mathrm{H})_{2} \mathrm{Al}^{i} \mathrm{Bu}_{2}$ is due to formation of an adduct, e.g. of the type $(\mathrm{SBI}) \mathrm{Zr}\left(\mathrm{Cl}^{\cdots} \mathrm{AlMe}_{3}\right)(\mu-\mathrm{H})_{2} \mathrm{AlR}_{2}$, with $\mathrm{R}={ }^{i} \mathrm{Bu}$ and/or Me .

## 2) Exchange Reaction:

The reaction of $(\mathrm{SBI}) \mathrm{ZrCl}(\mu-\mathrm{H})_{2} \mathrm{Al}^{i} \mathrm{Bu}_{2}$ to exchange either the Zr -bound Cl or an Al -bound ${ }^{i} \mathrm{Bu}$ with one of the methyl groups of $\mathrm{Al}_{2} \mathrm{Me}_{6}$, to yield $\mathrm{Al}_{2} \mathrm{Me}_{5} \mathrm{X}$ where $\mathrm{X}=\mathrm{Cl}$ or ${ }^{i} \mathrm{Bu}$, is represented by Equ. 10, with $\mathbf{A}$ representing the starting $\mathrm{ZrClH}_{2}$ complex, $\mathbf{X}_{2}$ the $\mathrm{AlMe}_{3}$ dimer, $\mathbf{B}$ the exchange product and $\mathbf{Y}$ the $\mathrm{Al}_{2} \mathrm{Me}_{5} \mathrm{X}$ product:

$$
\begin{equation*}
A+X_{2} \leftrightarrow B+Y \tag{10}
\end{equation*}
$$

The equilibrium constant K for this reaction is represented by Equ. 2:

$$
\begin{equation*}
K=\frac{[B][Y]}{[A]\left[X_{2}\right]} \tag{11}
\end{equation*}
$$

We can use the same derivation as for Equation 8, except [ $\mathbf{A} \mathbf{X}]$ is now replaced by $[\mathbf{B}]$.

$$
\begin{equation*}
\frac{1}{\Delta \delta}=\frac{1}{\Delta \delta_{\max }}+\frac{1}{\Delta \delta_{\max }} \cdot \frac{[A]}{[B]} \tag{12}
\end{equation*}
$$

Using the equilibrium constant, Equ. 11, this yields a Benesi-Hildebrand type relation (Equ. 13):

$$
\begin{equation*}
\frac{1}{\Delta \delta}=\frac{1}{\Delta \delta_{\max }}+\frac{1}{\Delta \delta_{\max }} \bullet \frac{[Y]}{K\left[X_{2}\right]} \tag{13}
\end{equation*}
$$

Since we are adding $\mathbf{X}_{\mathbf{2}}$ to $\mathbf{A},[\mathbf{Y}]$ is equal to $[\mathbf{B}]$, yielding:

$$
\begin{equation*}
\frac{1}{\Delta \delta}=\frac{1}{\Delta \delta_{\max }}+\frac{1}{\Delta \delta_{\max }} \bullet \frac{[B]}{K\left[X_{2}\right]} \tag{14}
\end{equation*}
$$

Rearranging to give $\mathrm{a} y=m x+b$ format gives:

$$
\begin{equation*}
\frac{1}{\Delta \delta}=\left(\frac{[B]}{\Delta \delta_{\max } K}\right) \cdot \frac{1}{\left[X_{2}\right]}+\frac{1}{\Delta \delta_{\max }} \tag{15}
\end{equation*}
$$

Alternatively Equ. 14 can be modified by using the following relationship which is derived by combining Equ. 3, 4 and 7:

$$
\begin{equation*}
\Delta \delta=\Delta \delta_{\max } \frac{[B]}{[A]+[B]} \tag{16}
\end{equation*}
$$

Solving for [B] and substituting into Equation 14 gives:

$$
\begin{equation*}
\frac{1}{\Delta \delta}=\frac{1}{\Delta \delta_{\max }}+\frac{\Delta \delta}{\Delta \delta_{\max }} \cdot \frac{[A]+[B]}{\Delta \delta_{\max } K\left[X_{2}\right]} \tag{17}
\end{equation*}
$$

With $[\mathrm{A}]+[\mathrm{B}]=[\mathrm{Zr}]_{\text {TOT }}$ and $\left[\mathrm{X}_{2}\right]=\left[\mathrm{Al}_{2} \mathrm{Me}_{6}\right]$, equation 17 can be rearranged to:

$$
\begin{equation*}
\left(\frac{\Delta \delta_{\max }}{\Delta \delta}-1\right) \frac{\Delta \delta_{\max }}{\Delta \delta}=\frac{[Z r]_{O T}}{K \cdot\left[A l_{2} M e_{6}\right]} \tag{18}
\end{equation*}
$$

The value of $\Delta \delta_{\text {max }}$ can be estimated from the chemical shift at the highest concentrations of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ or from the plot in Chart 1 . Assuming that K is small, the amount of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ added is approximately equal to the amount of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ in solution. Therefore, a plot of the left side of Equ. 18 against $[\mathrm{Zr}]_{\text {TOT }} /\left[\mathrm{Al}_{2} \mathrm{Me}_{6}\right]$ should give a straight line going through the origin, with a slope of $1 / \mathrm{K}$, which should thus be independent of $[\mathrm{Zr}]_{\text {тотт }}$.


Inspection of such a plot (Chart 2) shows that the data do not meet this requirement. Instead, the slope of the data for $[\mathrm{Zr}]_{\text {tot }}=7 \mathrm{mM}$ is about three times larger than that of the data for $[\mathrm{Zr}]_{\text {tot }}=$ 28 mM . The change in chemical shift of the $\mathrm{ZrH}_{2}$ signal upon addition of $\mathrm{Al}_{2} \mathrm{Me}_{6}$ to a solution of $(\mathrm{SBI}) \mathrm{Zr}(\mathrm{Cl})(\mu-\mathrm{H})_{2} \mathrm{Al}^{i} \mathrm{Bu}_{2}$ can thus not be due to an exchange reaction, e.g. of the Cl against a Me ligand.

