SUPPORTING INFORMATION

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

Steven M. Baldwin,[†] John E. Bercaw,[*, †] and Hans H. Brintzinger*, [‡]

Contribution from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, USA, and Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany

E-mail: Bercaw@caltech.edu; Hans.Brintzinger@uni-konstanz.de

NMR Spectra:

Figure S1. ^{1}H spectrum of $(C_5H_5)_2ZrH_2$ (**3**) with 1 equiv. HAl^iBu_2 and 1 equiv. $ClAl^iBu_2$ in benzene-d_6 at 25°C.

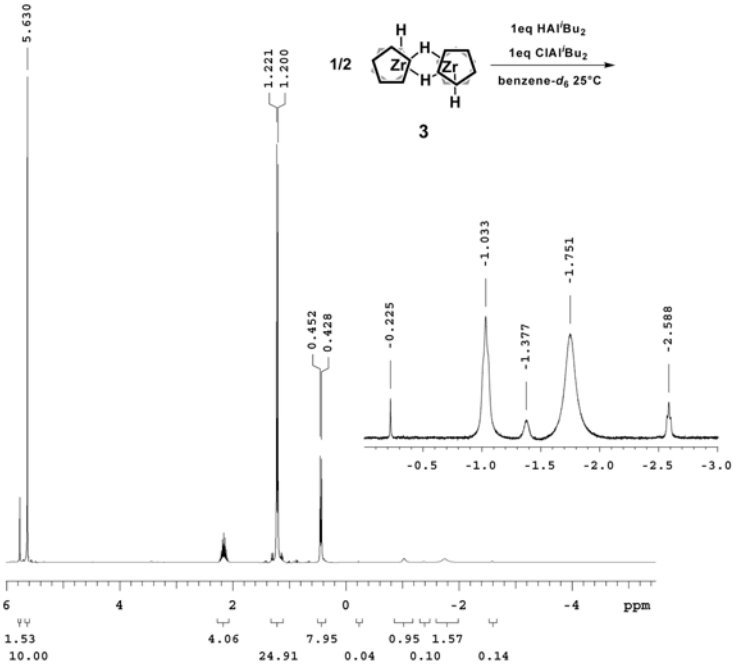


Figure S2. ^{1}H spectrum of $(C_5H_5)_2ZrH_2$ (**3**) with 1 equiv. HAl^iBu_2 and 2 equiv. $ClAl^iBu_2$ in benzene-d_6 at 25°C.

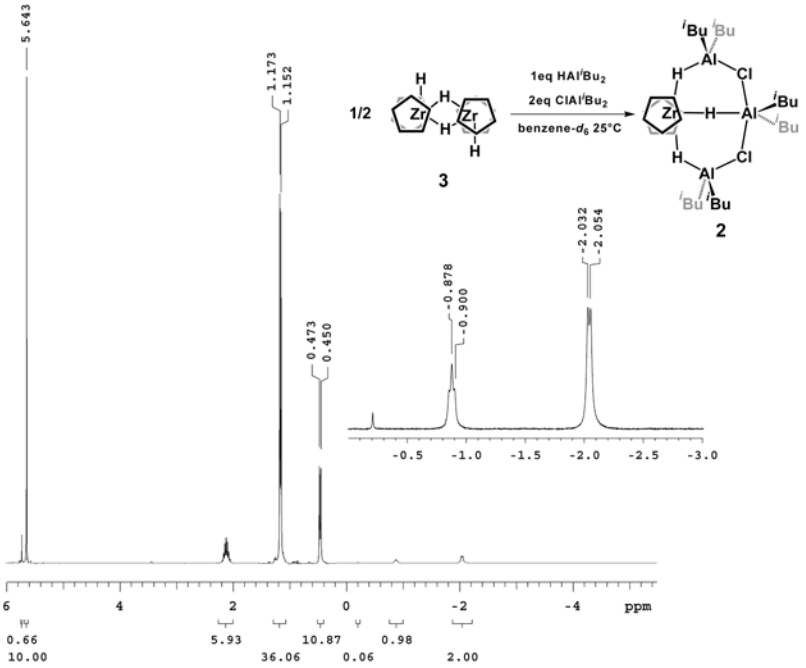


Figure S3. ^{1}H spectrum of $(C_5H_5)_2Zr(\mu\text{-}H)_3(Al^{i}Bu_2)_3(\mu\text{-}H)_3$ in toluene-d_8 at -60°C.

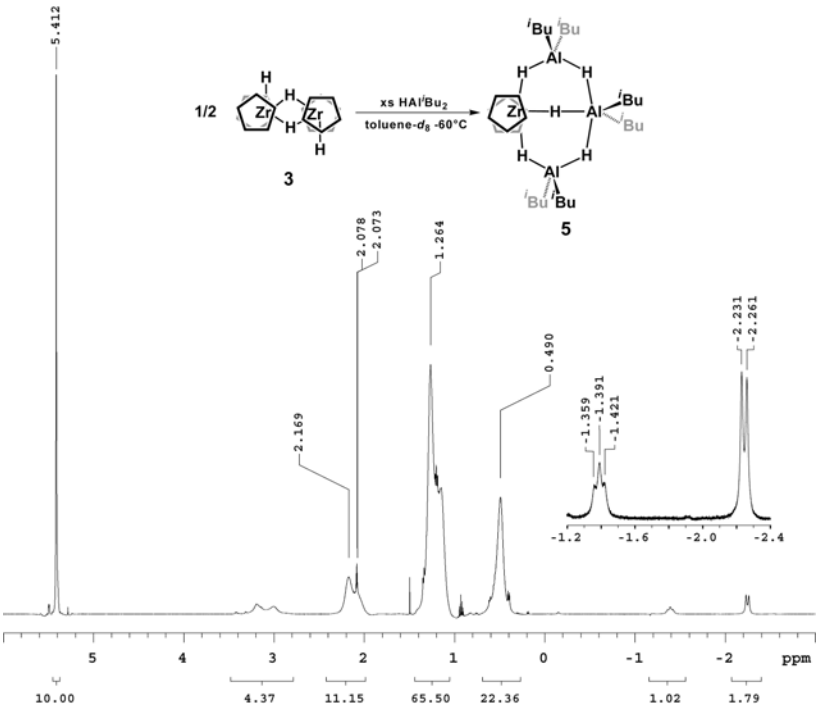


Figure S4. ^{1}H spectrum of (^{n}Bu-Cp)$_2$ZrCl$_2$ (**6**) with 3 equiv. HAl^{i}Bu$_2$ in benzene-d_6 at 25°C

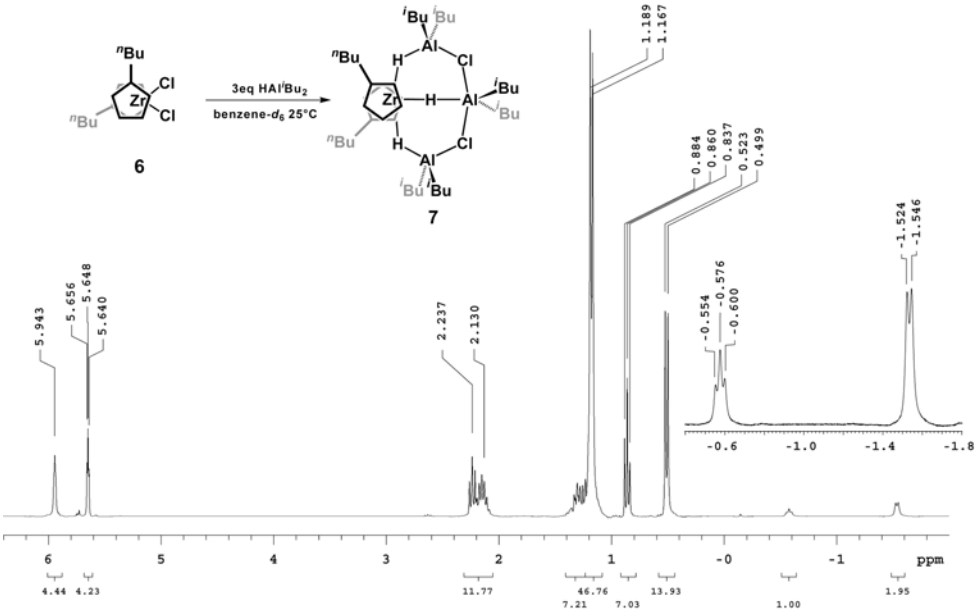


Figure S5. ^{1}H spectrum of (1,2-Me_2-C_5H_3)$_2$$ZrCl_2$ (**8**) with excess HAl^{i}Bu_2 in benzene-d_6 at 25°C.

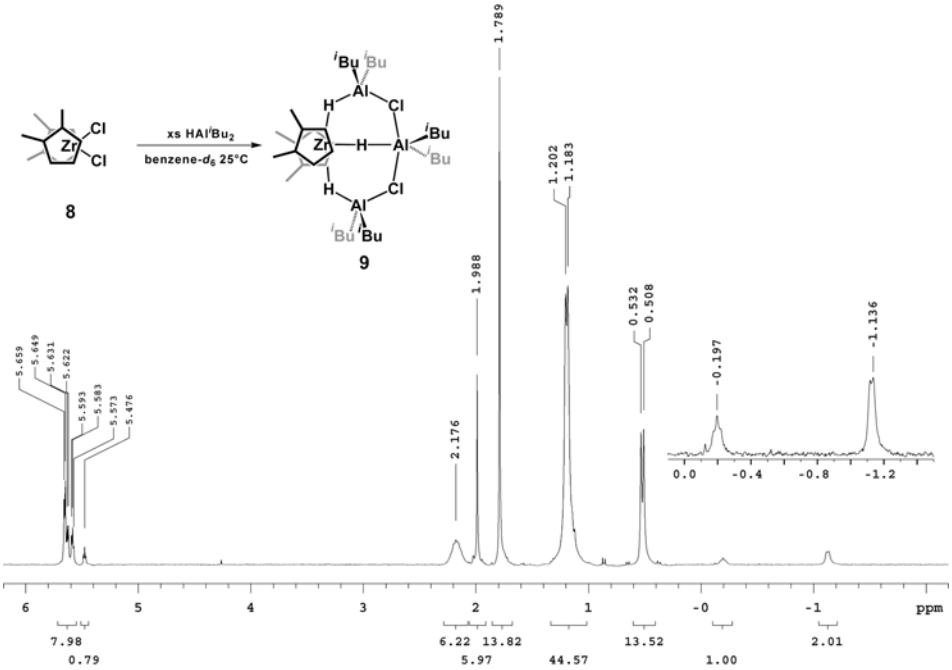


Figure S6. ^{1}H spectrum of (Me_3Si-C_5H_4)$_2$$ZrCl_2$ (**10**) with 2 equiv. HAl^{i}Bu_2 in toluene-d_8 at -75°C.

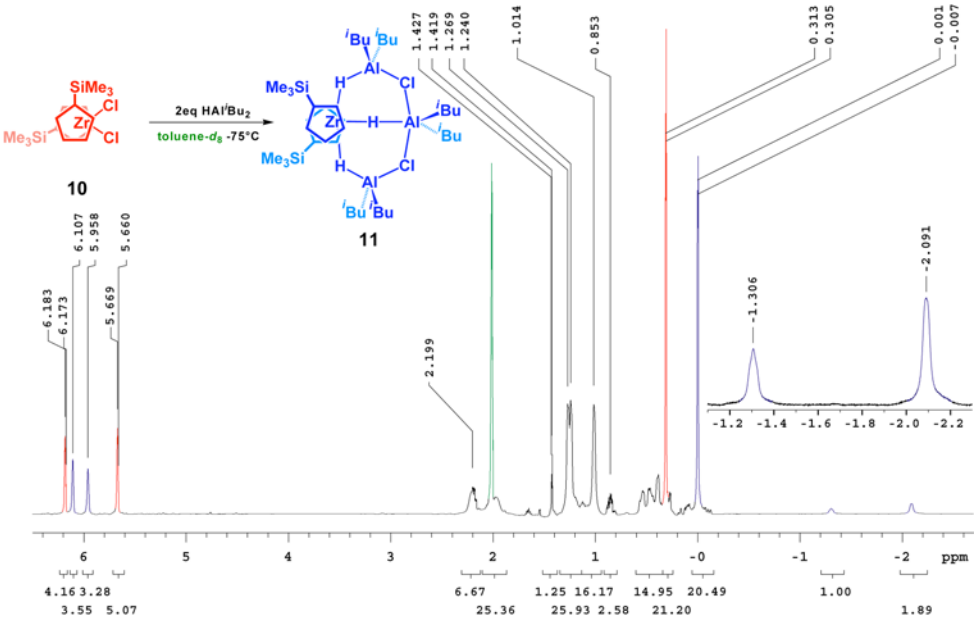


Figure S7. ^{1}H spectrum of $(C_5Me_5)_2ZrH_2$ (**13**) with 2 equiv. Al^iBu_3 to give $(C_5Me_5)_2ZrH^iBu$ (**14**) and $(C_5Me_5)_2Zr^iBu_2$ (**15**) in benzene-d_6 at 25°C.

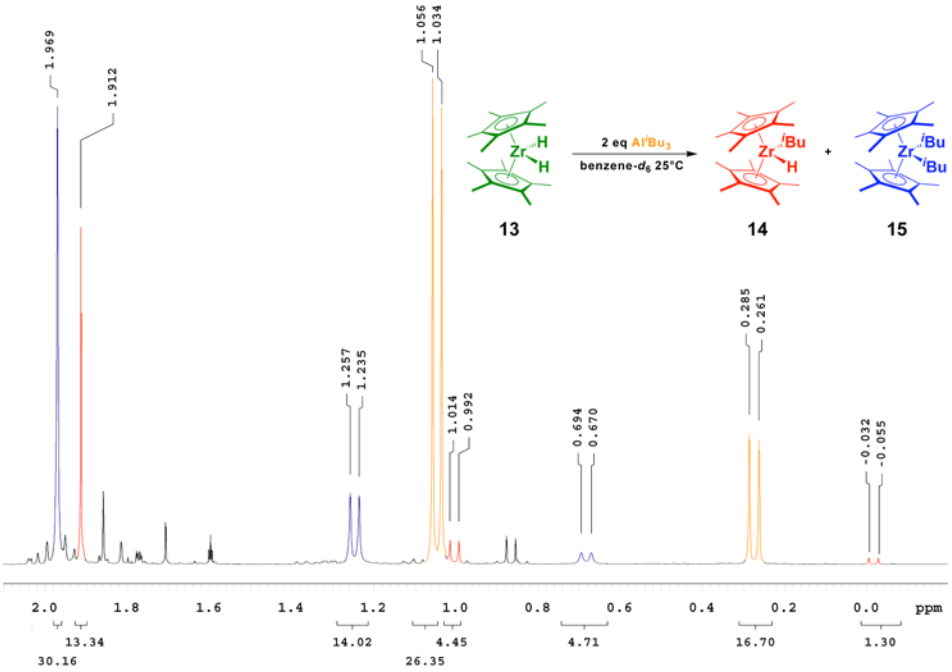


Figure S8. ^{1}H spectrum of (EBI)$ZrCl_2$ (**17**) with 2 equiv. HAl^iBu_2 in benzene-d_6 at 25°C.

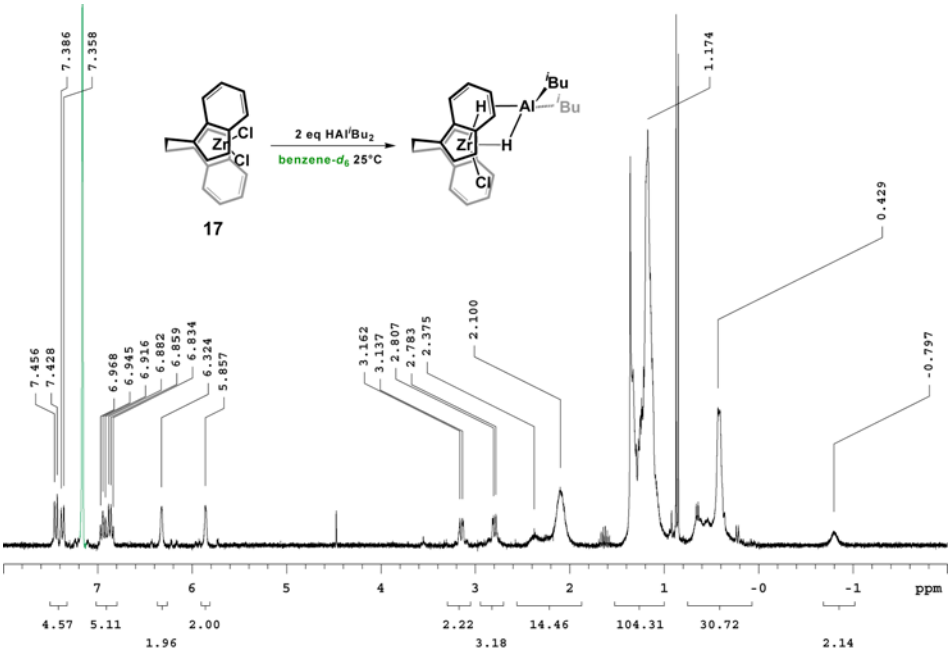


Figure S9. (EBTHI)$ZrCl_2$ (**18**) with 2 equiv. HAl^iBu_2 in benzene-d_6 at 25°C.

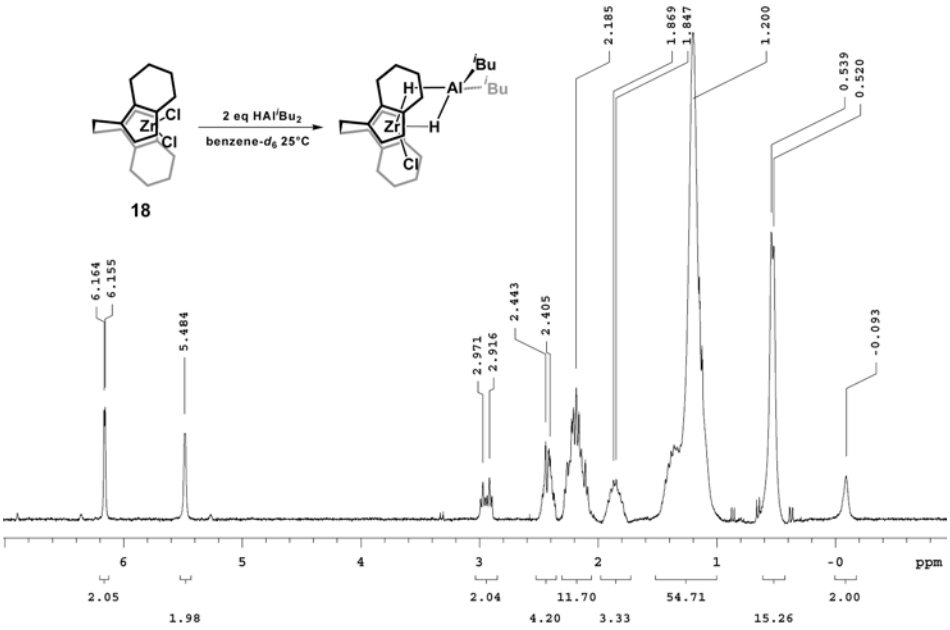


Figure S10. ^1H spectrum of $Me_2C(C_5H_4)_2ZrCl_2$ (**19**) with excess HAl^iBu_2 in benzene-d_6 at 25°C.

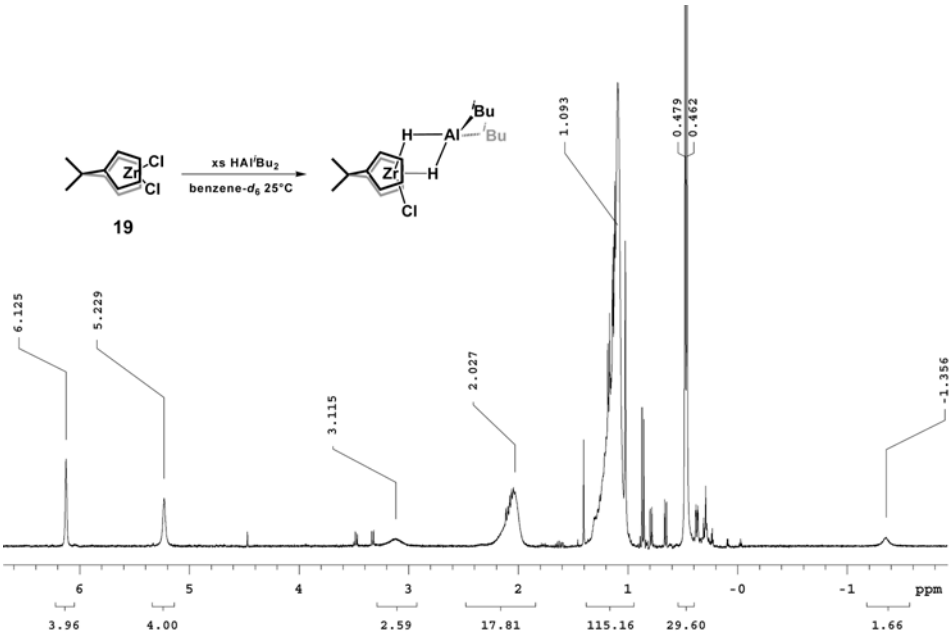


Figure S11. ^{1}H spectrum of $Me_2Si(C_5H_4)_2ZrCl_2$ (**19**) with 6 equiv. HAl^iBu_2 in benzene-d_6 at 25°C.

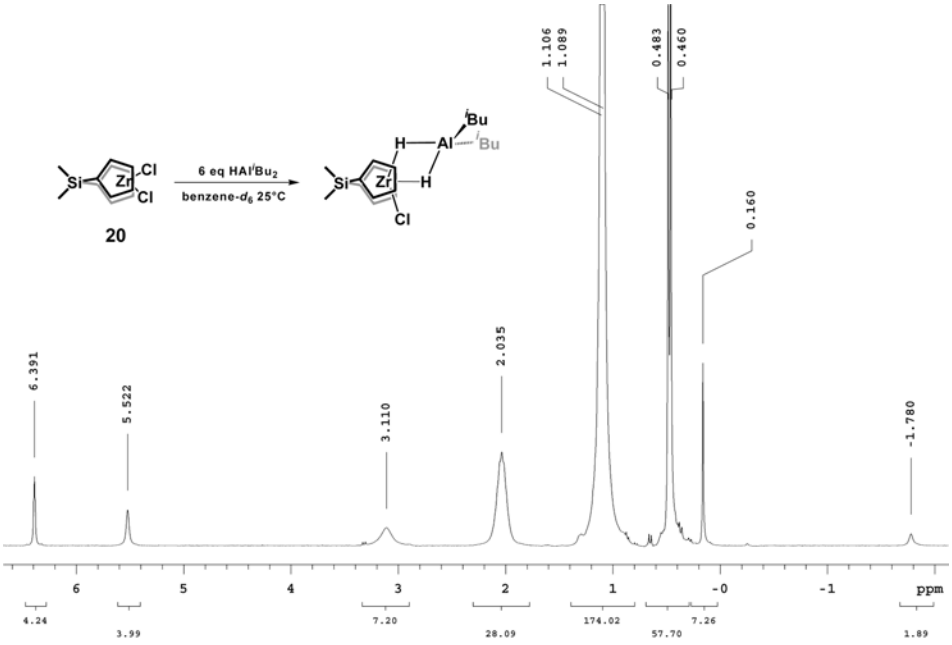


Figure S12. ^{1}H spectrum of $Me_2Si(2,4\text{-}Me_2\text{-}C_5H_2)_2ZrCl_2$ (**21**) with excess HAl^iBu_2 in benzene-d_6 at 25°C.

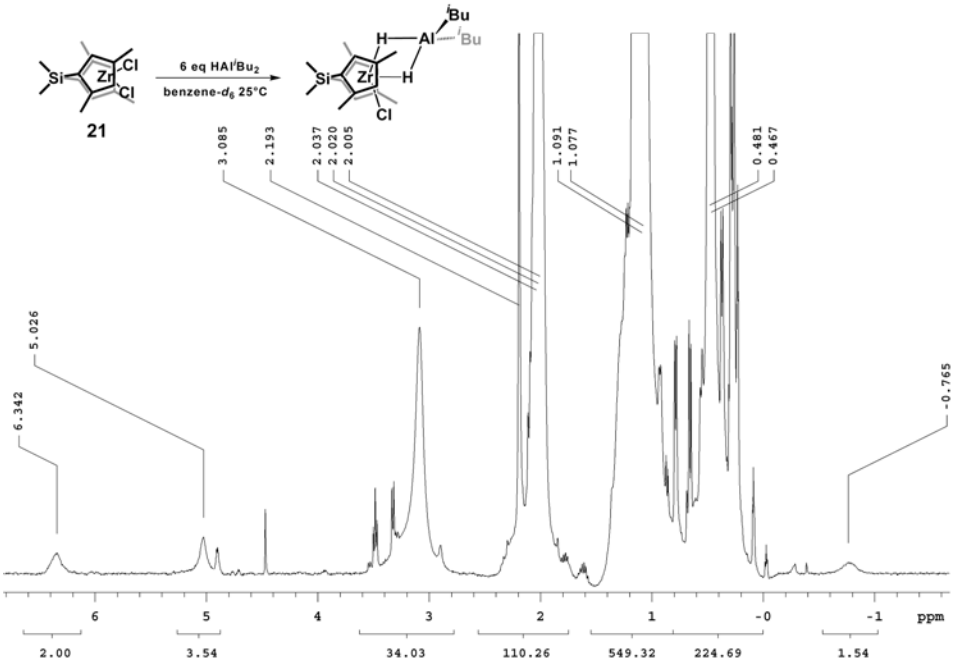


Figure S13. ^{1}H spectrum of $(Me_2Si)_2(C_5H_3)_2ZrCl_2$ (**22**) with 2 equiv. HAl^iBu_2 in toluene-d_8 at -75°C.

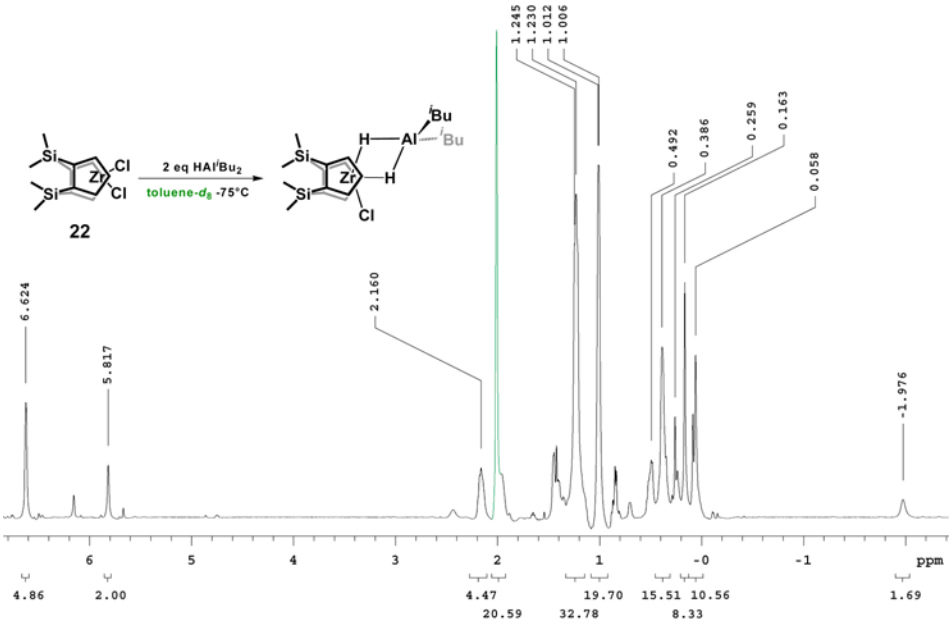


Figure S14. ^{1}H spectrum of $(Me_2Si)_2(2,4\text{-}^{i}Pr_2\text{-}C_5H_3)_2ZrCl_2$ (**23**) with 2 equiv. HAl^iBu_2 in toluene-d_8 at -75°C.

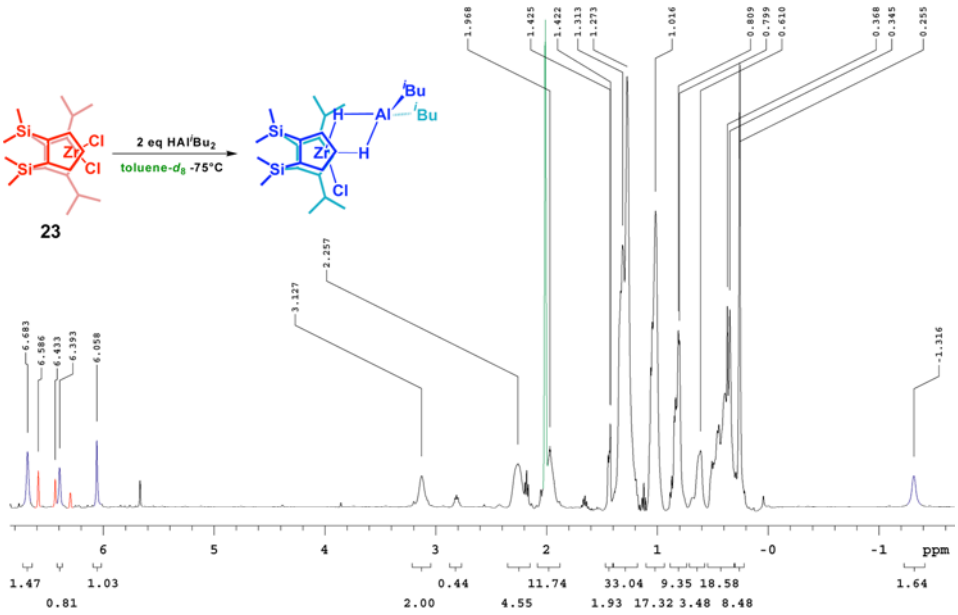


Figure S15. gCOSY of (EBTHI)ZrH(μ-H)$_2$Al^{i}Bu$_2$ (**25**) in toluene-d_8 at -75°C.

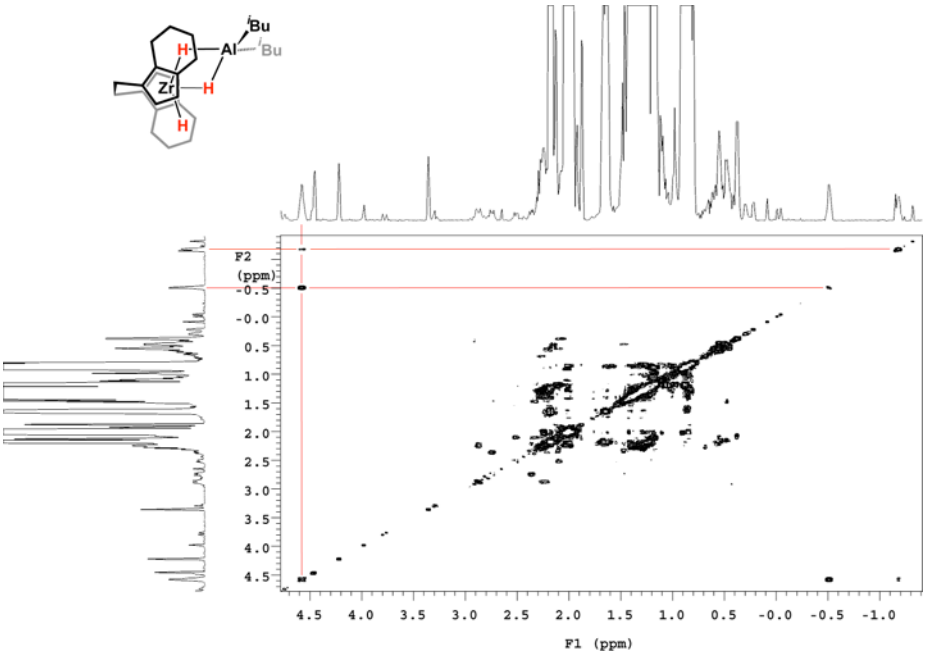


Figure S16. ^{1}H spectrum of ((EBTHI)ZrH(μ-H))$_2$ (**24**) with 4 equiv. HAl^{i}Bu$_2$ and 2 equiv. ClAl^{i}Bu$_2$ in benzene-d_6 at 25°C.

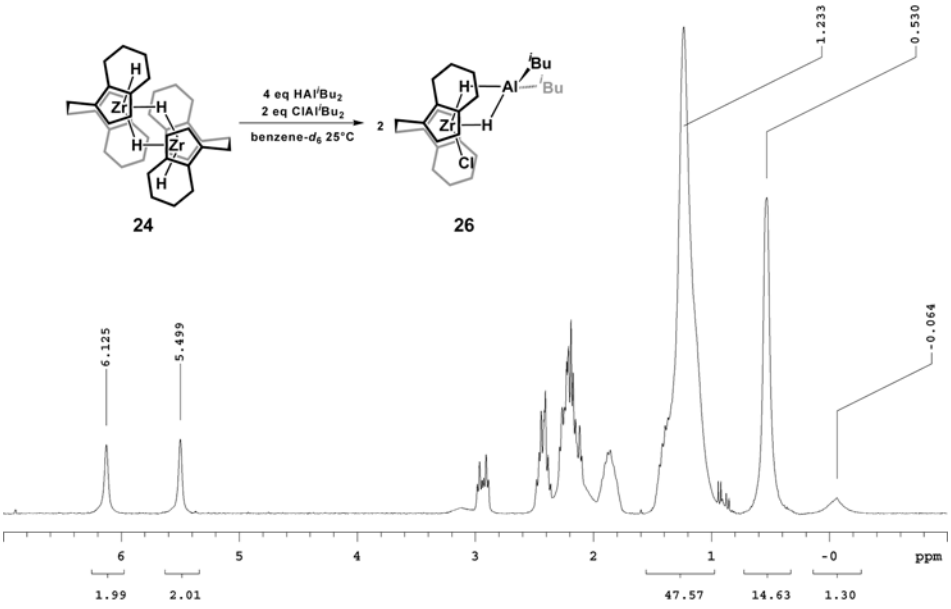


Figure S17. ^{1}H spectrum of ((EBTHI)ZrH(μ-H))$_2$ (**24**) with 4 equiv. HAl^{i}Bu$_2$ and 4 equiv. ClAl^{i}Bu$_2$ in benzene-d_6 at 25°C.

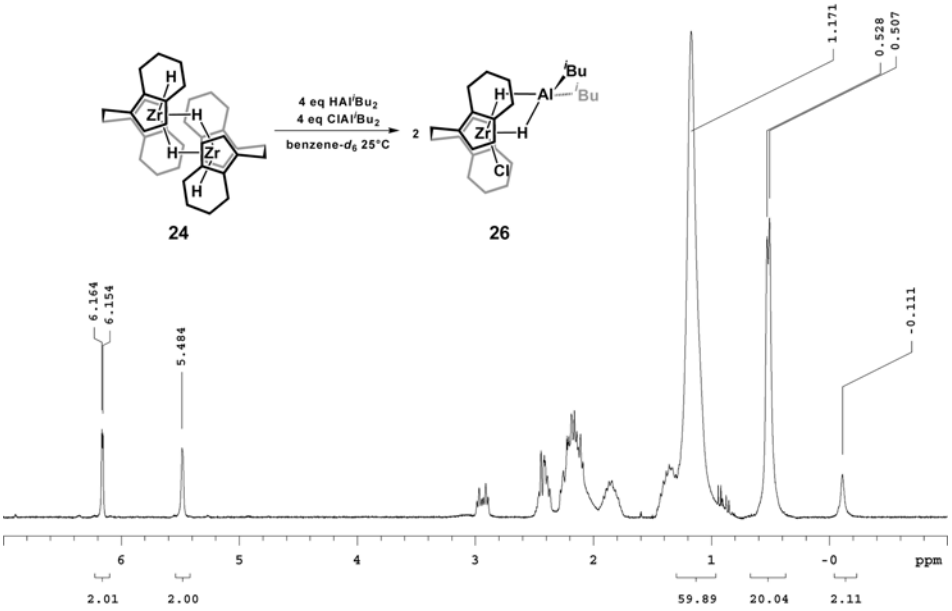


Figure S18. ^{1}H spectrum of *rac*-Me$_2$C(indenyl)$_2$ZrCl$_2$ (**27**) with 2 equiv. HAl^{i}Bu$_2$ in benzene-d_6 at 25°C.

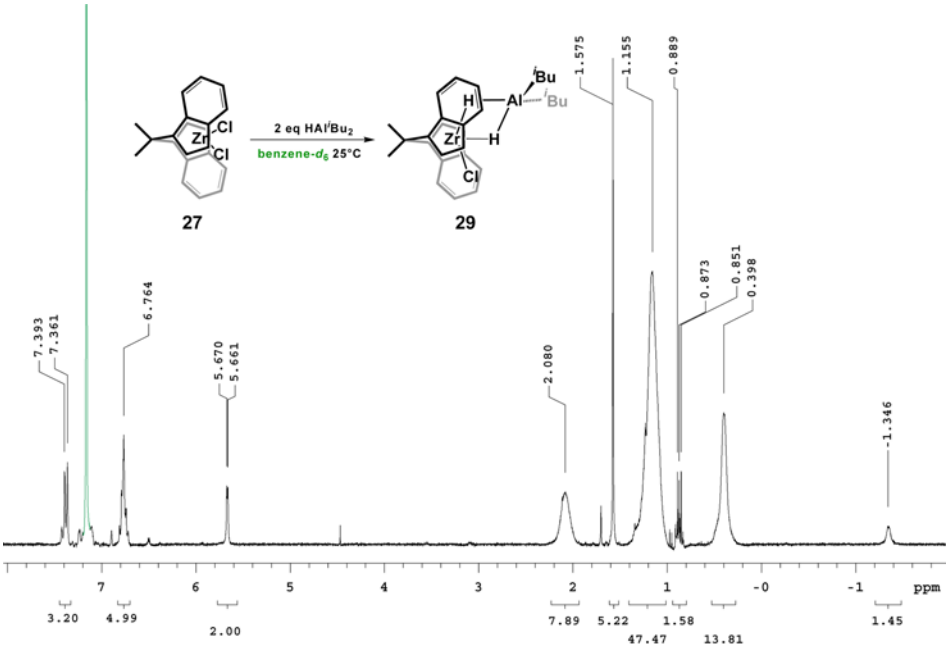


Figure S19. ^{1}H spectrum of *meso*-$Me_2C(indenyl)_2ZrCl_2$ (**28**) with 2 equiv. $HAl^{i}Bu_2$ in benzene-d_6 at 25°C.

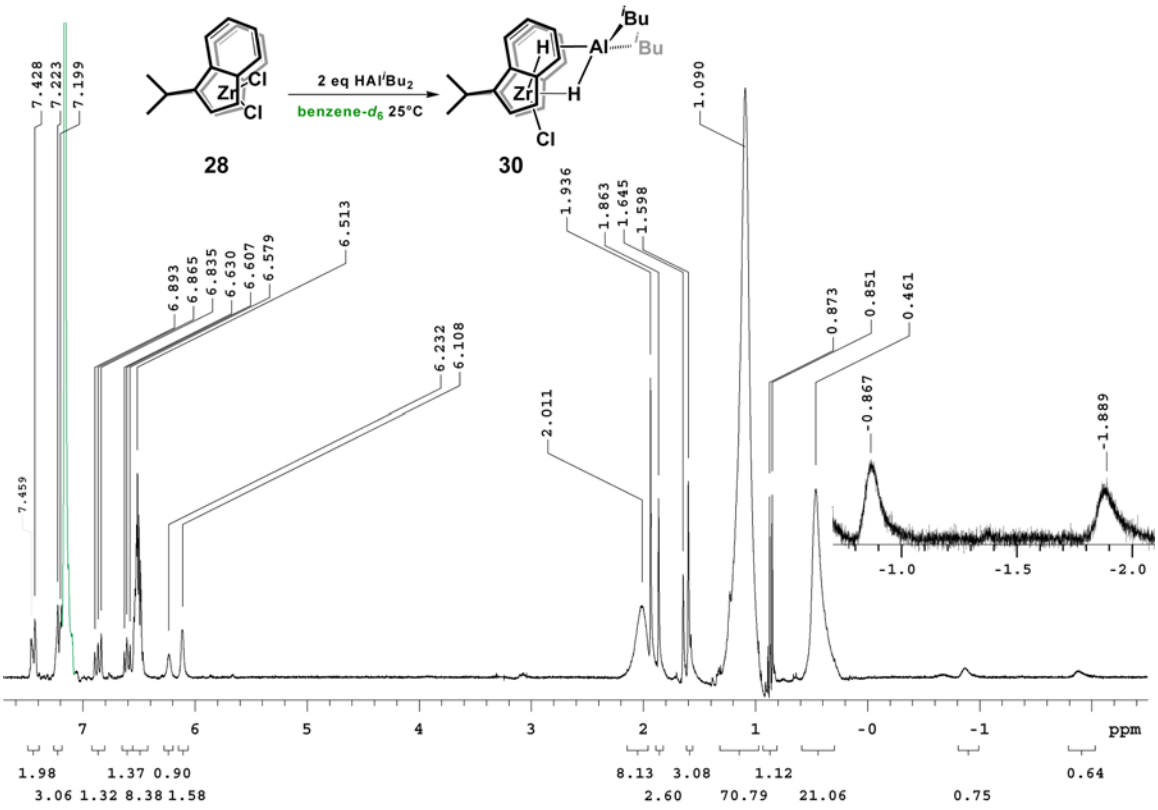


Figure S20. gCOSY of *rac*-$Me_2Si((2\text{-}Me_3Si\text{-}4\text{-}Me_3C\text{-}C_5H_2)ZrH(\mu\text{-}H)_2Al^{i}Bu_2$ (**32**) in toluene-d_8 at -75°C

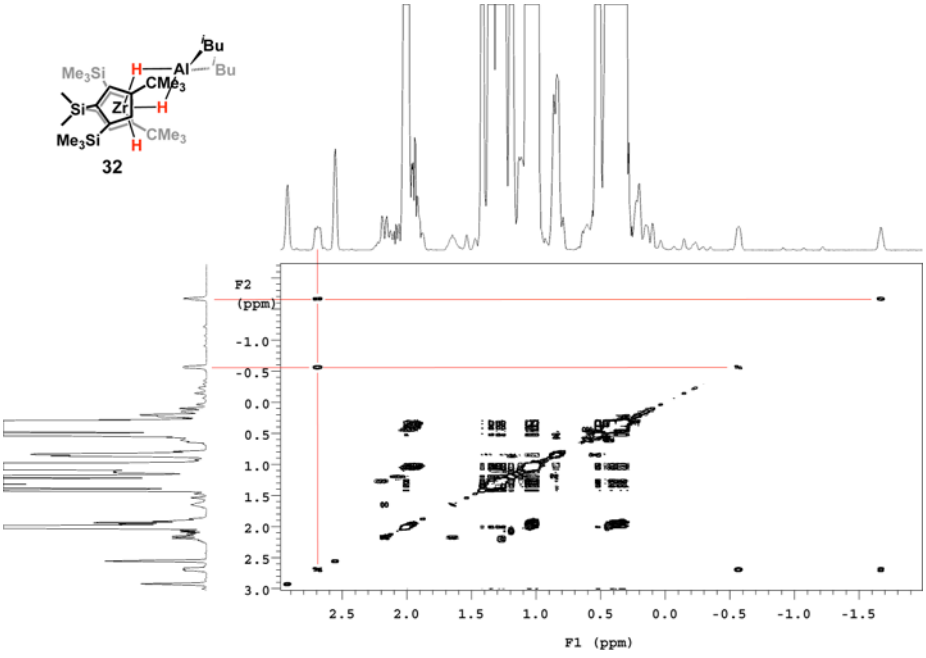


Figure S21. noedif of **32** in benzene-d_6 at 25°C irradiating the central hydride resonance (**A**) and the terminal unbridged hydride resonance (**B**).

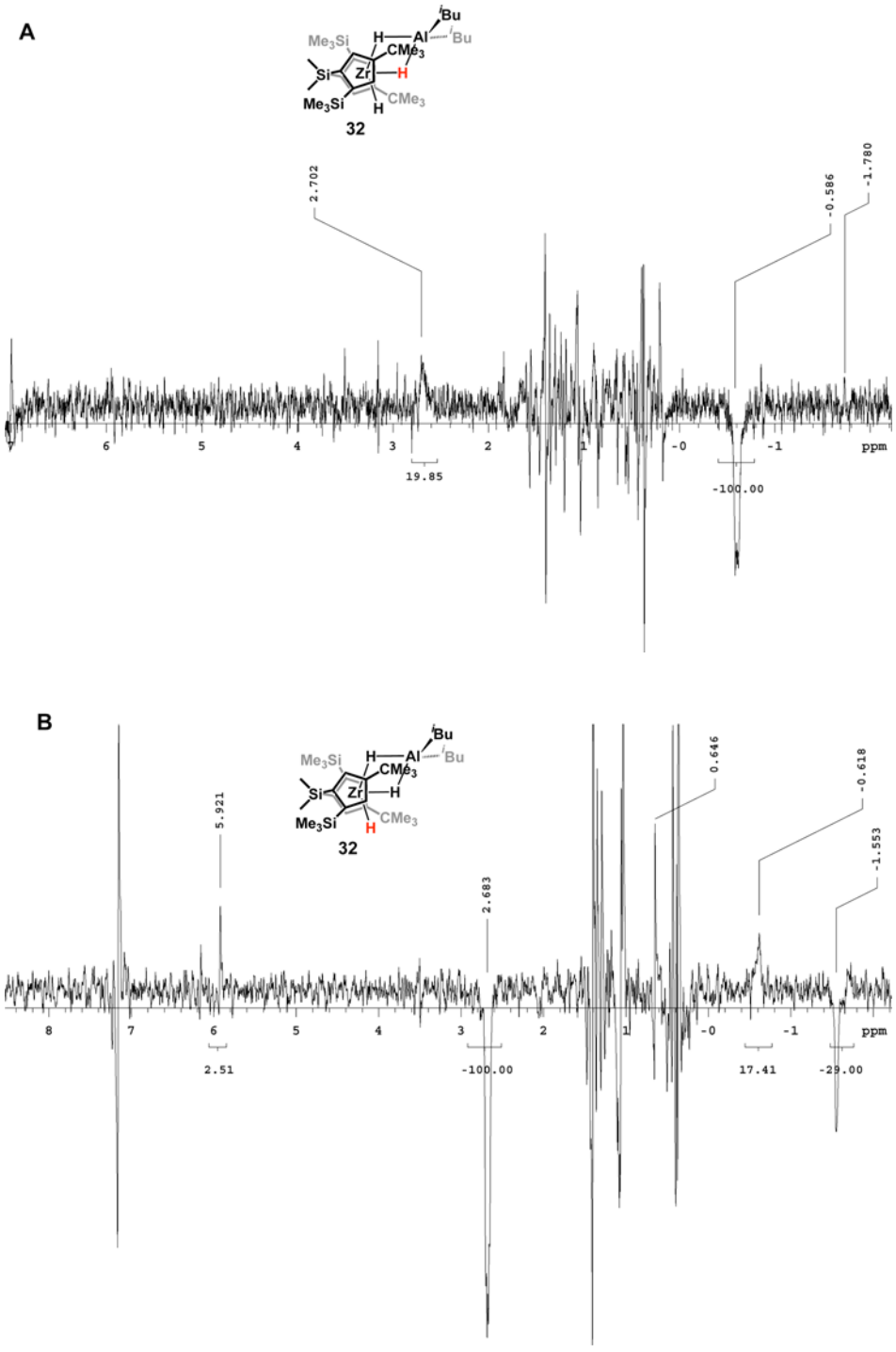


Figure S22. ^{1}H spectrum of *meso*-$Me_2Si(3\text{-}Me_3C\text{-}C_5H_3)_2ZrCl_2$ (**33**) with 2 equiv. $HAl^{i}Bu_2$ in toluene-d_8 at 25°C.

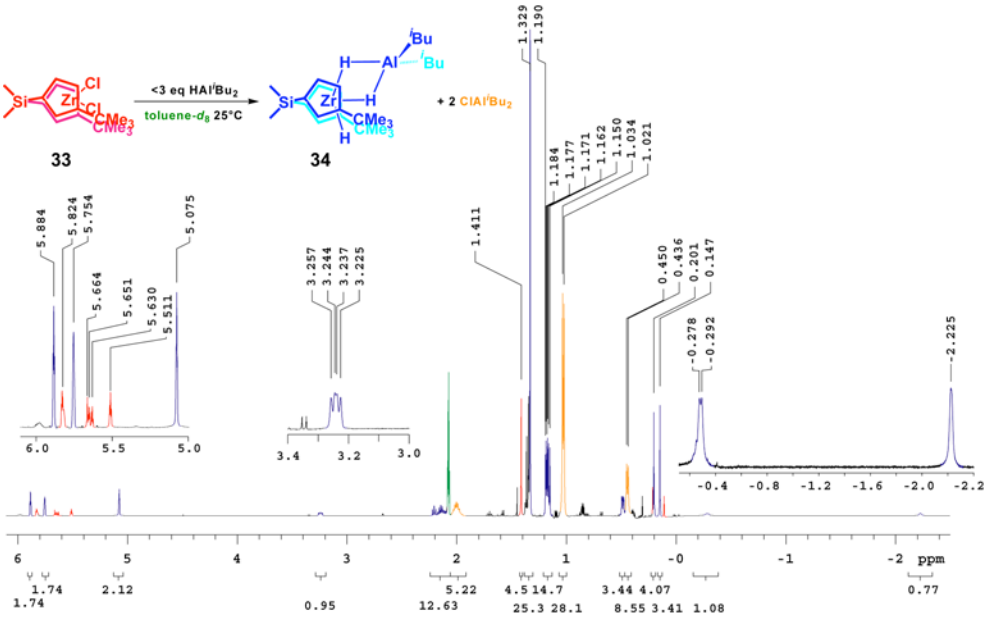


Figure S23. gCOSY of **33** with 2 equiv. $HAl^{i}Bu_2$ in toluene-d_8 at 25°C.

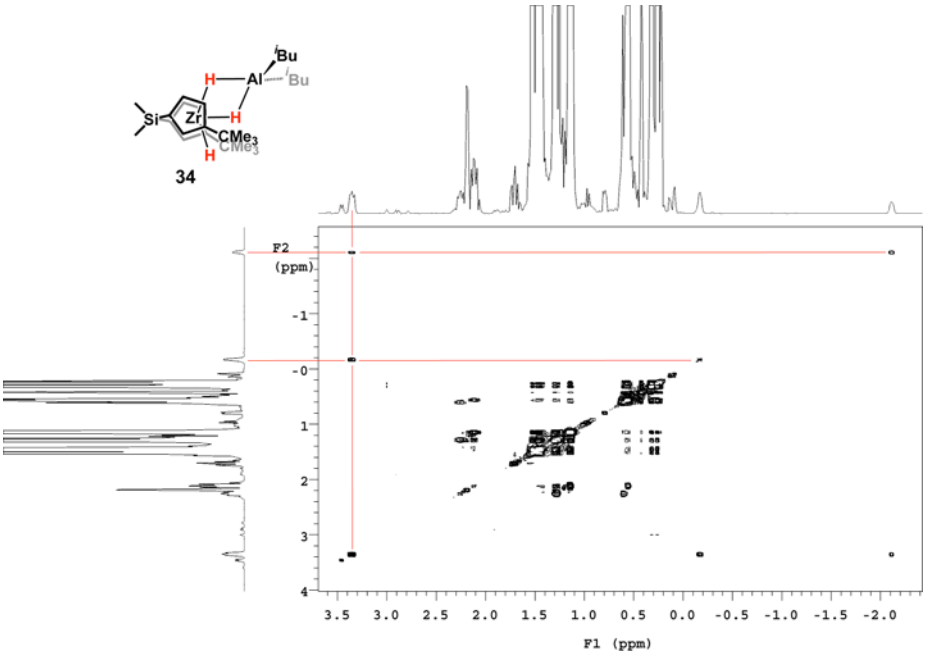


Figure S24. noedif of **33** with 3 equiv. $HAl^{i}Bu_2$ in benzene-d_6 at 25°C.

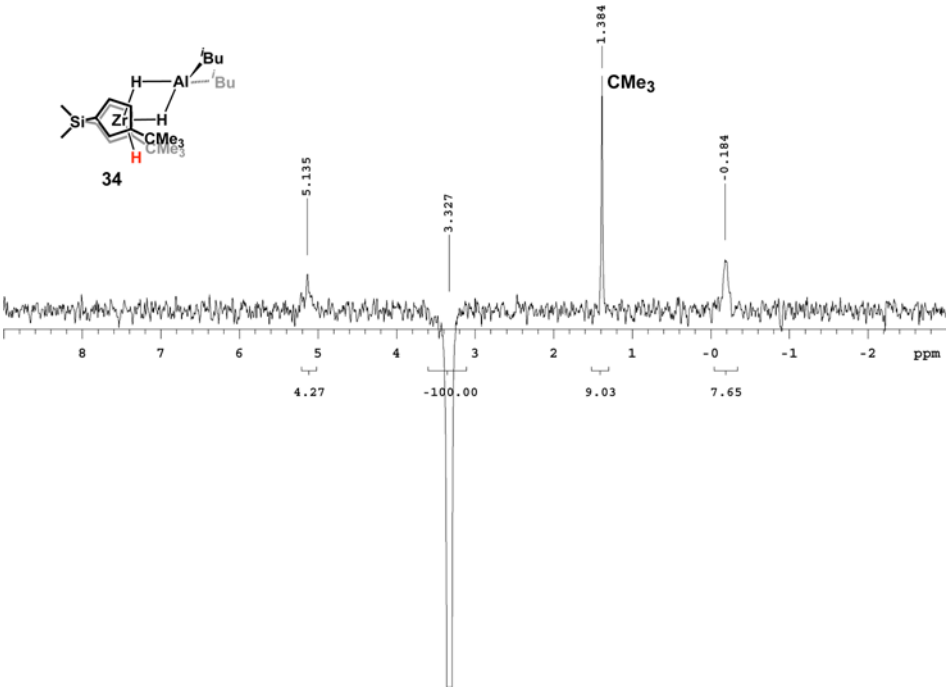


Figure S25. ^{1}H spectrum of $H_4C_2(C_5H_4)_2ZrCl_2$ (**35**) with 4 equiv. $HAl^{i}Bu_2$ in toluene-d_8 at 0°C.

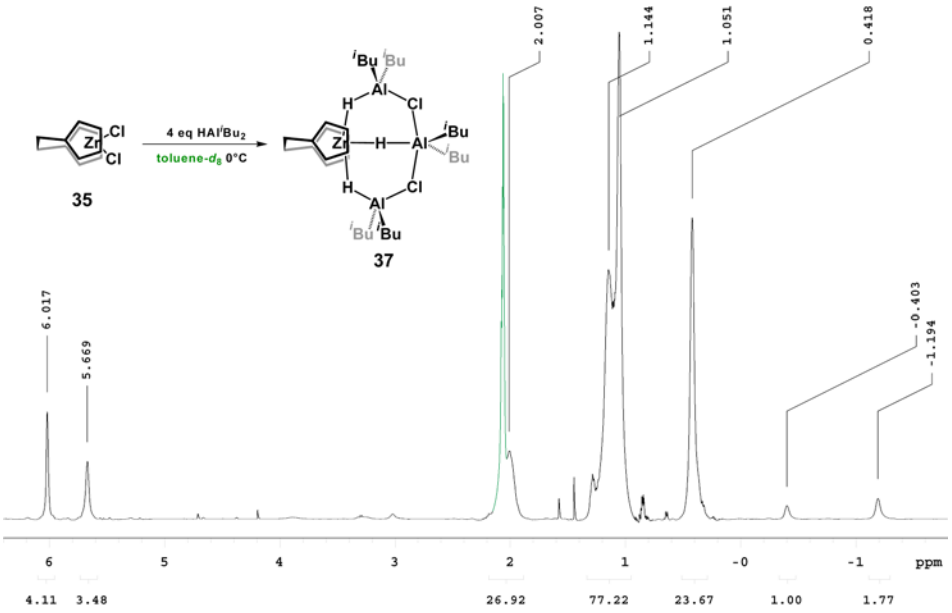


Figure S26. NOESY1D of $Me_4C_2(C_5H_4)_2ZrCl_2$ (**36**) with 4 equiv. HAl^iBu_2 in benzene-d_6 at 25°C.

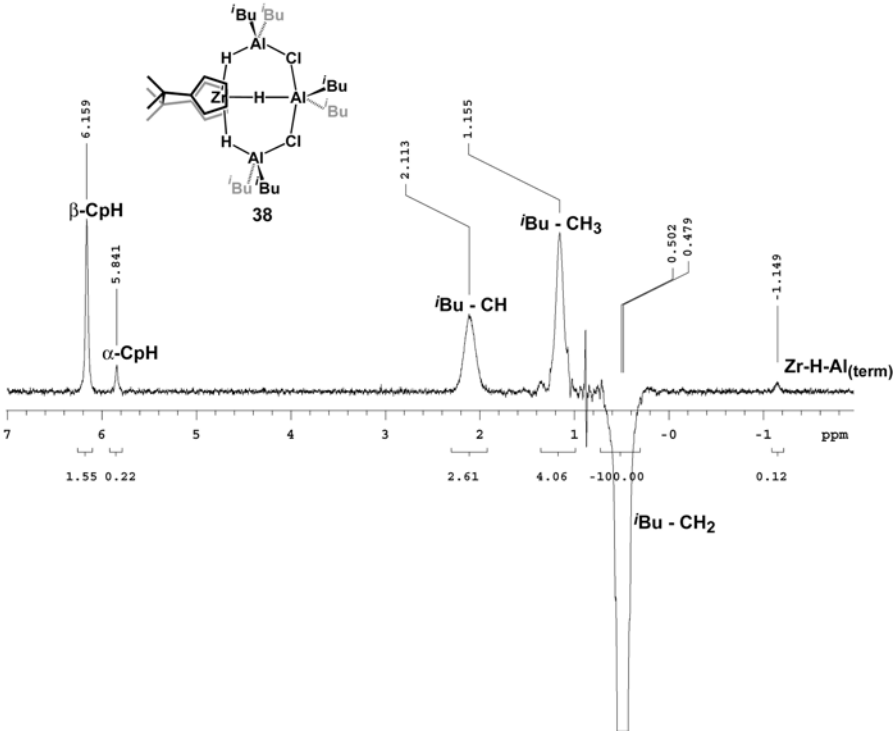
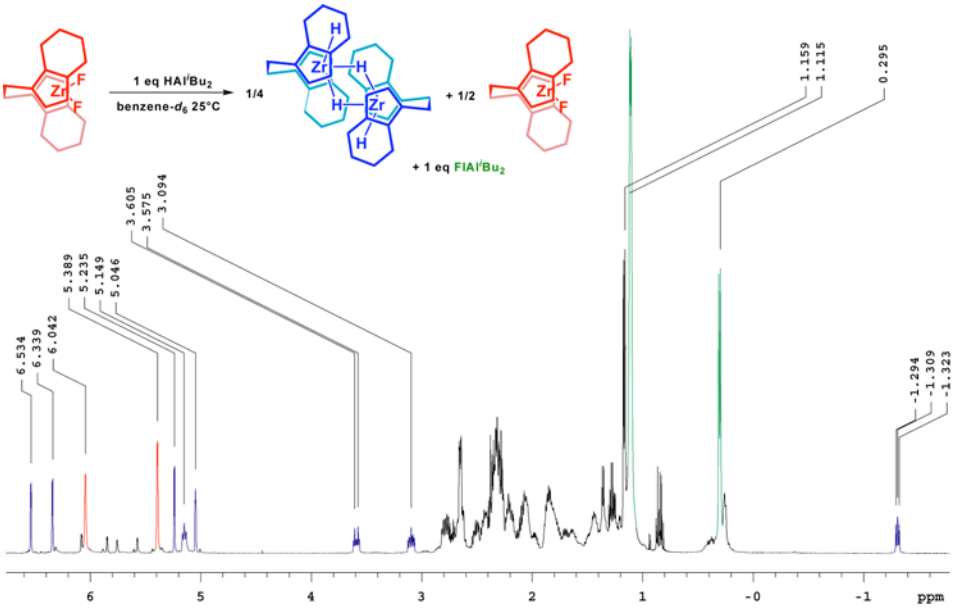


Figure S27. ^1H spectrum of $(EBTHI)ZrF_2$ with 1 equiv. HAl^iBu_2 in benzene-d_6 at 25°C.



Appendix S-1. Analysis of changes in the chemical shift of the ZrH_2 signal of (SBI)ZrCl(μ-H)$_2$Al^{i}Bu$_2$ upon addition of Al_2Me_6.

1) Adduct Formation:

Adduct formation of (SBI)ZrCl(μ-H)$_2$Al^{i}Bu$_2$ with Al_2Me_6, is represented by Equ. 1, with **A** representing the starting complex, $\mathbf{X_2}$ the $AlMe_3$ dimer and **AX** the adduct:

$$A + \frac{1}{2} X_2 \leftrightarrow AX \tag{1}$$

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

$$K = \frac{[AX]}{[A]\sqrt{[X_2]}} \tag{2}$$

Under conditions of rapid exchange between **A** and **AX** the chemical shift of the resulting signal, δ, is the weighted average of the chemical shifts of **A**, δ_A, and **AX**, δ_{AX} (Equ. 3).

$$\delta = \frac{[A]}{[AX]+[A]}\delta_A + \frac{[AX]}{[AX]+[A]}\delta_{AX} \tag{3}$$

The difference in chemical shift, Δδ, of the signal at any given concentration of added **X**, δ, and that of pure **A** is given by Equ. 4.

$$\Delta\delta = \delta - \delta_A \tag{4}$$

Combining Equ. 3 and Equ. 4 we get:

$$\Delta\delta = \left(\frac{[A]}{[AX]+[A]} - 1\right)\delta_A + \frac{[AX]}{[AX]+[A]}\delta_{AX} \tag{5}$$

Which simplifies to:

$$\Delta\delta = \frac{[AX]}{[AX]+[A]}(\delta_{AX} - \delta_A) \tag{6}$$

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

$$\Delta\delta_{\max} = \delta_{AX} - \delta_A \tag{7}$$

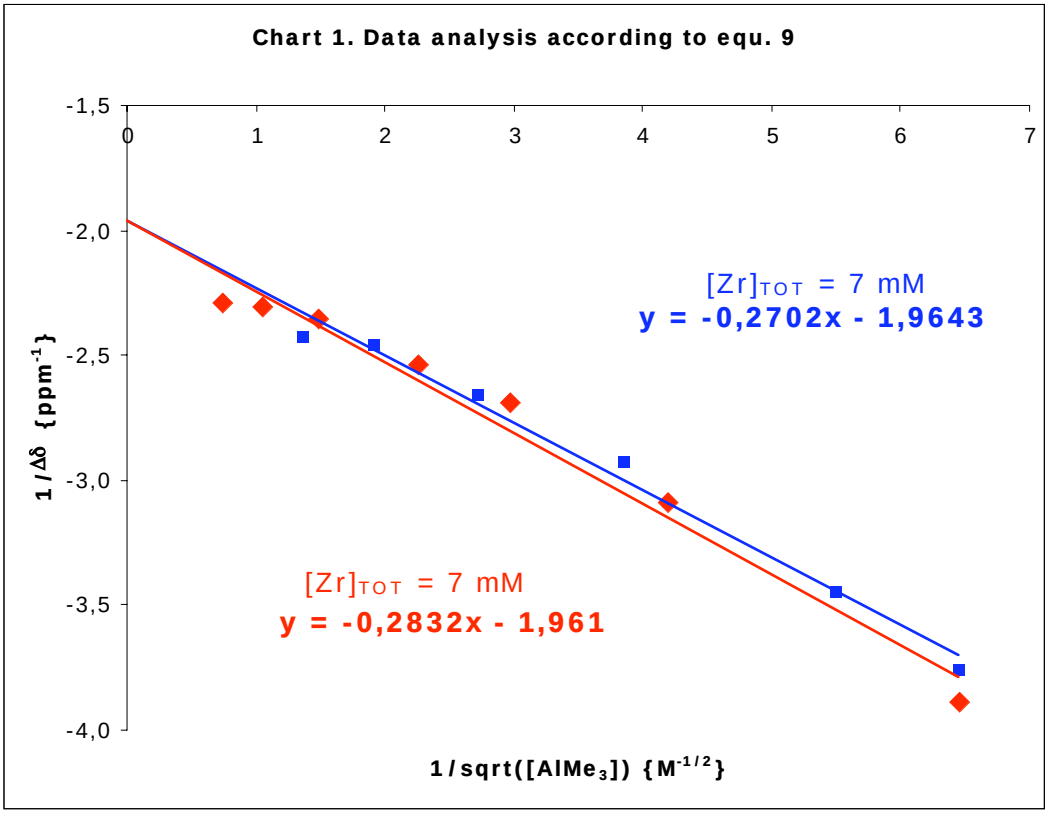
Taking the reciprocal of Equ. 6 and using Equ. 7 gives Equ. 8:

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{1}{\Delta\delta_{\max}} \bullet \frac{[A]}{[AX]} \tag{8}$$

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

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{max}} + \frac{1}{\Delta\delta_{max} K \sqrt{[X_2]}} \qquad (9)$$

Assuming that K is small, the amount of $\mathbf{X_2}$ added is approximately equal to the amount of $\mathbf{X_2}$ in solution. A plot of the reciprocal of the change in chemical shift against the reciprocal of the square root of the concentration of Al_2Me_6 added should thus be linear, with a slope of 1/K and a y-axis intercept of $1/\delta_{AX}$, neither of which should depend on $[Zr]_{TOT}$.



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 Al_2Me_6 to $AlMe_3$ in dilute solutions and/or from the fact that the most concentrated solutions of Al_2Me_6 contain up to 20 volume percent Al_2Me_6, such that these solution can no longer be considered to be ideal solutions of Al_2Me_6 in benzene. Nevertheless, the values of $1/\delta_{max}$ 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 ZrH_2 signal upon addition of Al_2Me_6 to a solution of (SBI)Zr(Cl)(μ-H)$_2$Al^{i}Bu$_2$ is due to formation of an adduct, e.g. of the type (SBI)Zr(Cl$^{\cdots}$AlMe$_3$)(μ-H)$_2$AlR$_2$, with R = ^{i}Bu and/or Me.

2) Exchange Reaction:

The reaction of (SBI)ZrCl(μ-H)$_2$Al^{i}Bu$_2$ to exchange either the Zr-bound Cl or an Al-bound ^{i}Bu with one of the methyl groups of Al_2Me_6, to yield Al_2Me_5X where X = Cl or ^{i}Bu, is represented by Equ. 10, with **A** representing the starting $ZrClH_2$ complex, $\mathbf{X_2}$ the $AlMe_3$ dimer, **B** the exchange product and **Y** the Al_2Me_5X product:

$$A + X_2 \leftrightarrow B + Y \tag{10}$$

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

$$K = \frac{[B][Y]}{[A][X_2]} \tag{11}$$

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

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{1}{\Delta\delta_{\max}} \bullet \frac{[A]}{[B]} \tag{12}$$

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

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{1}{\Delta\delta_{\max}} \bullet \frac{[Y]}{K[X_2]} \tag{13}$$

Since we are adding $\mathbf{X_2}$ to **A**, [**Y**] is equal to [**B**], yielding:

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{\max}} + \frac{1}{\Delta\delta_{\max}} \bullet \frac{[B]}{K[X_2]} \tag{14}$$

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

$$\frac{1}{\Delta\delta} = \left(\frac{[B]}{\Delta\delta_{\max} K}\right) \bullet \frac{1}{[X_2]} + \frac{1}{\Delta\delta_{\max}} \tag{15}$$

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

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

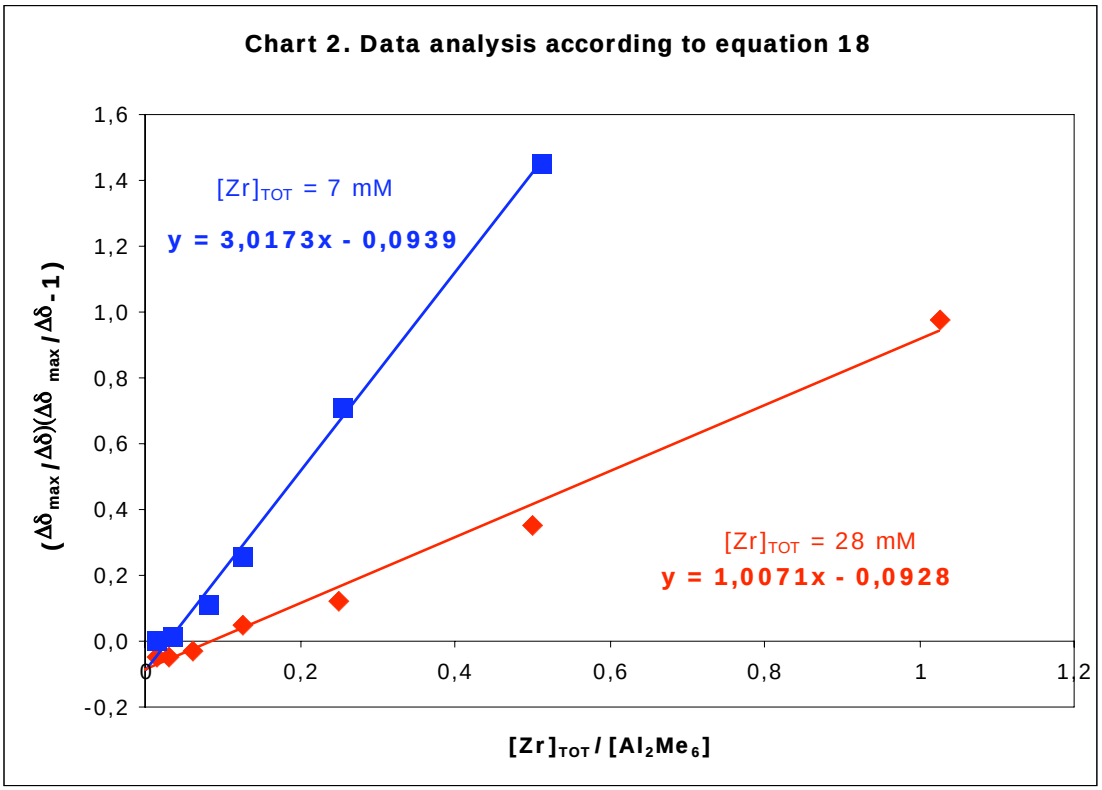
Solving for [**B**] and substituting into Equation 14 gives:

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{max}} + \frac{\Delta\delta}{\Delta\delta_{max}} \bullet \frac{[A]+[B]}{\Delta\delta_{max} K [X_2]} \qquad (17)$$

With [A] + [B] = $[Zr]_{TOT}$ and $[X_2] = [Al_2Me_6]$, equation 17 can be rearranged to:

$$\left(\frac{\Delta\delta_{max}}{\Delta\delta} - 1\right)\frac{\Delta\delta_{max}}{\Delta\delta} = \frac{[Zr]_{TOT}}{K \bullet [Al_2Me_6]} \qquad (18)$$

The value of $\Delta\delta_{max}$ can be estimated from the chemical shift at the highest concentrations of Al_2Me_6 or from the plot in Chart 1. Assuming that K is small, the amount of Al_2Me_6 added is approximately equal to the amount of Al_2Me_6 in solution. Therefore, a plot of the left side of Equ.18 against $[Zr]_{TOT}/[Al_2Me_6]$ should give a straight line going through the origin, with a slope of 1/K, which should thus be independent of $[Zr]_{TOT}$.



Inspection of such a plot (Chart 2) shows that the data do not meet this requirement. Instead, the slope of the data for $[Zr]_{tot}$ = 7 mM is about three times larger than that of the data for $[Zr]_{tot}$ = 28 mM. The change in chemical shift of the ZrH_2 signal upon addition of Al_2Me_6 to a solution of (SBI)Zr(Cl)(μ-H)$_2$Al^{i}Bu$_2$ can thus **not** be due to an exchange reaction, e.g. of the Cl against a Me ligand.