SUPPORTING INFORMATION


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NMR Spectra:

Figure S1. (C5H5)2ZrH2 (3) + 1 eq HAi'Bu + 1 eq ClAi'Bu2

Figure S2. (C5H5)2ZrH2 (3) + 1 eq HAi'Bu2 + 2 eq ClAi'Bu2

Figure S3. (C5H5)2ZrH2 (3) + xs HAi'Bu2 → (C5H5)2Zr(μ-H)3(Al'Bu2)3(μ-H)3 (5)

Figure S4. (Bu-Cp),ZrCl2 (6) + 2 HAi'Bu2 → (Bu-Cp),Zr(μ-H)3(Al'Bu2)3(μ-H)3 (7)

Figure S5. (1,2-Me2-C5H3)2Zr(μ-H)3(Al'Bu2)3(μ-H)3 (9)

Figure S6. (nBu-Cp)2ZrCl2 (6) + 2 HAi'Bu2 → (nBu-Cp)2Zr(μ-H)3(Al'Bu2)3(μ-H)3 (9)

Figure S7. (1,2-Me2-C5H3)2 (8) + xs HAi'Bu2 → (1,2-Me2-C5H3)2Zr(μ-H)3(Al'Bu2)3(μ-H)3 (9)

Figure S8. (EBI)ZrCl2 (17) + 2 HAi'Bu2 → (EBI)ZrCl(μ-H)2Al'Bu2

Figure S9. (EBTHI)ZrCl2 (18) + 2 HAi'Bu2 → (EBTHI)ZrCl(μ-H)2Al'Bu2

Figure S10. Me2C(C5H4)ZrCl2 (19) + xs HAi'Bu2 → Me2C(C5H4)ZrCl(μ-H)2Al'Bu2

Figure S11. Me2Si(C5H4)ZrCl2 (20) + 6 HAi'Bu2 → Me2Si(C5H4)ZrCl(μ-H)2Al'Bu2

Figure S12. Me2Si(2,4-Me2-C5H4)ZrCl2 (21) + xs HAi'Bu2 → Me2Si(2,4-Me2-C5H4)ZrCl(μ-H)2Al'Bu2

Figure S13. (Me2Si)2(C5H3)ZrCl2 (22) + 2 HAi'Bu2 → (Me2Si)2(C5H3)ZrCl(μ-H)2Al'Bu2

Figure S14. (Me2Si)2(2,4-Pr2-C5H)(C5H3)ZrCl2 (23) + 2 HAi'Bu2 → (Me2Si)2(2,4-Pr2-C5H)(C5H3)ZrCl(μ-H)2Al'Bu2

Figure S15. gCOSY for (EBTHI)ZrH(μ-H)2Al'Bu2 (25)

Figure S16. ((EBTHI)ZrH2)2 (24) + 4 HAi'Bu2 + 2 ClAl'Bu2 → (EBTHI)ZrCl(μ-H)2Al'Bu2

Figure S17. ((EBTHI)ZrH2)2 (24) + 4 HAi'Bu2 + 4 ClAl'Bu2 → (EBTHI)ZrCl(μ-H)2Al'Bu2

Figure S18. rac-Me2C(indenyl)2ZrCl2 (28) + 2 eq HAi'Bu2 → rac-Me2C(indenyl)2ZrCl(μ-H)2Al'Bu2

Figure S18. rac-Me2C(indenyl)2ZrCl2 (28) + 2 eq HAi'Bu2 → rac-Me2C(indenyl)2ZrCl(μ-H)2Al'Bu2
Figure S19. \( \textit{meso-} \text{Me}_2\text{C(indenyl)}_2\text{ZrCl}_2 \) (28) + 2 eq HAl\(^{i}\)Bu\(_2\) → \\
\( \textit{meso-} \text{Me}_2\text{C(indenyl)}_2\text{ZrCl}(\mu-\text{H})_2\text{Al}^{i}\text{Bu}_2 \)

Figure S20. gCOSY of \( \textit{rac-} \text{Me}_2\text{Si}((2-\text{Me}_3\text{Si}-4-\text{Me}_3\text{C}-\text{C}_5\text{H}_2)\text{ZrH}(\mu-\text{H})_2\text{Al}^{i}\text{Bu}_2 \) (32)

Figure S21. NOE of \( \textit{rac-} \text{Me}_2\text{Si}((2-\text{Me}_3\text{Si}-4-\text{Me}_3\text{C}-\text{C}_5\text{H}_2)\text{ZrH}(\mu-\text{H})_2\text{Al}^{i}\text{Bu}_2 \) (32)

Figure S22. \( \textit{meso-} \text{Me}_2\text{Si}(3-\text{Me}_3\text{C}-\text{C}_5\text{H}_2)_2\text{ZrCl}_2 \) (33) + 2 eq HAl\(^{i}\)Bu\(_2\) → \\
\( \textit{meso-} \text{Me}_2\text{Si}(3-\text{Me}_3\text{C}-\text{C}_5\text{H}_2)_2\text{ZrCl}(\mu-\text{H})_2\text{Al}^{i}\text{Bu}_2 \) (34)

Figure S23. gCOSY of \( \textit{meso-} \text{Me}_2\text{Si}(3-\text{Me}_3\text{C}-\text{C}_5\text{H}_2)_2\text{ZrCl}(\mu-\text{H})_2\text{Al}^{i}\text{Bu}_2 \) (34)

Figure S24. NOE of \( \textit{meso-} \text{Me}_2\text{Si}(3-\text{Me}_3\text{C}-\text{C}_5\text{H}_2)_2\text{ZrCl}(\mu-\text{H})_2\text{Al}^{i}\text{Bu}_2 \) (34)

Figure S25. H\(_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{ZrCl}_2 \) (35) + 4 eq HAl\(^{i}\)Bu\(_2\) → H\(_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Zr}(\mu-\text{H})_3(\text{Al}^{i}\text{Bu}_2)_3(\mu-\text{H})_3 \) (37)

Figure S26. NOE of Me\(_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Zr}(\mu-\text{H})_3(\text{Al}^{i}\text{Bu}_2)_3(\mu-\text{H})_3 \) (38)

Figure S27. ((EBTHI)ZrF\(_2\) + 1 eq HAl\(^{i}\)Bu\(_2\) → ((EBTHI)ZrH\(_2\)_2 + (EBTHI)ZrF\(_2\)

Appendix S-1. Analysis of changes in the chemical shift of the ZrH\(_2\) signal of (SBI)ZrCl(\(\mu\)-H)\(_2\)Al\(^{i}\)Bu\(_2\) upon addition of Al\(_2\)Me\(_6\).
Figure S1. \(^1\)H spectrum of (C\(_5\)H\(_5\))\(_2\)ZrH\(_2\) (3) with 1 equiv. HAl\(^t\)Bu\(_2\) and 1 equiv. ClAl\(^t\)Bu\(_2\) in benzene-\(d_6\) at 25°C.

Figure S2. \(^1\)H spectrum of (C\(_5\)H\(_5\))\(_2\)ZrH\(_2\) (3) with 1 equiv. HAl\(^t\)Bu\(_2\) and 2 equiv. ClAl\(^t\)Bu\(_2\) in benzene-\(d_6\) at 25°C.
Figure S3. $^1$H spectrum of $(\text{C}_5\text{H}_5)\text{Zr}(\mu-\text{H})_3\text{(Al}^3\text{Bu}_2)_3(\mu-\text{H})_3$ in toluene-$d_8$ at -60°C.

Figure S4. $^1$H spectrum of $(^6\text{Bu}\cdot\text{Cp})\text{ZrCl}_2$ (6) with 3 equiv. HAi'Bu$_2$ in benzene-$d_6$ at 25°C
Figure S5. $^1$H spectrum of (1,2-Me$_2$-C$_5$H$_3$)$_2$ZrCl$_2$ (8) with excess HAl'Bu$_2$ in benzene-$d_6$ at 25°C.

Figure S6. $^1$H spectrum of (Me$_3$Si-C$_5$H$_4$)$_2$ZrCl$_2$ (10) with 2 equiv. HAl'Bu$_2$ in toluene-$d_8$ at -75°C.
Figure S7. $^1$H spectrum of (C₅Me₅)₂ZrH₂ (13) with 2 equiv. Al′Bu₃ to give (C₅Me₅)₂ZrH′Bu (14) and (C₅Me₅)₂Zr′Bu₂ (15) in benzene-$d_6$ at 25°C.

Figure S8. $^1$H spectrum of (EBI)ZrCl₂ (17) with 2 equiv. HAl′Bu₂ in benzene-$d_6$ at 25°C.
Figure S9. (EBTHI)ZrCl₂ (18) with 2 equiv. HAi'Bu₂ in benzene-\textit{d}_6 at 25°C.

Figure S10. $^1$H spectrum of Me₂C(C₅H₄)₂ZrCl₂ (19) with excess HAi'Bu₂ in benzene-\textit{d}_6 at 25°C.
Figure S11. $^1$H spectrum of Me$_2$Si(C$_5$H$_4$)$_2$ZrCl$_2$ (19) with 6 equiv. HAl'Bu$_2$ in benzene-$d_6$ at 25°C.

Figure S12. $^1$H spectrum of Me$_2$Si(2,4-Me$_2$-C$_5$H$_2$)$_2$ZrCl$_2$ (21) with excess HAl'Bu$_2$ in benzene-$d_6$ at 25°C.
Figure S13. $^1$H spectrum of (Me$_2$Si)$_2$(C$_5$H$_3$)$_2$ZrCl$_2$ (22) with 2 equiv. HAl$^t$Bu$_2$ in toluene-$d_8$ at -75°C.

Figure S14. $^1$H spectrum of (Me$_2$Si)$_2$(2,4-$^t$Pr$_2$C$_5$H$_3$)$_2$ZrCl$_2$ (23) with 2 equiv. HAl$^t$Bu$_2$ in toluene-$d_8$ at -75°C.
Figure S15. gCOSY of (EBTHI)ZrH(μ-H)2AliBu2 (25) in toluene-d8 at -75°C.

Figure S16. $^1$H spectrum of ((EBTHI)ZrH(μ-H))2 (24) with 4 equiv. HA'iBu2 and 2 equiv. ClAI'Bu2 in benzene-d6 at 25°C.
Figure S17. $^1$H spectrum of ((EBTHI)ZrH(μ-H))$_2$ (24) with 4 equiv. HAi′Bu$_2$ and 4 equiv. ClAi′Bu$_2$ in benzene-$d_6$ at 25°C.

Figure S18. $^1$H spectrum of rac-Me$_2$C(indenyl)$_2$ZrCl$_2$ (27) with 2 equiv. HAi′Bu$_2$ in benzene-$d_6$ at 25°C.
Figure S19. $^1$H spectrum of meso-Me$_2$C(indenyl)$_2$ZrCl$_2$ (28) with 2 equiv. HAl'Bu$_2$ in benzene-$d_6$ at 25°C.

Figure S20. gCOSY of rac-Me$_3$Si((2-Me$_3$Si-4-Me$_3$C-C$_5$H$_2$)ZrH(μ-H)$_2$Al'Bu$_2$ (32) in toluene-$d_8$ at -75°C
Figure S21. noedif of 32 in benzene-$d_6$ at 25°C irradiating the central hydride resonance (A) and the terminal unbridged hydride resonance (B).
Figure S22. $^1$H spectrum of meso-Me$_2$Si(3-Me$_3$C-C$_5$H$_3$)$_2$ZrCl$_2$ (33) with 2 equiv. HAl$i$Bu$_2$ in toluene-$d_8$ at 25°C.

Figure S23. gCOSY of 33 with 2 equiv. HAl$i$Bu$_2$ in toluene-$d_8$ at 25°C.
**Figure S24.** noedif of 33 with 3 equiv. HAi′Bu2 in benzene-$d_6$ at 25°C.

**Figure S25.** $^1$H spectrum of $\text{H}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (35) with 4 equiv. HAi′Bu2 in toluene-$d_8$ at 0°C.
Figure S26. NOESY 1D of Me₄C₂(C₅H₄)₂ZrCl₂ (36) with 4 equiv. HA′Bu₂ in benzene-\textit{d}₆ at 25°C.

Figure S27. $^1$H spectrum of (EBTHI)ZrF₂ with 1 equiv. HA′Bu₂ in benzene-\textit{d}₆ at 25°C.
Appendix S-1. Analysis of changes in the chemical shift of the ZrH$_2$ signal of (SBI)ZrCl(\(\mu\)-H)$_2$Al\(^i\)Bu$_2$ upon addition of Al$_2$Me$_6$.

1) Adduct Formation:
Adduct formation of (SBI)ZrCl(\(\mu\)-H)$_2$Al\(^i\)Bu$_2$ with Al$_2$Me$_6$, is represented by Equ. 1, with \(A\) representing the starting complex, \(X_2\) the AlMe$_3$ dimer and \(AX\) the adduct:

\[
A + \frac{1}{2} X_2 \leftrightarrow AX
\]  

(1)

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

\[
K = \frac{[AX]}{[A][X_2]^{1/2}}
\]  

(2)

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

\[
\delta = \frac{[A]}{[AX]+[A]} \delta_A + \frac{[AX]}{[AX]+[A]} \delta_{AX}
\]  

(3)

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

\[
\Delta \delta = \delta - \delta_A
\]  

(4)

Combining Equ. 3 and Equ. 4 we get:

\[
\Delta \delta = \left( \frac{[A]}{[AX]+[A]} - 1 \right) \delta_A + \frac{[AX]}{[AX]+[A]} \delta_{AX}
\]  

(5)

Which simplifies to:

\[
\Delta \delta = \frac{[AX]}{[AX]+[A]} (\delta_{AX} - \delta_A)
\]  

(6)

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

\[
\Delta \delta_{\text{max}} = \delta_{AX} - \delta_A
\]  

(7)

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

\[
\frac{1}{\Delta \delta} = \frac{1}{\Delta \delta_{\text{max}}} + \frac{1}{\Delta \delta_{\text{max}}} \cdot \frac{[A]}{[AX]}
\]  

(8)
Together with the equilibrium constant, Equ. 2, this yields a Benesi-Hildebrand type relation (Equ. 9):

\[
\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\text{max}}} + \frac{1}{\Delta\delta_{\text{max}} K \sqrt{[X_2]}}
\]  

(9)

Assuming that K is small, the amount of X₂ added is approximately equal to the amount of X₂ in solution. A plot of the reciprocal of the change in chemical shift against the reciprocal of the square root of the concentration of Al₂Me₆ added should thus be linear, with a slope of 1/K and a y-axis intercept of 1/δₐₓ, neither of which should depend on [Zr]ₜₒᵗ.

![Chart 1. Data analysis according to equ. 9](image)

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 Al₂Me₆ to AlMe₃ in dilute solutions and/or from the fact that the most concentrated solutions of Al₂Me₆ contain up to 20 volume percent Al₂Me₆, such that these solution can no longer be considered to be ideal solutions of Al₂Me₆ in benzene. Nevertheless, the values of 1/δₐₓ and of 1/K derived from the data for [Zr] = 7 mM and from those for [Zr] = 28 mM are indistinguishable within their error.
margins. Our data are thus compatible with the view that the change in chemical shift of the ZrH2 signal upon addition of Al2Me6 to a solution of (SBI)Zr(Cl)(μ-H)2Al′Bu2 is due to formation of an adduct, e.g. of the type (SBI)Zr(Cl…AlMe3)(μ-H)2AlR2, with R = ′Bu and/or Me.

2) Exchange Reaction:
The reaction of (SBI)ZrCl(μ-H)2Al′Bu2 to exchange either the Zr-bound Cl or an Al-bound ′Bu with one of the methyl groups of Al2Me6, to yield Al2Me5X where X = Cl or ′Bu, is represented by Equ. 10, with A representing the starting ZrClH2 complex, X2 the AlMe3 dimer, B the exchange product and Y the Al2Me5X product:

\[
A + X_2 \leftrightarrow B + Y
\]  

(10)

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

\[
K = \frac{[B][Y]}{[A][X_2]}
\]  

(11)

We can use the same derivation as for Equation 8, except [AX] is now replaced by [B].

\[
\frac{1}{\Delta \delta} = \frac{1}{\Delta \delta_{\text{max}}} + \frac{1}{\Delta \delta_{\text{max}}} \cdot \frac{[A]}{[B]}
\]  

(12)

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

\[
\frac{1}{\Delta \delta} = \frac{1}{\Delta \delta_{\text{max}}} + \frac{1}{\Delta \delta_{\text{max}}} \cdot \frac{[Y]}{K[X_2]}
\]  

(13)

Since we are adding X2 to A, [Y] is equal to [B], yielding:

\[
\frac{1}{\Delta \delta} = \frac{1}{\Delta \delta_{\text{max}}} + \frac{1}{\Delta \delta_{\text{max}}} \cdot \frac{[B]}{K[X_2]}
\]  

(14)

Rearranging to give a y = mx+b format gives:

\[
\frac{1}{\Delta \delta} = \left( \frac{[B]}{\Delta \delta_{\text{max}} K} \right) \cdot \frac{1}{[X_2]} + \frac{1}{\Delta \delta_{\text{max}}}
\]  

(15)

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

\[
\Delta \delta = \Delta \delta_{\text{max}} \frac{[B]}{[A]+[B]}
\]  

(16)

Solving for [B] and substituting into Equation 14 gives:
\[
\frac{1}{\Delta \delta} = \frac{1}{\Delta \delta_{\text{max}}} + \frac{\Delta \delta}{\Delta \delta_{\text{max}}} \cdot \frac{[A] + [B]}{K[X_2]} 
\] (17)

With \([A] + [B] = [\text{Zr}]_{\text{TOT}}\) and \([X_2] = [\text{Al}_2\text{Me}_6]\), equation 17 can be rearranged to:

\[
\left(\frac{\Delta \delta_{\text{max}}}{\Delta \delta} - 1\right) \frac{\Delta \delta_{\text{max}}}{\Delta \delta} = \frac{[\text{Zr}]_{\text{TOT}}}{K \cdot [\text{Al}_2\text{Me}_6]} 
\] (18)

The value of \(\Delta \delta_{\text{max}}\) can be estimated from the chemical shift at the highest concentrations of \(\text{Al}_2\text{Me}_6\) or from the plot in Chart 1. Assuming that \(K\) is small, the amount of \(\text{Al}_2\text{Me}_6\) added is approximately equal to the amount of \(\text{Al}_2\text{Me}_6\) in solution. Therefore, a plot of the left side of Equ.18 against \([\text{Zr}]_{\text{TOT}}/[\text{Al}_2\text{Me}_6]\) should give a straight line going through the origin, with a slope of \(1/K\), which should thus be independent of \([\text{Zr}]_{\text{TOT}}\).

**Chart 2. Data analysis according to equation 18**

![Chart 2](image)

Inspection of such a plot (Chart 2) shows that the data do not meet this requirement. Instead, the slope of the data for \([\text{Zr}]_{\text{tot}} = 7 \text{ mM}\) is about three times larger than that of the data for \([\text{Zr}]_{\text{tot}} = 28 \text{ mM}\). The change in chemical shift of the \(\text{ZrH}_2\) signal upon addition of \(\text{Al}_2\text{Me}_6\) to a solution of \((\text{SBI})\text{Zr(Cl)}(\mu-\text{H})_2\text{Al}^i\text{Bu}_2\) can thus be due to an exchange reaction, e.g. of the Cl against a Me ligand.