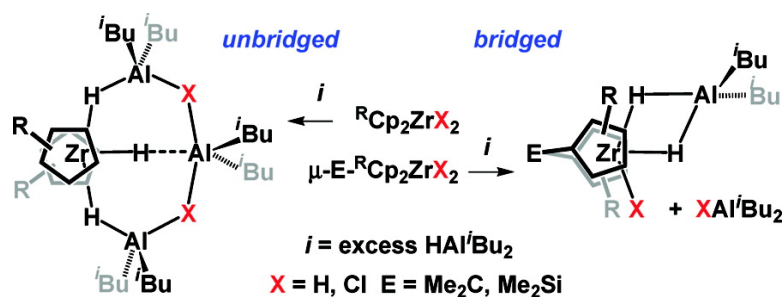Article

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

Steven M. Baldwin, John E. Bercaw, and Hans H. Brintzinger

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

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

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

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

Received July 15, 2008; E-mail: Bercaw@caltech.edu; Hans.Brintzinger@uni-konstanz.de

Abstract: Reactions of unbridged zirconocene dichlorides, $(R_nC_5H_{5-n})_2ZrCl_2$ (n = 0, 1, or 2), with diisobutylaluminum hydride (HAl^iBu_2) result in the formation of tetranuclear trihydride clusters of the type $(R_nC_5H_{5-n})_2Zr(\mu\text{-}H)_3(Al^iBu_2)_3(\mu\text{-}Cl)_2$, which contain three $[Al^iBu_2]$ units. Ring-bridged *ansa*-zirconocene dichlorides, $Me_2E(R_nC_5H_{4-n})_2ZrCl_2$ with E = C or Si, on the other hand, are found to form binuclear dihydride complexes of the type $Me_2E(R_nC_5H_{4-n})_2Zr(Cl)(\mu\text{-}H)_2Al^iBu_2$ with only one $[Al^iBu_2]$ unit. The dichotomy between unbridged and bridged zirconocene derivatives with regard to tetranuclear versus binuclear product formation is proposed to be connected to different degrees of rotational freedom of their C_5-ring ligands. Alkylaluminum-complexed zirconocene dihydrides, previously observed in zirconocene-based precatalyst systems activated by methylalumoxane (MAO) upon addition of HAl^iBu_2 or Al^iBu_3, are proposed to be species of the type $Me_2Si(ind)_2Zr(Me)(\mu\text{-}H)_2Al^iBu_2$, stabilized by interaction of their terminal Me group with a Lewis acidic site of MAO.

Introduction

In view of their manifold catalytic properties, a great variety of zirconocene hydride complexes as well as adducts of some of these entities with organoaluminum or other organometal hydrides have been isolated and characterized by spectroscopic and/or crystallographic methods.[1,2] From some reaction systems, mononuclear or binuclear zirconocene hydride cations have been isolated.[3–5] Most abundant, however, appear to be neutral—binuclear or oligonuclear—zirconocene hydride complexes, the Zr(IV) centers of which are incorporated in a [ZrH₃] core structure.

[ZrH₃] coordination patterns have been crystallographically characterized, e.g., in many dimeric zirconocene dihydrides,[6] in adducts of a zirconocene hydride moiety with another neutral metal hydride species,[7] e.g., with AlH_3,[8] or in an anionic $[(C_5Me_5)_2ZrH_3]^-$ entity in contact with suitable cations such as Li^+ or K^+.[9] Reaction systems derived from zirconocene dichloride or dihydride complexes by reaction with organoaluminum
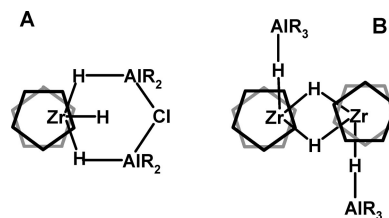

Figure 1. [ZrH₃] coordination geometries, proposed for alkylaluminum-complexed zirconocene hydride complexes in refs 10−15.

hydrides, which catalyze alkene hydrometallations or polymerizations, have been reported—based mainly on spectroscopic evidence—to contain oligonuclear species with hydride-bridged [ZrAl₂] or [Zr₂Al₂] cores, the Zr centers of which adopt, again, a [ZrH₃] coordination geometry (Figure 1, structures **A** and **B**, respectively).[10–15]

[†] California Institute of Technology.

[‡] Universität Konstanz.

(1) Review: Chen, E. Y.-X.; Rodriguez-Delgado, A. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Bochmann, M., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Vol. 4, p 878.

(2) Review on Zr(III) zirconocene hydride complexes: Lancaster, S. J. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Bochmann, M., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Vol. 4, p 753.

(3) Yang, X.; Stern, C. L.; Marks, T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375.

(4) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(5) (a) Carr, A. G.; Dawson, D. M.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1999**, *18*, 2933. (b) Bryliakov, K. P.; Talsi, E. P.; Semikolenova, N. V.; Zakharov, V. A.; Brand, J.; Alonso-Moreno, C.; Bochmann, M. *J. Organomet. Chem.* **2007**, *692*, 859.

(6) (a) Jones, S. B.; Peterson, J. L. *Inorg. Chem.* **1981**, *20*, 2889. (b) Choukroun, R.; Dahan, F.; Larsonneur, A. M.; Samuel, E.; Peterson, J.; Meunier, P.; Sornay, C. *Organometallics* **1991**, *10*, 37. (c) Larsonneur, A. M.; Choukroun, R.; Jaud, J. *Organometallics* **1993**, *12*, 3216. (d) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255. (e) Bai, G.; Müller, P.; Roesky, H. W.; Uson, I. *Organometallics* **2000**, *19*, 4675. (f) Chirik, P. J.; Henling, L. M.; Bercaw, J. E. *Organometallics* **2001**, *20*, 534. (g) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501. (h) Arndt, P.; Spannenberg, A.; Baumann, W.; Burlakov, V. V.; Rosenthal, U.; Becke, S.; Weiss, T. *Organometallics* **2004**, *23*, 4792.

(7) (a) Khan, K.; Raston, C. L.; Grady, J. E.; Skelton, B. W.; White, A. H. *Organometallics* **1997**, *16*, 3252. (b) Wehmschulte, R. J.; Power, P. P. *Polyhedron* **1999**, *18*, 1885.

(8) (a) Etkin, N.; Stephan, D. W. *Organometallics* **1998**, *17*, 763. (b) Sizov, A. I.; Zvukova, T. M.; Belsky, V. K.; Bulychev, B. M. *J. Organomet. Chem.* **2001**, *619*, 36.
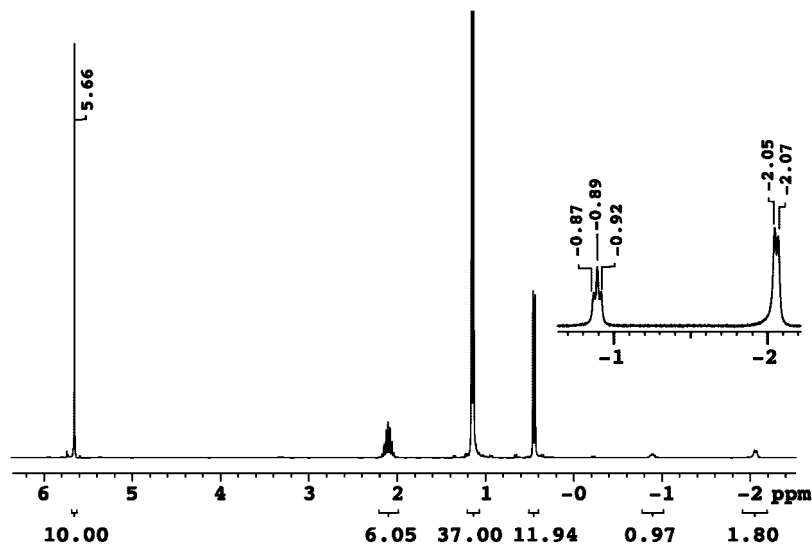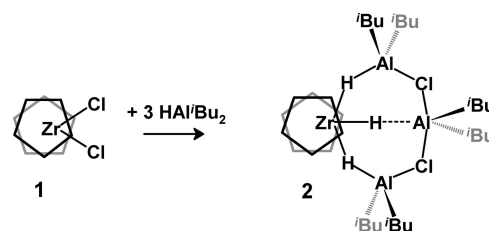
Figure 2. ^{1}H NMR spectrum of a 50 mM solution of $(C_5H_5)_2ZrCl_2$ (**1**) in benzene-d_6 at 25 °C after addition of 3 equiv of HAl^iBu_2.

Recently, however, zirconocene hydride complexes which deviate from the commonly observed [ZrH$_3$] coordination pattern have been encountered in methylalumoxane (MAO)-activated zirconocene precatalyst systems upon addition of HAl^iBu_2 or Al^iBu_3.[16] The ^{1}H NMR spectra of these species show only a single hydride resonance with an integral corresponding to two hydride units per Zr center, which indicates the presence of a [ZrH$_2$] unit with two equivalent H ligands.[16b] In order to characterize the species responsible for this NMR signal and the factors which govern the formation of [ZrH$_2$]-type as opposed to [ZrH$_3$]-type zirconocene hydride complexes, we have first re-evaluated some previously described reactions of un-bridged zirconocene complexes with diisobutylaluminum hydride, HAl^iBu_2,[17] and subsequently studied corresponding reactions of several *ansa*-zirconocene dichlorides.

Results and Discussion

1. Unbridged Zirconocene Complexes. In accord with earlier reports, we observe that excess HAl^iBu_2 reacts with $(C_5H_5)_2ZrCl_2$ (**1**) in benzene-d_6 at 25 °C to give a species with two characteristic hydride NMR signals, a triplet at −0.89 ppm with

(9) (a) Etkin, N.; Hoskin, A. J.; Stephan, D. W. *J. Am. Chem. Soc.* **1997**, *119*, 11420. (b) Fermin, M. C.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 12645.

(10) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *43*, C29.

(11) Shoer, L. I.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1977**, *136*, C19.

(12) (a) Parfenova, L. V.; Pechatkina, S. V.; Khaliliov, L. M.; Dzhemilev, U. M. *Russ. Chem. Bull.* **2005**, *54*, 316. (b) Parfenova, L. V.; Vil'danova, R. F.; Pechatkina, S. V.; Khaliliov, L. M.; Dzhemilev, U. M. *J. Organomet. Chem.* **2007**, *692*, 3424.

(13) Tritto, I.; Zucchi, D.; Destro, M.; Sacchi, M. C.; Dall'Occo, T.; Galimberti, M. *J. Mol. Catal. A: Chem.* **2000**, *160*, 107.

(14) Götz, C.; Rau, A.; Luft, G. *J. Mol. Catal. A: Chem.* **2002**, *184*, 95.

(15) Gonzales-Hernandes, R.; Chai, J.; Charles, R.; Perez-Camacho, O.; Kniajanski, S.; Collins, S. *Organometallics* **2006**, *25*, 5366.

(16) (a) Babushkin, D. E.; Brintzinger, H. H. *Chem. Eur. J.* **2007**, *13*, 5294. (b) Babushkin, D. E.; Panchenko, V. N.; Zakharov, V. A.; Brintzinger, H. H. *Macromol. Chem. Phys.* **2008**, *209*, 1210.

(17) For simplicity, diisobutylaluminum hydride is written here and in the following as a monomer, even though it is undoubtedly preponderantly present as a trimer in solution under our experimental conditions:(a) Ziegler, K.; Kroll, W.-R.; Larbig, W.; Steudel, O.-W. *Liebigs Ann. Chem.* **1960**, *629*, 53. (b) Hoffmann, E. G. *Liebigs Ann. Chem.* **1960**, *629*, 104. (c) Vestin, R.; Vestin, U.; Kowalewski, J. *Acta Chem. Scand., Ser. A* **1985**, *39*, 767.

Scheme 1

an intensity of 1H, and a doublet at −2.06 ppm with an intensity of 2H per zirconocene unit (Figure 2). This signal pattern has previously been ascribed to a trinuclear cluster, $(C_5H_5)_2ZrH_3(Al^iBu_2)_2Cl$, containing a [$(C_5H_5)_2ZrH_3$] moiety in contact with a chloride-bridged bis(diisobutylaluminum) unit (structure **A** in Figure 1).[11] This species has recently been proposed to be an (inactive) component in zirconocene-based reaction systems which catalyze the hydroalumination of α-olefins.[12]

The assignment of structure **A** to the product formed from $(C_5H_5)_2ZrCl_2$ and HAl^iBu_2 does not appear to be correct,[18] however. Careful integration of the isobutyl signals versus the C_5H_5 signal in reaction systems containing complex **1** and HAl^iBu_2 consistently yields a [Al^iBu_2]/[Zr] ratio of (3.02 ± 0.03):1. Even when **1** is used in excess, only the product with three [Al^iBu_2] units per zirconocene unit is observed, with an NMR spectrum identical to that described above, while unreacted **1** remains behind as a solid. The reaction of **1** with HAl^iBu_2 thus appears to lead to the immediate and complete formation of a tetranuclear cluster of composition $(C_5H_5)_2ZrH_3(Al^iBu_2)_3Cl_2$ (**2**, Scheme 1).

(18) An earlier formulation of this complex as a [ZrH$_3$Al$_2$Cl] cluster was based mainly on cryoscopy data which gave a molar mass close to that expected for **2** (ref 11). These cryoscopy measurements are likely to be complicated, however, by the low solubility of the dichloride starting compound and by the presence of some free $(HAl^iBu_2)_3$ in equilibrium with it.

(19) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405.

(20) Bickley, D. G.; Hao, N.; Bougeard, P.; Sayer, B. G.; Burns, R. C.; McGlinchey, M. J. *J. Organomet. Chem.* **1983**, *246*, 257.

(21) Attempts to isolate any crystalline products from the reaction systems described above were unsuccessful so far and are not likely to meet with success in view of the instability and the multiple degrees of conformational freedom of the diisobutylaluminum adducts considered.

Scheme 2
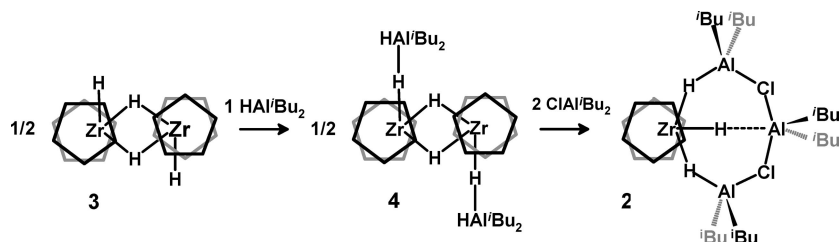
Table 1. ¹H NMR Signals of Unbridged Zirconocene Complexes and of Their Reaction Products with HAl^{i}Bu$_2$[a]

|	Zr—H	Al^{i}Bu$_2$	ligand
(C$_5$H$_5$)$_2$ZrCl$_2$ (**1**)			5.89 (s, 10H)
(C$_5$H$_5$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$ (**2**)	−0.89 (t, 1H, 7.4 Hz)	0.45 (d, 12H, 6.9 Hz)	5.66 (s, 10H)
	−2.03 (d, 2H, 6.8 Hz)	1.15 (d, 36H, 6.3 Hz)	
		2.10 (m, 6H, 6.6 Hz)	
((C$_5$H$_5$)$_2$ZrH)$_2$(μ-H)$_2$ (**3**)[b]	−3.45 (t, 2H, 7.3 Hz)		5.75 (s, 20H)
	3.85 (t, 2H, 7.3 Hz)		
((C$_5$H$_5$)$_2$ZrH···HAl^{i}Bu$_2$)$_2$(μ-H)$_2$ (**4**)[c]	−2.11 (br, 2H)	0.39 (d, 8H, 6.5 Hz)	5.40 (s, 20H)
	−3.05 (br, 2H)	1.18 (d, 24H, 5.0 Hz)	
		2.36 (br, 4H)	
(C$_5$H$_5$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-H)$_2$ (**5**)[c]	−1.46 (t, 1H, 15.5 Hz)	0.44 (br, 12H)	5.34 (s, 10H)
	−2.33 (d, 2H, 16.5 Hz)	1.25 (br, 36H)	
		2.16 (br, 6H)	
(^{n}Bu-C$_5$H$_4$)$_2$ZrCl$_2$ (**6**)			0.84 (t, 6H, 7.5 Hz)
			1.22 (s, 4H, 7.4 Hz)
			1.43 (p, 4H, 7.4 Hz)
			2.64 (t, 4H, 7.8 Hz)
			5.74 (pt, 4H, 2.7 Hz)
			5.92 (pt, 4H, 2.6 Hz)
(^{n}Bu-C$_5$H$_4$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$ (**7**)	−0.58 (t, 1H, 6.9 Hz)	0.51 (d, 12H, 7.2 Hz)	0.86 (t, 6H, 7.5 Hz)
	−1.54 (d, 2H, 6.9 Hz)	1.18 (d, 36H, 6.6 Hz)	2.24 (t, 4H, 7.1 Hz)[d]
		2.15 (m, 6H, 6.6 Hz)	5.65 (br, 4H)
			5.94 (br, 4H)
(1,2-Me$_2$-C$_5$H$_3$)$_2$ZrCl$_2$ (**8**)			5.47 (t, 2H, 3.0 Hz)
			5.62 (d, 4H, 3.0 Hz)
(1,2-Me$_2$-C$_5$H$_3$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$ (**9**)	−0.20 (t, 1H, 7.2 Hz)	0.52 (d, 12H, 7.2 Hz)	5.58 (t, 2H, 3.0 Hz)
	−1.13 (d, 2H, 6.3 Hz)	1.19 (d, 36H, 5.7 Hz)	5.65 (d, 4H, 3.0 Hz)
		2.18 (br, 6H)	
(Me$_3$Si-C$_5$H$_4$)$_2$ZrCl$_2$ (**10**)			0.33 (s, 18H)
			5.93 (pt, 4H, 2.5 Hz)
			6.39 (pt, 4H, 2.5 Hz)
(Me$_3$Si-C$_5$H$_4$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$ (**11**)[c]	−1.31 (br, 1H)	all broad	0.00 (s, 18H)
	−2.09 (br, 2H)		5.96 (br, 4H)
			6.11 (br, 4H)
(C$_5$Me$_5$)$_2$ZrCl$_2$ (**12**)			1.85 (s, 30H)
(C$_5$Me$_5$)$_2$ZrH$_2$ (**13**)	7.50 (s, 2H)		2.02 (s, 30H)
(C$_5$Me$_5$)$_2$ZrH^{i}Bu (**14**)	6.13 (s, 1H)	−0.03 (d, 2H, 6.9 Hz)	1.91 (s, 30H)
		1.02 (d, 6H, 6.6 Hz)	
		2.39 (m, 1H, 6.5 Hz)	
(C$_5$Me$_5$)$_2$Zr^{i}Bu$_2$ (**15**)		0.69 (d, 4H, 7.2 Hz)	1.85 (s, 30H)
		1.25 (d, 12H, 6.6 Hz)	
		2.22 (m, 2H, 6.4 Hz)	

[a] In benzene-d_6 at 25 °C. [b] From ref 20. [c] In toluene-d_8 at −75 °C. [d] Two resonances overlap with ^{i}Bu signals.

In order to verify that three [Al^{i}Bu$_2$] units and two Cl bridges are indeed present in the reaction product, we have designed the experiment outlined in Scheme 2: the zirconocene dihydride, **3**,[19,20] reacts with 1 equiv of HAl^{i}Bu$_2$ per zirconocene unit to

(22) Geometry optimizations, based on Hartree−Fock methods (Spartan software package, 3-21G basis set), yield for a simplified model for compound **2**, with isobutyl groups replaced by methyl groups, a geometry close to the C_2-symmetric structure shown in Scheme 1 but with both staggered C$_5$-rings rotated by 18°. Calculations by methods based on density functional theory (DFT), performed at the University of Hamburg, yield an energy, lower by ca. 6 kcal/mol than that of the C_2-symmetric geometry shown in Scheme 1, for an unsymmetric structure with one four-membered Zr(μ-H)$_2$Al ring and a tetracoordinate geometry of the middle Al center (ref 23).

(23) Burger, P. Private communication, 2007.

form species **4**, characterized by a 1:1 pair of hydride signals at −2.12 and −3.06 ppm in toluene-d_8 solution at −75 °C (Table 1), which had been seen also for adducts of the dimeric zirconocene dihydride complex **3** with various aluminum trialkyl compounds (structure **B** in Figure 1).[10−12,14] Addition of 1 equiv of ClAl^{i}Bu$_2$ per zirconocene to such a reaction system—which would be required to form species **A**—gives instead four broad signals between −1 and −3 ppm, which indicate the presence of several mutually interconverting hydride products (Supporting Information Figure S1). Clean formation of the trihydride species **2** with sharp hydride signals at −0.89 ppm (t, 1H) and −2.06 ppm (d, 2H) is observed, however, when exactly 2 equiv of ClAl^{i}Bu$_2$ are added to the reaction system containing 1 equiv

Scheme 3
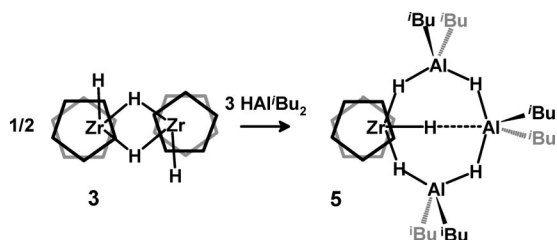
Scheme 4

each of $(C_5H_5)_2ZrH_2$ and of HAl^iBu_2 (Supporting Information Figure S2). The exclusive and complete formation of species **2** via this alternative route (Scheme 2) corroborates its composition $(C_5H_5)_2ZrH_3(Al^iBu_2)_3Cl_2$.

Further support for this assignment comes from the observation that reaction of the dimeric dihydride **3** with 2 equiv of $ClAl^iBu_2$ yields a 2:1 mixture of the hydride cluster **2** and the dichloride **1**, in accord with the stoichiometry expected from eq 1.

$$1/2((C_5H_5)_2ZrH_2)_2 +$$
$$2ClAl^iBu_2 \rightarrow 2/3(C_5H_5)_2ZrH_3(Al^iBu_2)_3Cl_2 + 1/3(C_5H_5)_2ZrCl_2$$
$$(1)$$
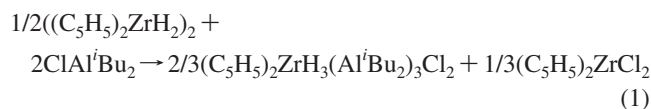
Although we were not able to obtain crystals of complex **2** suitable for a diffractometric structure determination,[21] we propose for this complex the structure shown in Schemes 1 and 2, as a representation of its—presumably time-averaged—C_2-symmetric NMR characteristics. Whether the central Al center of this complex is indeed five-coordinate, as represented in Scheme 1, must be left to future studies.[22]

When the dimeric zirconocene dihydride **3** is reacted, rather than with $ClAl^iBu_2$, with 3 equiv of HAl^iBu_2 per zirconocene unit in toluene-d_8, one observes, at -75 °C, two hydride NMR signals with an intensity ratio of 2:1, a doublet at -2.32 ppm and a triplet at -1.46 ppm (Supporting Information Figure S3). These signals closely resemble those assigned to the [ZrH$_3$] core of species **2** (Table 1). On the basis of this similarity and on the observation of an additional signal at 3.18 ppm with an integral of 2H, which we assign to two bridging [Al–H–Al] units, the product of this reaction is likely to be the cluster **5**, i.e., an analogue to complex **2** with hydride instead of chloride bridges (Scheme 3).

When the temperature of this reaction system is increased from -75 to 0 °C, the Zr–H signals of complex **5** at -2.32 and -1.46 ppm coalesce with each other and with the [Al–*H*–Al] signal at 3.18 ppm. At 25 °C finally, all of these signals become so broad as to be hardly detectable. Facile exchange between lateral and central Zr–H positions and of both of these with the peripheral [Al–H–Al] units is indicated by this observation. The entirely H-bridged species **5** thus appears much more prone to undergo exchange reactions than its congener **2**, which contains two Al–Cl–Al bridges. At above-ambient temperatures, the appearance of violet colorations indicates that decomposition occurs in this system.

Similar spectra as for the system **1**/HAl^iBu_2 are observed when unbridged zirconocene dichlorides with substituted C$_5$-rings are reacted with HAl^iBu_2 in benzene or toluene solution (Table 1). Reactions of $(^nBu\text{-}C_5H_4)_2ZrCl_2$ (**6**), $(1,2\text{-}Me_2\text{-}C_5H_3)_2ZrCl_2$ (**8**), or $(Me_3Si\text{-}C_5H_4)_2ZrCl_2$ (**10**) with 2 equiv of HAl^iBu_2 each give a species with a doublet and a triplet Zr–H signal at ca. -1 ppm and -0.2 ppm, respectively (Scheme 4). Integrals of these and the respective ^iBu and ring ligand signals
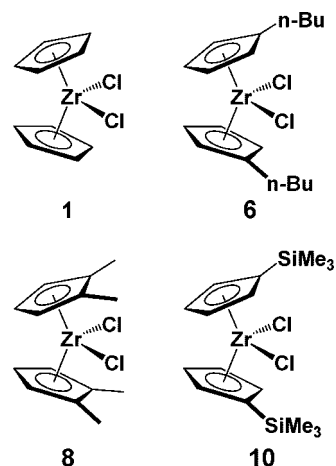
are in accord with the presence of tetranuclear trihydride clusters, **7**, **9**, and **11** (Table 1, Supporting Information Figures S4–S6), respectively. In comparison to their unsubstituted analogue **2**, the Zr–H signals of all these complexes appear shifted to lower fields by ca. 0.5–1 ppm, presumably due to changes in the electron density of their substituted ring ligands.

In distinction to the reaction systems discussed so far, permethylzirconocene dichloride, $(C_5Me_5)_2ZrCl_2$ (**12**), does not give a hydride complex when reacted with 2 equiv of HAl^iBu_2 in benzene-d_6 solution at 25 °C. Instead, a slight shift of its ^1H NMR signal indicates that its Cl ligands might form an adduct with HAl^iBu_2. The dihydride complex $(C_5Me_5)_2ZrH_2$ (**13**), on the other hand, reacts with 1–2 equiv of Al^iBu_3 to give mixtures of the monohydride monoisobutyl complex $(C_5Me_5)_2ZrH^iBu$ (**14**) and the diisobutyl complex $(C_5Me_5)_2Zr^iBu_2$ (**15**) (Supporting Information Figure S7). A 10-fold excess of either Al^iBu_3 or HAl^iBu_2 in benzene-d_6 solution at 25 °C converts the dihydride **13** practically completely to the diisobutyl complex $(C_5Me_5)_2Zr^iBu_2$ (**15**).[24] Remarkably enough, bulky ^iBu groups, rather than hydride units, are thus preferentially transferred from Al to the sterically shielded Zr center of $(Me_5C_5)_2ZrCl_2$.

Apparently, formation of a trihydridic [ZrH$_3$] unit in combination with an array of spatially demanding [Al$^iBu_2$] units is disfavored by steric factors in this case. Hydride units present in these reaction systems thus appear to be more favorably accommodated in hydride-bridged alkylaluminum clusters, rather than in a Zr–H moiety, if formation of the otherwise preferred [Zr–H–Al] bridges is precluded by steric factors.

2. Bridged Zirconocene Complexes. Neutral, alkylaluminum-complexed zirconocene dihydride complexes have been observed, by a ZrH$_2$ signal at ca. -2.0 ppm, to form in catalyst systems containing $rac\text{-}Me_2Si(1\text{-indenyl})_2ZrCl_2$, ((SBI)ZrCl$_2$, **16**), and MAO upon addition of excess Al^iBu_3 or HAl^iBu_2.[16b] In the following, we seek to ascertain structural assignments for these alkylaluminum-complexed *ansa*-zirconocene hydrides, which differ from their unbridged congeners discussed above by the presence of only two—instead of three—hydride ligands at their Zr centers.

(SBI)ZrCl$_2$ was found to react with a 2–5-fold excess of HAl^iBu_2 in benzene or toluene solutions at room temperature to form a hydride product, which obviously contains a [ZrH$_2$] group, as indicated by a broad singlet at -1.29 ppm with an integral corresponding to two protons per zirconocene unit.[16b]

(24) Reaction of the dihydride complex **13** with excess AlMe$_3$ gives an unstable intermediate, which decomposes to a yet unidentified product.

Table 2. ^{1}H NMR Signals of Bridged Zirconocene Complexes and Their Reaction Products with HAl^{i}Bu$_2$ and/or ClAl^{i}Bu$_2^a$

	Zr−H	Al^{i}Bu$_2^b$	ligand C$_5$−H^c
rac-Me$_2$Si(indenyl)$_2$ZrCl$_2$ ((SBI)ZrCl$_2$, **16**)			5.76 (d, 2H, 3.3 Hz) 6.81 (d, 2H, 3.3 Hz)
rac-Me$_2$Si(indenyl)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2$	−1.29 (br, 2H)	0.41 1.16 2.10	5.86 (d, 2H, 3.0 Hz) 6.92 (d, 2H, 2.7 Hz)
rac-C$_2$H$_4$(indenyl)$_2$ZrCl$_2$ ((EBI)ZrCl$_2$, **17**)			5.75 (d, 2H, 3.3 Hz) 6.47 (d, 2H, 3.3 Hz)
rac-C$_2$H$_4$(indenyl)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2$	−0.80 (br, 2H)	0.42 1.17 2.10	5.88 (br, 2H) 6.32 (br, 2H)
Me$_2$C(C$_5$H$_4$)$_2$ZrCl$_2$ (**19**)			5.19 (pt, 4H, 3 Hz) 6.42 (pt, 4H, 3 Hz)
Me$_2$C(C$_5$H$_4$)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2$	−1.36 (br, 2H)	0.47 1.09 2.04	5.23 (br, 4H) 6.13 (br, 4H)
Me$_2$Si(C$_5$H$_4$)$_2$ZrCl$_2$ (**20**)			5.52 (pt, 4H, 2.9 Hz) 6.81 (pt, 4H, 2.9 Hz)
Me$_2$Si(C$_5$H$_4$)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2$	−1.75 (br, 2H)	0.47 1.13 2.08	5.52 (br, 4H) 6.40 (br, 4H)
Me$_2$Si(2,4-Me$_2$-C$_5$H$_2$)$_2$ZrCl$_2$ (**21**)			5.05 (d, 2H, 2 Hz) 6.39 (d, 2H, 2 Hz)
Me$_2$Si(2,4-Me$_2$-C$_5$H$_2$)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2$	−0.77 (br, 2H)	0.48 1.08 2.02	5.03 (br, 2H) 6.34 (br, 2H)
(Me$_2$Si)$_2$(C$_5$H$_3$)$_2$ZrCl$_2$ (**22**)^d			6.14 (t, 2H, 2.8 Hz) 6.72 (d, 4H, 2.7 Hz)
(Me$_2$Si)$_2$(C$_5$H$_3$)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2^{d,e}$	−1.72 (s, 2H)	0.42 1.12 2.08	5.98 (br, 2H) 6.76 (br, 4H)
(Me$_2$Si)$_2$(2,4-^{i}Pr$_2$-C$_5$H)(C$_5$H$_3$)ZrCl$_2$ (**23**)			6.36 (t, 1H, 2.7 Hz) 6.46 (s, 1H) 6.75 (d, 2H, 2.7 Hz)
(Me$_2$Si)$_2$(2,4-^{i}Pr$_2$-C$_5$H)(C$_5$H$_3$)ZrCl(μ-H)$_2$Al^{i}Bu$_2^{d,f}$	−1.27 (s, 2H)	0.3−0.5^g 1.0−1.3 2.0−2.25	6.06 (br, 1H) 6.42 (br, 1H) 6.71 (br, 2H)
rac-C$_2$H$_4$(4,5,6,7-tetrahydroindenyl)$_2$ZrCl$_2$ ((EBTHI)ZrCl$_2$, **18**)			5.27 (d, 2H, 3 Hz) 6.36 (d, 2H, 3 Hz)
rac-C$_2$H$_4$(4,5,6,7-tetrahydroindenyl)$_2$ZrH)$_2$(μ-H)$_2$ (**24**)	−1.29 (t, 2H, 7.5 Hz) 5.18 (t, 2H, 7.2 Hz)		5.07 (br, 2H) 5.27 (d, 2H, 2.4 Hz) 6.37 (d, 2H, 2.7 Hz) 6.57 (br, 2H)
rac-C$_2$H$_4$(4,5,6,7-tetrahydroindenyl)$_2$ZrH(μ-H)$_2$Al^{i}Bu$_2$ (**25**)^{d,f}	−1.17 (br, 1H) −0.53 (br, 1H) −4.57 (br, 1H)	0.4−0.7^g 1.1−1.4 2.0−2.4	4.94 (br, 1H) 5.15 (br, 1H) 5.73 (br, 1H) 6.34 (br, 1H)
rac-C$_2$H$_4$(4,5,6,7-tetrahydroindenyl)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2$ (**26**)	−0.09 (br, 2H)	0.53 1.20 2.18	5.49 (br, 2H) 6.16 (d, 2H, 2.7 Hz)
rac-Me$_2$C(indenyl)$_2$ZrCl$_2$ (**27**)			5.67 (d, 2H, 3.6 Hz) 6.50 (d, 2H, 3.6 Hz)
rac-Me$_2$C(indenyl)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2$ (**29**)	−1.35 (br, 2H)	0.40 1.16 2.08	5.67 (d, 2H, 2.7 Hz) 6.76^g
meso-Me$_2$C(indenyl)$_2$ZrCl$_2$ (**28**)			5.53 (d, 2H, 3.6 Hz) 6.54 (d, 2H, 3.3 Hz)
meso-Me$_2$C(indenyl)$_2$ZrCl(μ-H)$_2$Al^{i}Bu$_2$ (**30**)	−1.89 (br, 1H) −0.87 (br, 1H)	0.46 1.09 2.01	6.11 (br, 2H) 6.23 (br, 2H)
rac-Me$_2$Si(2-Me$_3$Si-4-Me$_3$C-C$_5$H$_2$)$_2$ZrCl$_2$ (**31**)			6.17 (d, 2H, 1.8 Hz) 7.23 (d, 2H, 2.1 Hz)
rac-Me$_2$Si(2-Me$_3$Si-4-Me$_3$C-C$_5$H$_2$)$_2$ZrH(μ-H)$_2$Al^{i}Bu$_2$ (**32**)	−1.56 (br, 1H) −0.60 (d, 1H, 8.2 Hz) 2.68 (dd, 1H, 5.5, 9.4 Hz)	0.3−0.5 1.0−1.25 1.9−2.3	5.75 (d, 1H, 2.1 Hz) 5.93 (d, 2H, 1.5 Hz) 6.36 (d, 1H, 1.8 Hz)
meso-Me$_2$Si(3-Me$_3$C-C$_5$H$_3$)$_2$ZrCl$_2$ (**33**)			5.56 (t, 2H, 3.0 Hz) 5.89 (t, 2H, 2.3 Hz) 6.86 (dd, 2H, 3.0, 2.1 Hz)
meso-Me$_2$Si(3-Me$_3$C-C$_5$H$_3$)$_2$ZrH(μ-H)$_2$Al^{i}Bu$_2$ (**34**)	−2.17 (d, 1H, 5 Hz) −0.21 (d, 1H, 10.2 Hz) 3.31 (dd, 1H, 5.1, 9.9 Hz)	0.54 (d, 4H, 7.2 Hz) 1.21 (m, 12H) 2.19 (m, 2H, 6.8 Hz)	5.12 (br, 2H) 5.79 (br, 2H) 5.94 (br, 2H)
H$_4$C$_2$(C$_5$H$_4$)$_2$ZrCl$_2$ (**35**)			5.46 (pt, 4H, 2.5 Hz) 6.50 (pt, 4H, 2.5 Hz)
H$_4$C$_2$(C$_5$H$_4$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$ (**37**)	−1.11 (br, 2H) −0.32 (br, 1H)	0.47 1.13 2.1	5.72 (br, 4H) 6.07 (br, 4H)
Me$_4$C$_2$(C$_5$H$_4$)$_2$ZrCl$_2$ (**36**)			5.65 (pt, 4H, 2.7 Hz) 6.51 (pt, 4H, 2.7 Hz)
Me$_4$C$_2$(C$_5$H$_4$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$ (**38**)	−1.14 (br, 2H) −0.15 (br, 1H)	0.49 1.17 2.12	5.84 (br, 4H) 6.16 (br, 4H)

^{a} In benzene-d_6 at 25 °C. ^{b} Complex-bound and free XAl^{i}Bu$_2$ exchange-averaged. ^{c} Remaining resonances omitted because of overlap with XAl^{i}Bu$_2$. ^{d} In toluene-d_8. ^{e} At −75 °C. ^{f} At −50 °C. ^{g} Complex-bound and free XAl^{i}Bu$_2$ partly decoalesce.
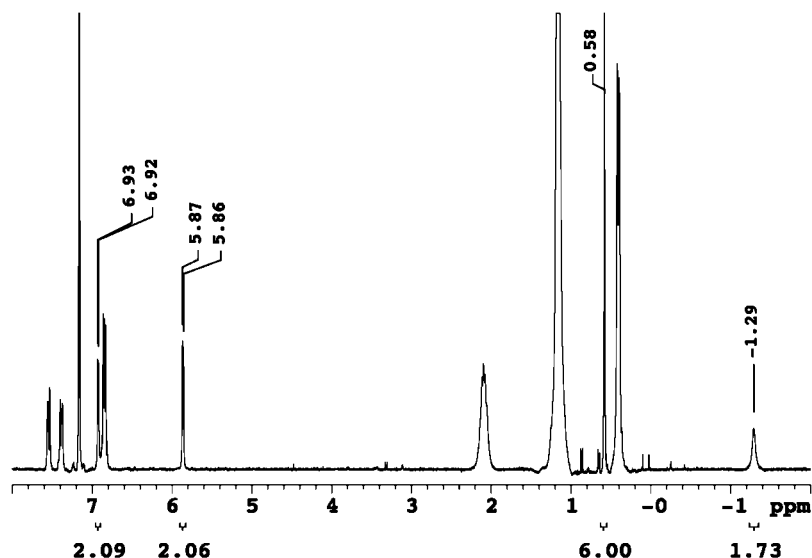
Figure 3. ^{1}H NMR spectrum of a 50 mM solution of (SBI)ZrCl$_2$ (**16**) in benzene-d_6 at 25 °C after addition of 3 equiv of HAl^{i}Bu$_2$.
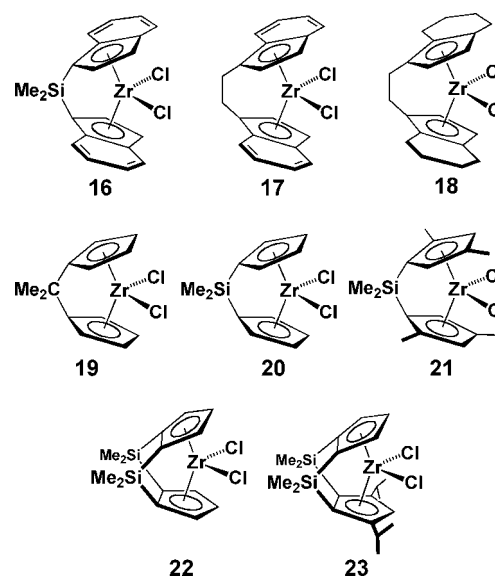
The (SBI) ligand resonances of this product are shifted only slightly from their positions in the dichloride complex **16** (Figure 3, Table 2), thus indicating the presence of a neutral zirconocene species with an intact (SBI) ligand framework.[25] Integration of the ^{i}Bu signals indicates that approximately four [Al^{i}Bu$_2$] units are present in solution per zirconocene unit. Use of lower ratios of HAl^{i}Bu$_2$ over (SBI)ZrCl$_2$ leaves parts of the latter unreacted. A finite concentration of free HAl^{i}Bu$_2$ thus has to be present in these solutions to bring the conversion of the *ansa*-zirconocene dichloride into the dihydride complex to completion.

Products with a single high-field signal due to a ZrH$_2$ group are observed also upon reaction of HAl^{i}Bu$_2$ with several other singly or doubly bridged zirconocene dichlorides, shown in Scheme 5, such as *rac*-C$_2$H$_4$(indenyl)$_2$ZrCl$_2$ ((EBI)ZrCl$_2$, **17**), *rac*-C$_2$H$_4$(4,5,6,7-tetrahydroindenyl)$_2$ZrCl$_2$ ((EBTHI)ZrCl$_2$, **18**),[26] Me$_2$C(C$_5$H$_4$)$_2$ZrCl$_2$ (**19**), Me$_2$Si(C$_5$H$_4$)$_2$ZrCl$_2$ (**20**), *rac*-Me$_2$Si(2,4-Me$_2$-C$_5$H$_2$)$_2$ZrCl$_2$ (**21**), (Me$_2$Si)$_2$(C$_5$H$_3$)$_2$ZrCl$_2$ (**22**), or (Me$_2$Si)$_2$(3,5-^{i}Pr$_2$-C$_5$H)(C$_5$H$_3$)ZrCl$_2$ (**23**).

Formation of a dihydride complex from each of these *ansa*-zirconocene dichlorides by reaction with HAl^{i}Bu$_2$ (Table 2, Supporting Information Figures S8–S14) requires the concurrent formation of 2 equiv of the chloroaluminum species ClAl^{i}Bu$_2$. This Lewis acidic byproduct is likely to remain in association with the comparatively Lewis basic zirconocene dihydride. In order to decide whether one or both of the resulting ClAl^{i}Bu$_2$ entities are complexed to each of the *ansa*-zirconocene dihydride species, we have investigated related, Cl-free reaction systems, using an *ansa*-zirconocene dihydride as a starting material.

Particularly useful in this regard proved the easily accessible and well-characterized dimeric dihydride, ((EBTHI)ZrH)$_2$(μ-H)$_2$ (**24**).[6g,h] The Zr–H signals of this compound, a triplet at 5.17 ppm for its terminal Zr–H groups and another triplet at −1.29 ppm for its Zr–H–Zr bridges, disappear when 1 equiv of HAl^{i}Bu$_2$ is added to a solution of **24**. A new species is formed, which gives rise, in toluene-d_8 solution at −75 °C, to two bridging Zr–H signals, at −1.17 ppm and −0.53 ppm, a

(25) Ligand and hydride signals shown in Figure 3 were found to remain essentially unchanged down to −75 °C by variable-temperature ^{1}H NMR.

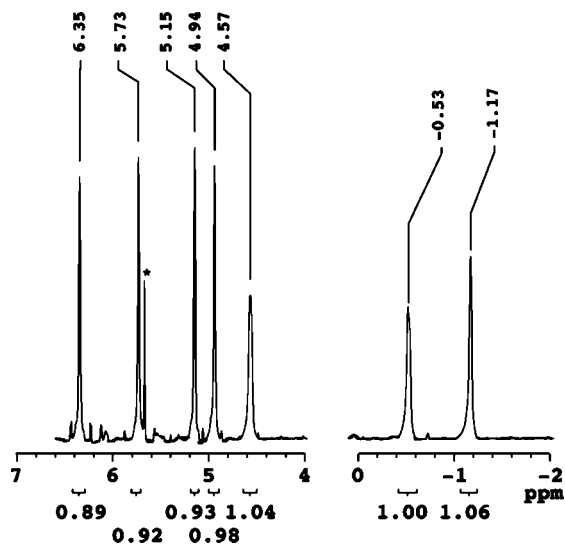(26) This observation contradicts a report in ref 6h, which claims that **18** does not react with HAl^{i}Bu$_2$.

Scheme 5

terminal Zr–H signal at 4.57 ppm, and four separate ligand C$_5$–H signals (Figure 4, Table 2). A gradient correlation spectroscopy (gCOSY) analysis shows coupling between the terminal and each of the two bridging [Zr–H] units but not between the latter two (Supporting Information Figure S15). On the basis of the similarity of this Zr–H NMR pattern to that reported by Wehmschulte and Powers for the structurally characterized species (C$_5$H$_5$)$_2$Zr(H)(μ-H)$_2$Al(H)C$_6$H$_2$^{t}Bu$_3$, we assign the signals shown in Figure 4 to the trihydride (EBT-HI)ZrH(μ-H)$_2$Al^{i}Bu$_2$ (**25**, Scheme 6).

The signals shown in Figure 4 are strongly broadened at higher temperatures, with the onset of this coalescence being critically dependent on the [HAl^{i}Bu$_2$]/[Zr] ratio used. The signals of (EBTHI)ZrH(μ-H)$_2$Al^{i}Bu$_2$ are not observable at any temperature in the presence of 4 equiv of HAl^{i}Bu$_2$, whereas in the presence of 2 equiv of HAl^{i}Bu$_2$ the observation of sharp signals requires cooling to −90 °C. Sharp signals as in Figure 4 can be observed even at room temperature, however, together with those of the initial ((EBTHI)ZrH)$_2$(μ-H)$_2$, when only 0.5 equiv of HAl^{i}Bu$_2$ is added per zirconocene, so as to minimize the

Figure 4. ^{1}H NMR spectrum of a 15 mM solution of ((EBTHI)ZrH)$_2$(μ-H)$_2$ (**24**) in toluene-d_8 at -50 °C after addition of 1 equiv of HAl^{i}Bu$_2$ ($*$, solvent impurity).

Scheme 6
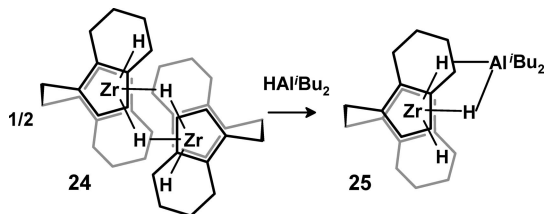
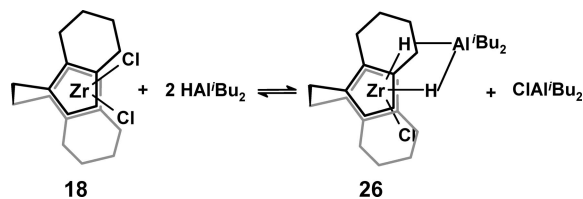*Scheme 7*
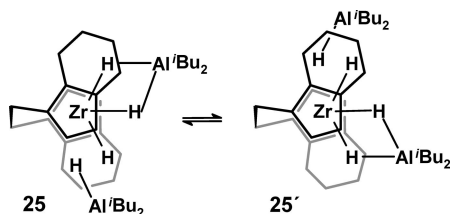
presence of any free HAl^{i}Bu$_2$ in the reaction system. This acceleration of exchange processes by excess HAl^{i}Bu$_2$ indicates that an associative exchange reaction with free HAl^{i}Bu$_2$ induces a dynamic side exchange in complex **25** (cf., Scheme 7).

On the basis of our understanding of this reaction system, we surmise that the dihydride complex formed upon addition of HAl^{i}Bu$_2$ to the dichloride (EBTHI)ZrCl$_2$ (**18**) is the cluster **26**, i.e., an analogue of the trihydride complex **25** in which the terminal hydride is replaced by a chloride, while both hydride ligands are bridging to an [Al^{i}Bu$_2$] unit, as indicated by their high-field chemical shift. When this view is tested by adding, instead of HAl^{i}Bu$_2$, 1 equiv of ClAl^{i}Bu$_2$ per Zr to a toluene-d_8 solution of ((EBTHI)ZrH)$_2$(μ-H)$_2$, we observe, together with the expected dihydride cluster **26**, a mixture of the dichloride **18**, the trihydride cluster **25**, and free HAl^{i}Bu$_2$, i.e., a decay of **26** under release of HAl^{i}Bu$_2$. When this decay of **26** is suppressed, however, by addition of 2 equiv of HAl^{i}Bu$_2$, one observes indeed exactly the same signals as in the reaction system containing the dichloride **18** and excess HAl^{i}Bu$_2$ (Supporting Information Figure S16). This reaction sequences shows unequivocally that of the 2 equiv of chloride, originally contained in the zirconocene dichloride complex, only one is retained in the reaction

Scheme 8

Scheme 9
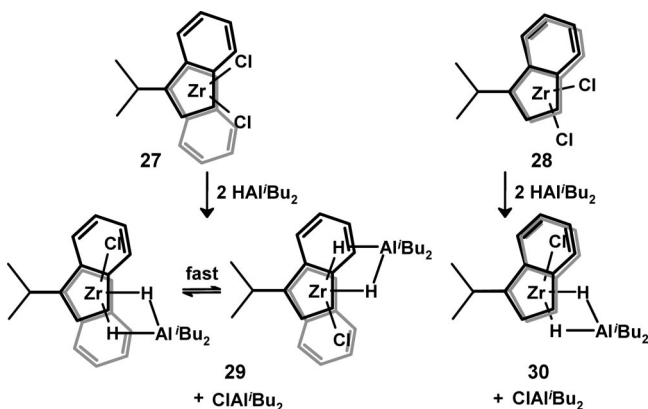
product, whereas 1 equiv of ClAl^{i}Bu$_2$ is apparently released into solution (Scheme 8). Accordingly, addition of a second equiv of ClAl^{i}Bu$_2$ to the reaction system made up of the dihydride **24** and 2 equiv of HAl^{i}Bu$_2$ and 1 equiv of ClAl^{i}Bu$_2$ per Zr leaves the positions and integrals of the previous signals unchanged (Supporting Information Figure S17). It causes, however, a sharpening of the signals assigned to the dihydride cluster **26**, quite obviously by accelerating an associative side exchange of this species analogous to that described in Scheme 7.

The view that addition of HAl^{i}Bu$_2$ to one of the *ansa*-zirconocene dichlorides shown in Scheme 5 gives the corresponding zirconocene monochloride dihydride clusters containing one Al^{i}Bu$_2$ unit is supported by experiments with a pair of racemic and meso-configured Me$_2$C(indenyl)$_2$ZrCl$_2$ complexes, *rac*-**27** and *meso*-**28** (Scheme 9). The racemic dihydride cluster **29** gives, as expected, a single ZrH$_2$ signal at -1.35 ppm (Supporting Information Figure S18). Its meso counterpart **30**, on the other hand, in which the (μ-H)$_2$Al^{i}Bu$_2$ moiety is likely to stay on the open side of the complex, yields two separate ZrH signals at -1.89 and -0.87 ppm (Supporting Information Figure S19). The close coincidence of the average of these two values with the chemical shift of the ZrH$_2$ group in the racemic isomer supports the notion that the latter has a similarly unsymmetric structure as the meso isomer and that the appearance of a single ZrH$_2$ resonance in this—and by implication also in the other—racemic complexes arises from a rapid side exchange of the type shown in Scheme 9.

A remarkable mode of reaction with HAl^{i}Bu$_2$, which differs from that described above for the bridged dichloride complexes **17**–**24**, is observed for the ^{t}Bu-substituted complexes **31** and **33** (Scheme 10). When complex **31**, *rac*-Me$_2$Si(2-Me$_3$Si-4-Me$_3$C-C$_5$H$_2$)$_2$ZrCl$_2$, in which both C$_5$-ring ligands are shielded by a Me$_3$Si and a Me$_3$C group, is reacted with 2 equiv of HAl^{i}Bu$_2$ in toluene-d_8 at -50 °C, about half of it is converted to a new species with three Zr—H signals at -1.67, -0.62, and 2.65 ppm. A gCOSY analysis (Supporting Information Figure S20), which shows coupling of the signal at 2.65 ppm with both of the high-field Zr—H signals but no coupling between these

Scheme 10
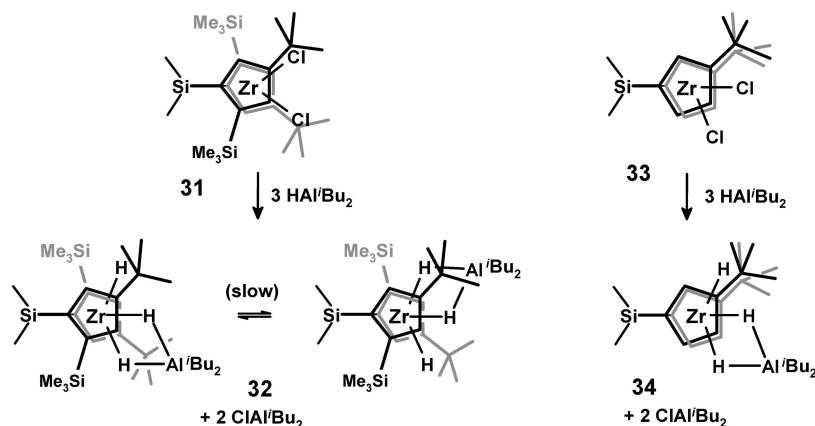
high-field signals, and the observation of duplicate sets of CH, Me₃C, and Me₃Si ligand signals are closely analogous to the NMR pattern described above for the trihydride complex (EBTHI)ZrH(μ-H)₂Al^{i}Bu₂ (**25**). We can thus conclude that a trihydride complex carrying one [Al^{i}Bu₂] unit, *rac*-Me₂Si(2-Me₃Si-4-Me₃C-C₅H₂)₂ZrH(μ-H)₂Al^{i}Bu₂ (**32**), is formed by reaction of HAl^{i}Bu₂ with the dichloride **31** (Scheme 10). In this reaction system, 2 equiv of ClAl^{i}Bu₂ are apparently displaced by HAl^{i}Bu₂ from the Zr center and released into solution. This Cl/H displacement appears to be an equilibrium reaction, as shown by an almost complete (ca. 90%) conversion of **31** to **32** in the presence of a 10-fold excess of HAl^{i}Bu₂ (Figure 5). In distinction to the (EBTHI)Zr trihydride complex **25**, the hydride signals of complex **32** do not coalesce or broaden even at room temperature in the presence of excess HAl^{i}Bu₂. Side exchange, while still observable here in polarization transfer experiments (Supporting Information Figure S21), is undoubtedly greatly hindered by the α-positioned Me₃Si groups, which block the approach of HAl^{i}Bu₂ required for the associative exchange outlined in Scheme 7.

A related case concerns a reaction system which contains, together with 2 equiv of HAl^{i}Bu₂, the dichloride *meso*-Me₂Si(3-Me₃C-C₅H₃)₂ZrCl₂ (**33**). This complex differs from the previous representative **31** by the absence of the α-positioned Me₃Si groups and by the placement of both *tert*-butyl substituents on the same side of the complex. The reaction product *meso*-

Me₂Si(3-Me₃C-C₅H₃)₂ZrH(μ-H)₂Al^{i}Bu₂ (**34**) is characterized, in toluene-d_8 at −50 °C, by three sharp Zr−H signals at −2.25, −0.28, and 3.22 ppm and by a single set of three C₅-ring CH and one *tert*-butyl signal, in accord with its C_s symmetry (Supporting Information Figure S22). The NMR spectrum observed for complex **34** at −50 °C persists essentially unchanged also at temperatures up to 25 °C. Here, as in the meso-configured bisindenyl complex **30** discussed above, we see no signs for any side exchange of the Zr(μ-H)₂Al^{i}Bu₂ moiety (Supporting Information Figure S24). Apparently, the latter is locked into one side of the complex molecule by the *tert*-butyl groups, which make the other side of the complex inaccessible.[27] In distinction to all other cases discussed so far, we observe here even at room temperature separate ^{i}Bu signals for 2 equiv of free ClAl^{i}Bu₂ (0.48 (d 8H, 7.0 Hz), 1.05 (d 24 H, 6.7 Hz) and 2.03 ppm (m, 4H, 6.8 Hz)) and for 1 equiv of a complex-bound [Al^{i}Bu₂] unit (0.54 (d 4H, 7.2 Hz), 1.21 (m 12H) and 2.19 ppm (m, 2H, 6.8 Hz)). This attests to the efficient shielding of complex **34** against associative exchange reactions and confirms the stoichiometry of the reaction shown in Scheme 10.

The observation that bridged zirconocene dichloride complexes with bulky substituents in a β-position of each C₅-ring react with HAl^{i}Bu₂ to give the trihydride clusters Cp$^x_2$ZrH(μ-H)₂Al^{i}Bu₂, instead of the otherwise prevailing chlorodihydride clusters Cp$^x_2$ZrCl(μ-H)₂Al^{i}Bu₂, can be explained by the serious mutual repulsion, which Cl ligands and β-^{t}Bu substituents in *ansa*-zirconocenes are known to suffer.[28] Much of this repulsion is likely to be released when a Zr−Cl bond with a length of ca. 245 pm is replaced by a much shorter Zr−H bond (ca. 195 pm), which allows the hydride ligand to escape from repulsive contacts by staying on the "inside" of the β-^{t}Bu substituent. This steric shielding appears to favor the formation of the trihydride cluster over its chlorodihydride congener; at the same time, it will largely suppress an associative approach of HAl^{i}Bu₂ or ClAl^{i}Bu₂ from the side of the terminal hydride.

3. Bridged versus Unbridged Zirconocene Complexes. All of our results presented so far thus indicate a clear dichotomy between unbridged and bridged zirconocene complexes: all unbridged representatives discussed in section 1 of this report
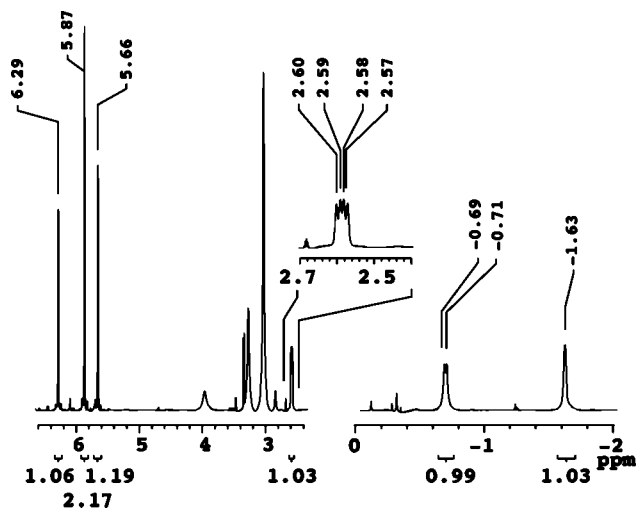

Figure 5. ¹H NMR spectrum of a 48 mM solution of *rac*-Me₂Si(2-Me₃Si-4-Me₃C-C₅H₂)₂ZrCl₂ (**31**) in toluene-d_8 at 25 °C after addition of 10 equiv of HAl^{i}Bu₂.

(27) A significant NOE, which connects the signals of the *tert*-butyl and the terminal Zr−H groups in complex **34**, indicates that these groups are in close proximity.

(28) (a) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359. (b) Brintzinger, H. H.; Prosenc, M. H.; Schaper, F.; Weeber, A.; Wieser, U. *J. Mol. Struct.* **1999**, *485–486*, 409.
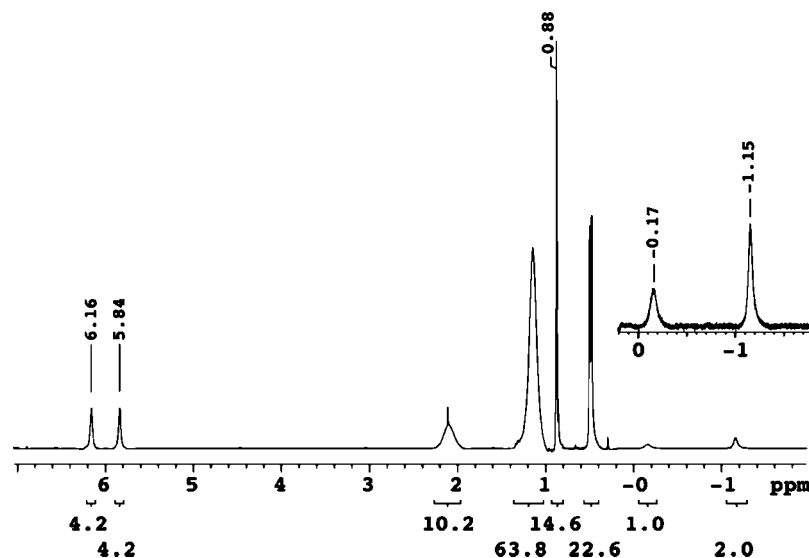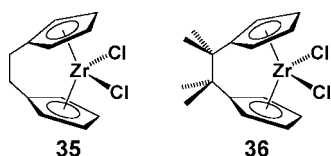
Figure 6. ^{1}H NMR spectrum of a 30 mM solution of $Me_4C_2(C_5H_4)_2ZrCl_2$ (**36**) in benzene-d_6 at 25 °C after addition of 4 equiv of HAl^iBu_2.

Scheme 11

react with HAl^iBu_2 to form clusters containing three $[Al^iBu_2]$ units and a $[ZrH_3]$ coordination core.[29] All the bridged complexes shown in Scheme 5, on the other hand, react with HAl^iBu_2 to give an adduct with only one $[Al^iBu_2]$ unit. The vast majority of these contain a $[ZrClH_2]$ coordination core; only the most heavily congested *ansa*-zirconocenes with β-^tBu substituents are found to contain a $[ZrH_3]$ core in contact with a single Al^iBu_2 unit. In the following, we search for possible causes for this dichotomy between unbridged and bridged zirconocene complexes.

With regard to steric factors, bridged zirconocenes should be at least as accessible for contacts with further $[Al^iBu_2]$ units as their unbridged counterparts. Especially the totally unsubstituted *ansa*-zirconocenes **19** and **20** would appear to be more open than their unbridged congeners **1**, **6**, **8**, or **10**, yet even they differ from the latter by an apparent incapability to expand their binuclear $[Zr(Cl)(\mu-H)_2Al^iBu_2]$ coordination geometry to the tetranuclear $[Zr(\mu-H)_3(Al^iBu_2)_3(\mu-Cl)_2]$ alternative. The preference of unbridged complexes for the latter coordination mode does not appear to be based on electronic factors either: Several observables, such as reduction potentials of dichloride complexes or CO stretching frequencies in the corresponding Zr(II) dicarbonyl derivatives, as well as single-electron affinities determined by DFT-based calculations, all point toward a net electron-withdrawing effect of a Me_2C or Me_2Si bridge[30] and, hence, toward a greater tendency of bridged than of unbridged zirconocenes to accept an electron-rich hydride in exchange for a less donating chloride ligand.[31]

The only remaining explanation would thus appear to be that the dichotomy between unbridged and bridged zirconocenes with

regard to their reactions with HAl^iBu_2 is connected to different degrees of rotational freedom of the C_5-ring ligands in these two classes of complexes. In order to test this hypothesis, we have studied reactions of HAl^iBu_2 with two ethanediyl-bridged zirconocenes, **35** and **36** (Scheme 11). In distinction to their congeners with Me_2C- and Me_2Si-bridges, which enforce a strictly eclipsed conformation of their C_5-ring ligands, ethanediyl-bridged titanocene and zirconocene complexes are known to deviate significantly from an eclipsed C_5-ring conformation. Crystal structures reported for complexes **35** and **36**[30,32] reveal dihedral bridgehead–centroid–centroid–bridgehead angles of 21° and 15°, respectively. This and the observation of ^{1}H NMR spectra with time-averaged C_{2v} symmetry in solutions of **35** and **36** indicate an essentially unobstructed fluctuation between right- and left-handed deviations from C_{2v} symmetry, i.e., a significant measure of torsional freedom of the C_5-rings in these ethanediyl-bridged complexes.

Reactions of complexes **35** and **36** with 4 equiv of HAl^iBu_2 do indeed give the trialuminum trihydrides $H_4C_2(C_5H_4)_2Zr(\mu-H)_3(Al^iBu_2)_3(\mu-Cl)_2$ (**37**) and $Me_4C_2(C_5H_4)_2Zr(\mu-H)_3(Al^iBu_2)_3(\mu-Cl)_2$ (**38**), respectively, as judged by their typical NMR doublet and triplet signals between −0.5 and −2 ppm with integral ratios of 2:1, which are characteristic for complexes of this type (Figure 6, Table 2, Supporting Information Figure S25). The outcome of this test reaction, which sets complexes **35** and **36** clearly apart from their single-atom bridged congeners **19**, **20**, and **22**, strongly indicates that the accessibility of a staggered C_5-ring conformation is the decisive criterion for the dichotomy between unbridged zirconocene complexes vis-à-vis those with a single-atom bridge with regard to their respective reactions with HAl^iBu_2.[33]

Formation of a trialuminum cluster $[Zr(\mu-H)_3(Al^iBu_2)_3(\mu-Cl)_2]$ apparently requires that the Al-bound CH_2 groups of its $[Al^iBu_2]$ units fit snugly into spatial niches in the C–H periphery of the C_5-ring ligands. This appears to be achieved more favorably with staggered than with eclipsed C_5-rings. The view that the Al-bound CH_2 groups of these complexes are in close contact with C_5-ring H atoms, is supported by the observation of a significant nuclear Overhauser effect (NOE) signal for complex **38**, which connects these Al–CH_2 groups with the β-H atoms
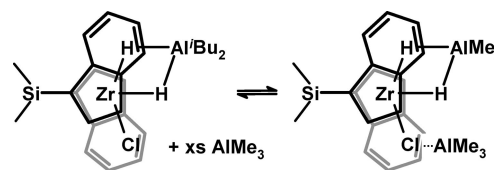
(29) An exception to this rule is the complex $(C_5H_5)_2Zr(H)(\mu-H)_2Al(H)(1,3,5-$ $^tBu_3C_6H_3)$ described in ref 7b, where the exceptional steric demand of the supermesityl group appears to preclude the approach of further AlR_2X units.

of the C_5-ring ligands (Supporting Information Figure S26).[34] In ethanediyl-bridged complexes with bisindenyl and bis(tetrahydroindenyl) ligands, such as **17** and **18**, however, the increased steric bulk of the annulated/substituted ring ligands appears to be sufficient to restrict reactions with HAl^{i}Bu$_2$ again to the formation of [ZrCl(μ-H)$_2$Al^{i}Bu$_2$] rather than [Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$] clusters.

Our results show that either a chloride or a hydride can occupy the terminal position in hydride-bridged monoaluminum clusters formed by typical *ansa*-zirconocenes, depending on the ligand framework of the zirconocene complex studied. In order to assess the scope of related hydride-complex formation reactions, other representatives of the general class of heterobinuclear ZrX(μ-H)$_2$Al^{i}Bu$_2$ clusters were sought for. Reaction of the fluoride analogue of complex **18**, (EBTHI)ZrF$_2$, with 1 or 2 equiv of HAl^{i}Bu$_2$ is found to yield, in accord with previous studies,[6h] the dihydride **24** as the only zirconocene product, with no indication for an intermediate of the kind (EBTHI)ZrF(μ-H)$_2$Al^{i}Bu$_2$ (Supporting Information Figure S27). This might thus be a case where the coexistence of "hard" fluoride and "soft" hydride coligands is unfavorable, such that the reaction leads to the disjoined products, i.e., to ((EBTHI)ZrH$_2$)$_2$ and (FAl^{i}Bu$_2$)$_n$.

With a view toward "softer" coligands, we have tried to find evidence for the existence of clusters of the type [ZrMe(μ-H)$_2$AlR$_2$] containing a methyl group as a terminal ligand. When the chloride-containing complex (SBI)ZrCl(μ-H)$_2$Al^{i}Bu$_2$ is treated with AlMe$_3$, a shift of its Zr–H signal from 1.22 ppm to a limiting value of 1.65 ppm, reached at high excess of AlMe$_3$ ([AlMe$_3$]/[Zr] = 128), indicates the occurrence of some reaction. Product formation, as measured by the change in chemical shift, $\Delta\delta$(Zr–H), is found to be a function of the absolute concentration [AlMe$_3$], however, rather than of the ratio [AlMe$_3$]/[Zr] (Supporting Information Appendix S-1). The product thus appears to be an adduct, most likely with AlMe$_3$ attached to

(30) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525.

(31) Neither do hydride affinities, calculated by DFT-based methods as enthalpy differences for the hypothetical reaction (C$_5$H$_5$)$_2$ZrH$_2$ + H$^-$ → (C$_5$H$_5$)$_2$ZrH$_3^-$, indicate any preferred hydride uptake when the interanular wedge angle is increased to values characteristic for *ansa*-zirconocenes complexes such as **19** or **20** (ref 23).

(32) Bühl, M.; Hopp, G.; von Philipsborn, W.; Beck, S.; Prosenc, M.-H.; Rief, U.; Brintzinger, H. H. *Organometallics* **1996**, *15*, 778.

(33) Possible steric interactions of the Al-bound ^{i}Bu groups directly with the interannular bridging units would be expected to be stronger with a Me$_4$C$_2$ bridge, due to its greater spatial extension, than with a C$_2$H$_4$ bridge—probably more comparable to that with a Me$_2$C bridge. The observation that the reactions of **35** and **36** with HAl^{i}Bu$_2$ result in hydride complexes of the same type would thus rule out direct steric interactions between Al^{i}Bu$_2$ groups and bridging units as a decisive criterion for the relative stabilities of [ZrCl(μ-H)$_2$Al^{i}Bu$_2$] vs [Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$] species.

(34) A significant NOE signal connects the signal at 0.875 ppm due to the CH$_3$ groups of the interanular bridge of complex **38** with the C$_5$–H signal at 5.839 ppm and identifies the latter as being due to the α-positioned H atoms and that at 6.161 ppm as the resonance of the β-H atoms. This order of the chemical shifts of α- and β-positioned C$_5$–H atoms, which we find also for the dimeric dihydride **24** and for the dihydride cluster **26** (see the Supporting Information), groups these five-coordinate hydride-bridged zirconocene complexes together with typical four-coordinate, 16-electron dichloride complexes (cf., Gutmann, S.; Burger, P.; Prosenc, M.-H.; Brintzinger, H. H. *J. Organomet. Chem.* 1990, *397*, 21). This indicates that the Zr centers of these hydride-bridged complexes do not reach a full 18-electron complement and might explain why pentacoordination, rather than an even more electron-deficient tetracoordination, is prevalent in these hydride-bridged complexes.

Scheme 12

the terminal Cl ligand of (SBI)ZrCl(μ-H)$_2$Al^{i}Bu$_2$,[35] rather than the sought-for Me-versus-Cl exchange product (Scheme 12).

When the dimethyl complex (SBI)ZrMe$_2$ is reacted with slightly more than 2 equiv of HAl^{i}Bu$_2$ in benzene or toluene solution, at room temperature or at −75 °C, several Zr–H signals appear between ca. −0.5 and −2 ppm. This observation, and an intense darkening of the reaction mixture in the course of 1−2 h,[36] indicate that any (SBI)ZrMe(μ-H)$_2$Al^{i}Bu$_2$ formed in this reaction would decay to other species, possibly to complexes which contain their Zr center in a reduced oxidation state. The sought-for species (SBI)ZrMe(μ-H)$_2$Al^{i}Bu$_2$ might be in equilibrium with HAl^{i}Bu$_2$ and (SBI)Zr(Me)H; the latter is likely to form, by reductive elimination of methane,[37,38] the Zr(II) species (SBI)Zr. This would then most probably lead to further decay reactions under the prevailing reaction conditions.

Conclusions

Our results show that reactions with HAl^{i}Bu$_2$ give different reaction products—tetranuclear trihydrides [Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_3$(μ-Cl)$_2$] versus binuclear dihydrides [ZrCl(μ-H)$_2$Al^{i}Bu$_2$]—from unbridged zirconocenes and from zirconocene dichlorides with a single-atom bridge, respectively. Binuclear complexes [ZrH(μ-H)$_2$Al^{i}Bu$_2$], which contain a Zr–H instead of a Zr–Cl unit, are formed when HAl^{i}Bu$_2$ is reacted with a zirconocene dihydride or with a zirconocene dichloride carrying particularly congested ring ligands. A terminal Zr–Me group instead of a Zr–Cl or Zr–H unit, however, appears to render otherwise analogous binuclear dihydrides prone to decay, possibly due to reductive CH$_4$ elimination.[38]

On the basis of these results, we would propose that the zirconocene dihydride complexes, which are formed in (SBI)-

(35) Either Me or ^{i}Bu can occupy terminal Zr(μ-H)$_2$Al-alkyl positions in such a complex. A closely related exchange of terminal ^{i}Bu and Me groups between the cation (SBI)Zr(μ-Me)$_2$AlMe$_{2-x}$^{i}Bu$_x^+$ and mixed alkylaluminum dimers, Al$_2$(μ-Me)$_2$Me$_{4-x}$^{i}Bu$_x$, has been shown to occur to an extent which is close to statistical expectations (ref 16a). This Me vs ^{i}Bu exchange was found to leave the chemical shift of the μ-Me groups unchanged; in the present case, such an exchange is thus unlikely to cause the changing chemical shifts of the (μ-H)$_2$ signal.

(36) Similar decay reactions appear to proceed upon addition of HAl^{i}Bu$_2$ to mixtures of (SBI)ZrMe$_2$ and AlMe$_3$ in various ratios. Addition of HAl^{i}Bu$_2$ to 1:1 mixtures of (SBI)ZrMe$_2$ and B(C$_6$F$_5$)$_3$, in the absence as in the presence of excess AlMe$_3$, appears to lead to partial transfer of C$_6$F$_5$ groups from boron to aluminum, as indicated by signals at −124.8, −155.2, and −163.7 ppm in the ^{19}F NMR spectra of the reaction mixtures (cf., Bochmann, M.; Sarsfield, M. J. Organometallics 1998, *17*, 5908).

(37) ((EBTHI)ZrH$_2$)$_2$ in C$_6$D$_6$ reacts with excess AlMe$_3$—in the absence as in the presence of MAO—to give mainly the dimethyl complex (EBTHI)ZrMe$_2$, together with some hydride species with a resonance at −1.542 ppm; several C$_5$–H signals between 5 and 6 ppm indicate the formation of additional products. In these cases, evolution of CH$_4$ is evident by the appearance of its characteristic sharp signal at 0.16 ppm, while this spectral region is obscured by the Me$_2$Si resonances in reactions systems involving (SBI)Zr derivatives.

(38) Alkane elimination from zirconocene alkyl hydrides: (a) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2241. (b) Chirik, P. J.; Bercaw, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 393. (c) McAllister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

ZrCl$_2$/MAO reaction systems upon addition of HAl^{i}Bu$_2$,[16b] are species of the type (SBI)Zr(Me$\cdots$MAO)(μ-H)$_2$AlMe$_2$, in which the terminal Zr—Me group is bound, without being cationized,[39] to a Lewis acidic Al site of MAO.[40] Interaction of excess AlMe$_3$—always present in these reaction systems—with minor fractions of a MAO-free species (SBI)Zr(Me)(μ-H)$_2$AlMe$_2$, on the other hand, might make side exchange in this species fast enough to give the symmetrized ZrH$_2$ signal observed for zirconocene dihydride complexes in these reaction media.[16b] Such a "mild" sequestration of the Zr—Me group would be analogous to that observed in reaction systems (C$_5$H$_5$)$_2$ZrMe$_2$/ MAO at relatively low [Al]$_{MAO}$/[Zr] ratios of 20–50,[41] and might be sufficient to suppress an otherwise prevalent methane elimination, at least to a substantial degree. A residual extent of CH$_4$ release even from these MAO-stabilized complexes might explain the ubiquitous formation of methane from "working" zirconocene-based polymerization catalysts[42] and, likewise, the still enigmatic formation of zirconocene species with a long-wavelength absorbance, at ca. 600 nm, possibly due to a zirconocene species containing Zr in a reduced oxidation state,[43] in reaction systems containing (SBI)ZrCl$_2$ and MAO upon addition of HAl^{i}Bu$_2$.[16b] Further fates of such reduced zirconocene species, i.e., their contribution to irreversible catalyst deactivation and/or their reconversion to active cationic catalyst species, remain a topic for future investigations.

Experimental Section

All operations were carried out under a protective dinitrogen atmosphere, either in a glovebox or on a vacuum manifold. Benzene-d_6, toluene-d_8, and other solvents used were dried by vacuum transfer either from sodium benzophenone or from "titanocene".[44] Zirconocene complexes used as starting materials were either purchased from Strem Chemicals, Newburyport (**1**, **6**, **12**, and **17**), obtained as gifts from Dr. M. Ringwald, MCAT, Konstanz ((EBTHI)ZrF$_2$,[45] **27**, **28**,[46] and **36**[47]) and from BASELL Polyolefins, Frankfurt/Main (**16**[48]), or prepared in our laboratories according to published procedures (**3**,[49] **8**,[50] **10**,[51] **13**,[52] **18**,[53] **19**,[54] **20**,[55] **21**,[56]

22,[57] **23**,[58] **24**,[6g,h] **31**,[59] **33**,[28a,60] and **35**[30,61]). Trimethylaluminum, triisobutylaluminum, diisobutylaluminum hydride, and diisobutylaluminum chloride were used as obtained from Aldrich Chemical Co., Milwaukee. **CAUTION:** *alkylaluminum compounds are pyrophoric and must be handled with special precautions* (see, e.g., Shriver, D.F. *The Manipulation of Air-sensitive Compounds*; Robert E. Krieger Publishing Company; Malabar, Florida, 1982).

Reaction mixtures for NMR measurements were prepared by dissolving a weighed amount of solid zirconocene starting compound, in an oven-dried J Young NMR tube, in benzene-d_6 or toluene-d_8 under inert atmosphere. Aluminum reagents were added as neat liquids via microliter syringes. NMR spectra were obtained using Varian Inova 400, 500, or Mercury 300 spectrometers. Chemical shifts are referenced to residual solvents peaks, 7.160 ppm for benzene and 7.000 ppm for the central aromatic proton resonance of toluene.

Supporting Information Available: Additional figures and appendix outlining the 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$_2$Me$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

JA8054723

(39) The ^{1}H NMR signals of this alkylaluminum-complexed dihydride species are close to those of other neutral complexes, such as (SBI)ZrCl$_2$ and (SBI)ZrMe$_2$, rather than to those of the cationic species [(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ MeMAO$^-$ or [(SBI)ZrMe$^+\cdots$MeMAO$^-$] (ref 16b).

(40) The UV–vis spectra of the reaction products of HAl^{i}Bu$_2$ with (SBI)ZrCl$_2$ alone and of HAl^{i}Bu$_2$ with (SBI)ZrCl$_2$/MAO reaction systems are quite similar to each other; both show broad absorbance bands around 380 and 340 nm (ref 16b).

(41) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2000**, *201*, 558.

(42) (a) Kaminsky, W.; Piehl, C. *J. Mol. Catal. A: Chem.* **2004**, *213*, 15. (b) Kaminsky, W.; Bark, A.; Steiger, R. *J. Mol. Catal.* **1992**, *74*, 109.

(43) Lyakin, O. Y.; Bryliakov, K. P.; Panchenko, V. N.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2007**, *208*, 1168.

(44) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

(45) Spannenberg, A.; Arndt, P.; Baumann, W.; Burlakov, V. V.; Rosenthal, U.; Becke, S.; Weiss, T. *Organometallics* **2004**, *23*, 3819.

(46) Voskoboynikov, A. Z.; Agarkov, A. Yu.; Chernyshev, E. A.; Beletskaya, I. P.; Churakov, A. V.; Kuz'mina, L. G. *J. Organomet. Chem.* **1997**, *530*, 75.

(47) Schwemlein, H.; Brintzinger, H. H. *J. Organomet. Chem.* **1983**, *254*, 69.

(48) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1511.

(49) Wailes, P. C.; Weigold, H. *Inorg. Synth.* **1979**, *19*, 223.

(50) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772.

(51) Lappert, M. F.; Riley, P. I.; Yarrow, P. I. W.; Atwood, J. L.; Hunter, W. E.; Zaworothko, M. J. *J. Chem. Soc., Dalton Trans.* **1981**, 814.

(52) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733. (b) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

(53) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63.

(54) Nifant'ev, I. E.; Churakov, A. V.; Urazovskii, I. F.; Mkoyan, Sh. G.; Atovmyan, L. O. *J. Organomet. Chem.* **1992**, *435*, 37.

(55) Köpf, H.; Klouras, N. *Z. Naturforsch.* **1983**, *38B*, 321.

(56) Hüttenhofer, M.; Prosenc, M.-H.; Rief, U.; Schaper, F.; Brintzinger, H. H. *Organometallics* **1996**, *15*, 4816.

(57) Cano, A.; Cuenca, T.; Gomez-Sal, P.; Royo, B.; Royo, P. *Organometallics* **1994**, *13*, 1688.

(58) Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988.

(59) Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171.

(60) Yoder, J. C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1998**, *17*, 4946.

(61) In deviation from ref 30, ethylene-1,2-dicyclopentadiene was prepared by reaction of dicyclopentadienyl magnesium with ethylene-1,2-ditosylate in tetrahydrofuran at room temperature. In this manner, the yield of the dilithium salt of ethylene-1,2-dicyclopentadiene was increased from ca. 10% to ca. 60%.