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# Cationic Alkylaluminum-Complexed Zirconocene Hydrides: NMR-Spectroscopic Identification, Crystallographic Structure Determination, and Interconversion with Other Zirconocene Cations

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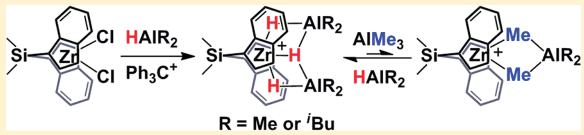
*Supporting Information*

**ABSTRACT:** The *ansa*-zirconocene complex *rac*-$Me_2Si(1\text{-indenyl})_2ZrCl_2$ ((SBI)$ZrCl_2$) reacts with diisobutylaluminum hydride and trityl tetrakis(perfluorophenyl)borate in hydrocarbon solutions to give the cation $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$, the identity of which is derived from NMR data and supported by a crystallographic structure determination. Analogous reactions proceed with many other zirconocene dichloride complexes. $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ reacts reversibly with $ClAl^iBu_2$ to give the dichloro-bridged cation $[(SBI)Zr(\mu\text{-}Cl)_2Al^iBu_2]^+$. Reaction with $AlMe_3$ first leads to mixed-alkyl species $[(SBI)Zr(\mu\text{-}H)_3(AlMe_x{}^iBu_{2-x})_2]^+$ by exchange of alkyl groups between aluminum centers. At higher $AlMe_3$/Zr ratios, $[(SBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$, a constituent of methylalumoxane-activated catalyst systems, is formed in an equilibrium, in which the hydride cation $[(SBI)Zr(\mu\text{-}H)_3(AlR_2)_2]^+$ strongly predominates at comparable $HAl^iBu_2$ and $AlMe_3$ concentrations, thus implicating the presence of this hydride cation in olefin polymerization catalyst systems.

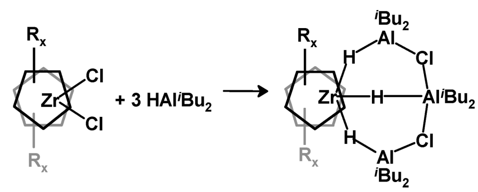



## INTRODUCTION

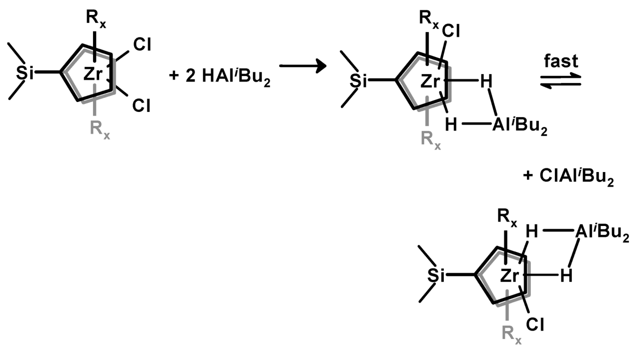
Alkylaluminum-complexed zirconocene hydride complexes have been shown to be present in a variety of catalytic systems, for example, for hydro- and carboalumination reactions of unsaturated substrates, including their asymmetric variants.[1] While there is still some uncertainty concerning the compositions and structures of the complexes occurring in these reaction systems,[2] we have recently shown that two types of neutral complexes can arise in such reaction systems containing diisobutylaluminum hydride, $HAl^iBu_2$,[3] depending on the type of zirconocene used.[4] Trihydride complexes containing three $\{Al^iBu_2\}$ units connected by two Cl-bridges are formed in the presence of $HAl^iBu_2$ from most unbridged zirconocene dichlorides (Scheme 1). Ring-bridged *ansa*-zirconocene precursors, on the other hand, react with $HAl^iBu_2$ to yield in most cases chloro dihydride complexes containing only one $\{Al^iBu_2\}$ unit (Scheme 2). This dichotomy appears to be caused by steric interference due to the ecclipsed ring-ligand conformation, which is enforced by a single-atom interannular bridge.[4]

Apart from such neutral species, alkylaluminum-complexed zirconocene hydrides might also give rise to cationic species, particularly in zirconocene-based reaction systems containing methylalumoxane (MAO) or other "cationization" reagents generally employed for olefin polymerization catalysis.[5] Cationic zirconocene hydride species, stabilized by complex formation either with an anion,[6] with a neutral Lewis base,[7] or, in the context of the work reported herein, with some neutral hydride species,[6d,8] have been identified by NMR and, in many instances, also

Scheme 1




Scheme 2

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crystallographically characterized.[6a,6b,7a−7f,8] The question thus arises: which kinds of cationic zirconocene hydride species might be present in "cationized", alkylaluminum-containing polymerization catalyst systems? In such catalyst systems, alkylaluminium-complexed hydrides have occasionally been observed by NMR,[9] but their identity does not yet appear to be unequivocally established. We have thus explored the nature of cationic species produced in reaction systems containing a zirconocene dichloride in the presence of an alkylaluminum hydride and a cationization reagent. Here, we report the results of these experiments that have focused mainly on the often-studied *ansa*-zirconocene complex (SBI)$ZrCl_2$. A cationic alkylaluminum-complexed zirconocene hydride of this complex has recently been shown by some of us to catalyze olefin polymerization and hydroalumination.[10]

## ■ RESULTS AND DISCUSSION

**1. The Reaction System (SBI)$ZrCl_2$/$HAl^iBu_2$/[$Ph_3C$][B($C_6F_5$)$_4$].** In a typical experiment, a 4 mM benzene-$d_6$ solution of the neutral complex (SBI)Zr(Cl)($\mu$-H)$_2$Al$^i$Bu$_2$ is obtained by reaction of (SBI)$ZrCl_2$ with 5 equiv of $HAl^iBu_2$.[4] When the neutral species is then treated with 1 equiv of trityl tetrakis(perfluorophenyl)borate, [$Ph_3C$][B($C_6F_5$)$_4$], at room temperature, the reaction mixture immediately assumes a bluish-green tint. $^1$H NMR of the solution reveals a single product characterized by a doublet at −2.25 ppm with $^2J_{HH} \approx 8$ Hz and an integration of 2 H per zirconocene unit (Figure 1), which is indicative of a $ZrH_2$ group. A gCOSY reveals that this doublet is coupled to a triplet at 0.30 ppm, which is partly obscured by Al−C$H_2$ signals (Figure 2). This triplet must then be due to a third Zr-bound hydride ligand, such that this set of hydride signals is to be assigned to a zirconocene complex with three Zr-bound hydride ligands, one in central position and two in lateral positions. The complete conversion of 1 equiv of the trityl salt to triphenyl methane ($\delta$ 5.42 pm) implies the formation of a zirconocene monocation. For a proper balancing of charges, this cation would have to contain two {$Al^iBu_2{}^+$} units, presumably in contact with the Zr-bound hydride ligands.

The {$Al^iBu_2{}^+$} units of the resulting cationic complex, [(SBI)Zr($\mu$-H)$_3$(Al$^i$Bu$_2$)$_2$]$^+$, give rise to C*H* and C*H*$_3$ signals centered at 1.77 and 0.94 ppm, respectively, and to a C*H*$_2$ signal with a well-resolved diastereotopic splitting of 0.11 ppm, centered at 0.20 ppm. Integration of these signals, which are well separated from those of the free {$^i$BuAl} species present, clearly support the presence of two {$Al^iBu_2{}^+$} moieties per zirconocene unit. Formation of $ClAl^iBu_2$ can be deduced from a characteristic splitting of the Al−H resonance into three separate resonances due to the formation of mixed ($XAl^iBu_2$)$_3$ trimers, with X = H and Cl,[11] and

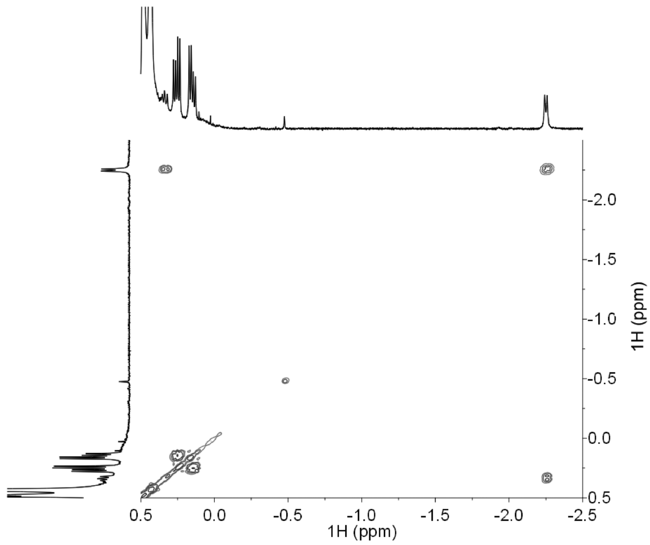


**Figure 2.** High-field region of gCOSY of the cation [(SBI)Zr($\mu$-H)$_3$(Al$^i$Bu$_2$)$_2$]$^+$ (reaction conditions as in Figure 1).

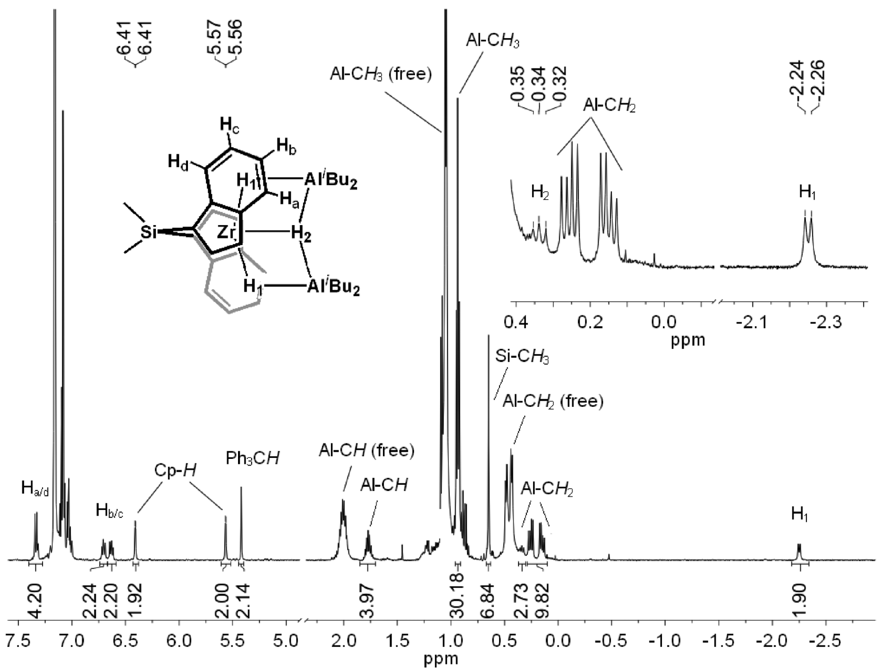


**Figure 1.** $^1$H NMR spectrum of the cationic hydride [(SBI)Zr($\mu$-H)$_3$(Al$^i$Bu$_2$)$_2$]$^+$ in benzene-$d_6$ solution, obtained by treating a 4 mM solution of (SBI)$ZrCl_2$ first with 5 equiv of $HAl^iBu_2$ and then with 1 equiv of [$Ph_3C$][B($C_6F_5$)$_4$] (25 °C, 500 MHz).


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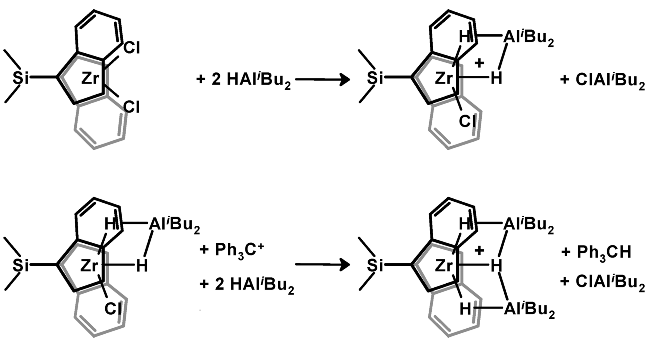
**Scheme 3**



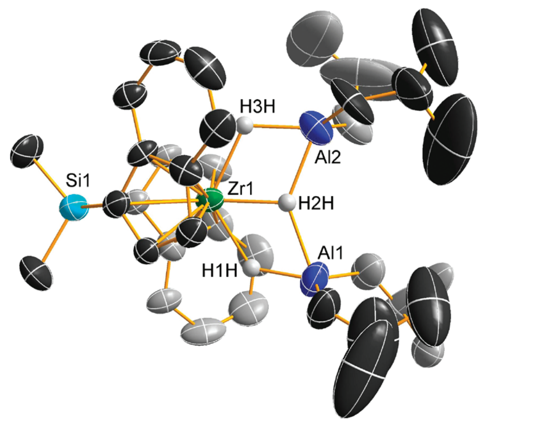




**Figure 3.** Structure of one of the two unique $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ cations in the asymmetric unit of crystals of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]\cdot{}^1/_2$toluene (thermal ellipsoids at 50% probability, hydride positions taken from the difference Fourier map; other H atoms omitted).

from the observation of isobutyl $^1$H resonances of free $ClAl^iBu_2$ at −25 °C (Supporting Information). Conversion of $(SBI)ZrCl_2$ to the hydride cation, $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$, can thus be described as outlined in Scheme 3.

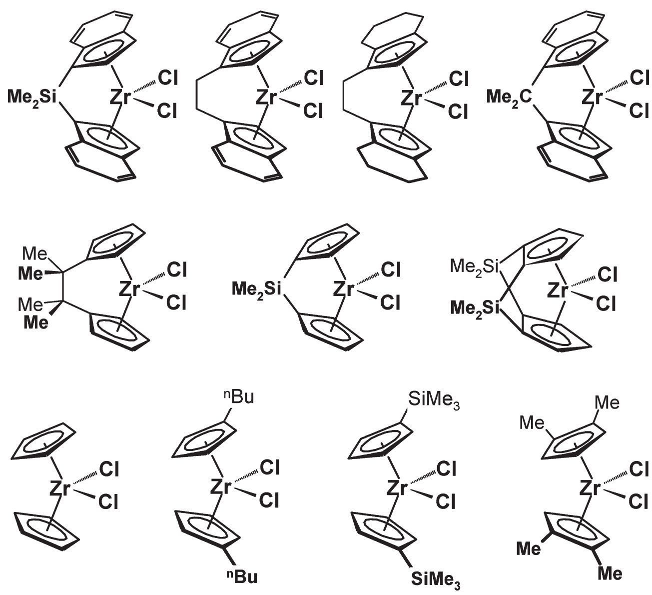
The observation of separate signals for complex-bound and free Al-isobutyl groups implies that exchange between these units is slow on the NMR time scale. Coalescence of these signals did not occur upon heating such a reaction system before the cation decomposed at 75 °C, but an EXSY study performed at room temperature revealed substantial exchange between complex-bound and free Al-isobutyl groups. At mixing times of 300 ms, sizable EXSY crosspeaks are observed between the respective isobutyl signals of the hydride cation and those of $\{Al^iBu\}$ units in solution, but not between the hydride signals of these species (see the Supporting Information). This indicates that a rather fast exchange occurs primarily between the peripheral isobutyl residues of the cation $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ and those of free $HAl^iBu_2$, while the $\{Zr(\mu\text{-}H)_3Al_2\}$ core of the zirconocene hydride cation remains inert on this time scale.

Yellow, thermally unstable crystals of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+[B(C_6F_5)_4]^-$ were obtained from toluene at −40 °C. An X-ray crystallographic determination, conducted at −100 °C (see the Supporting Information), revealed a structure in the noncentrosymmetric space group $P2_12_12_1$, with two $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ cations of opposite chirality and two $[B(C_6F_5)_4]^-$ anions per asymmetric unit along with a molecule of toluene. Structural refinement resulted in closely similar geometries for both of the cations, one of which is shown in Figure 3.

While the quality of the structure suffers from considerable disorder with regard to the orientation of the Al-bound isobutyl groups, the geometry of the $\{Zr(\mu\text{-}H)_3Al_2\}$ core, with hydride positions located in the difference Fourier map, clearly supports the structural assignments derived from the NMR data discussed above. The coordination of three adjacent hydride ligands to the metal center of this cation represents a structural motif, which is found in numerous neutral and cationic, mononuclear, and dinuclear zirconocene hydride complexes,[12] as well as in neutral, di-, and multinuclear hydrides of the lanthanide metals.[13] None of these classes provides any precedent, however, for the particular structure represented in Figure 3.

**2. Alkylaluminum-Complexed Hydride Cations Derived from Other Metallocene Complexes.** In addition to $(SBI)ZrCl_2$, we have studied several other zirconocene dichlorides (Scheme 4) with regard to their reactions with excess $HAl^iBu_2$ and 1 equiv of $[Ph_3C][B(C_6F_5)_4]$. As with $(SBI)ZrCl_2$, we observe in each case mutually coupled doublet and triplet high-field signals with intensities of 2H and 1H per zirconocene unit, respectively (Table 1). In some cases, the signals of complex-bound isobutyl *CH*, *CH*$_2$, and/or *CH*$_3$ groups are sufficiently apart from their uncomplexed counterparts to allow their separate integration, which supports the presence of two $Al^iBu_2$ moieties per zirconocene unit. There is no reasonable doubt, therefore, that each of the zirconocene dichlorides shown in Scheme 4 forms a cationic hydride complex containing two $Al^iBu_2$ units, in complete analogy to $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$.

**Scheme 4**




While all the zirconocene complexes studied here, ring-bridged and unbridged alike, uniformly give the previously unreported type of alkylaluminum-complexed zirconocene hydride cation described above, the relative positions of the two Zr-hydride signals differ among the hydride cations listed in Table 1. For all of the complexes with a single-atom bridge, the doublet of the lateral Zr−$H_2$ group appears at higher fields than the central Zr−$H$ triplet, whereas all of the hydride cations without interannular

**Table 1. $^1$H NMR Data of $\{^i Bu_2Al\}$-Complexed Zirconocene 'Hydride Cations ($[(F_5C_6)_4B]^-$ Salts in Benzene-$d_6$ Solution, 25 °C, $\delta$ in ppm, 300 MHz)**

| complex[a] | $ZrH_3$ | $Al-CH_2CH(CH_3)_2$ | ligand[b] |
|---|---|---|---|
| *rac*-$Me_2Si(indenyl)_2Zr$ = (SBI)Zr[24] | −2.25 (d, 2H, 8 Hz) | 0.26 (dd, 4H, 14, 7 Hz)[c] | 5.57 (d, 2H, 3 Hz) |
| | 0.34 (t, 1H, 8 Hz) | 0.15 (dd, 4H, 14, 7 Hz)[c] | 6.41 (d, 2H, 3 Hz) |
| | | 0.94 (t, 24H, 7 Hz)[d] | 0.65 (s, $(CH_3)_2Si$) |
| | | | 1.77(n, 4H, 7 Hz) |
| *rac*-$C_2H_4(indenyl)_2Zr$[25] | −1.72 (d, 2H, 8 Hz) | 0.19 (dd, 7, 3 Hz)[e] | 5.56 (d, 2H, 3 Hz) |
| | −0.29 (t, 1H, 8 Hz) | 0.93[d,e] | 5.74 (d, 2H, 3 Hz) |
| | | 1.74 (n, 4H, 7 Hz) | |
| *rac*-$C_2H_4$(4,5,6,7-tetrahydroindenyl)$_2$Zr[25] | −1.08 (t, 1H, 7 Hz) | 0.35 (m)[e] | 5.26 (d, 2H, 3 Hz) |
| | −0.46 (d, 2H, 6 Hz) | 0.96 (dt, 9, 5 Hz)[e] | 5.81 (d, 2H, 3 Hz) |
| | | 1.88 (n, 7 Hz)[e] | |
| *rac*-$Me_2C(indenyl)_2Zr$[26] | −1.72 (d, 2H, 7 Hz) | 0.25 (qd, 8H, 15, 7, 7 Hz) | 5.33 (t, 2H, 3 Hz) |
| | −0.82[f] | 0.91 (dd, 24H, 6, 4 Hz) | 6.49 (d, 2H, 3 Hz) |
| | | 1.76 (m, 4H) | 1.69 (s, $(CH_3)_2C$) |
| $Me_4C_2(C_5H_4)_2Zr$[27] | −1.60 (t, 1H, 7 Hz) | 0.36 (d, 8H 7 Hz) | 5.73 (pt, 4H, 3 Hz) |
| | −1.37 (d, 2H, 7 Hz) | 0.95 (d, 24H, 7 Hz) | 5.95 (pt, 4H, 3 Hz) |
| | | 1.86 (m, 4H, 7 Hz) | 0.88 (s, $(CH_3)_4C_2$) |
| $Me_2Si(C_5H_4)_2Zr$[28] | −2.04 (d, 2H, 9 Hz) | 0.34 (d, 7 Hz) | 5.24 (br, 4H) |
| | −1.27 (t, 1H, 8 Hz) | 0.86 (m) | 6.22 (br, 4H) |
| | | 1.82 (m) | 0.17 (s, $(CH_3)_2Si$) |
| $(Me_2Si)_2(C_5H_3)_2Zr$[29] | −2.03 (d, 2H, 8 Hz) | 0.34 (dd, 8H, 28, 7 Hz) | 5.94 (t, 2H, 2.7 Hz) |
| | −1.04 (t/s, 1H, 8 Hz) | 0.92 (m, 36H) | 6.49 (d, 4H, 2.7 Hz) |
| | | 1.82 (m, 4H) | −0.08 (s, $(CH_3)_2Si$) |
| $(C_5H_5)_2Zr$[30] | −2.39 (t, 1H, 8 Hz) | 0.28 (d, 8H, 7 Hz) | 5.59 (s, 10H) |
| | −2.27 (d, 2H, 8 Hz) | 0.92 (d, 24H, 7 Hz) | |
| | | 1.81 (n, 4H, 7 Hz) | |
| $(^nBuC_5H_4)_2Zr$[30] | −1.97 (t, 1H, 8 Hz) | 0.40 (d, 7 Hz) [e] | 5.67 (d, 4H, 2 Hz) |
| | −1.61 (d, 2H, 8 Hz) | 0.96 (d, 7 Hz)[e] | 5.73 (d, 4H, 3 Hz) |
| | | 1.87 (m)[e] | |
| $(Me_3SiC_5H_4)_2Zr$[31] | −2.30 (br, 1H) | 0.46[e] | 6.01 (br, 4H) |
| | −1.84 (d, 2H, 9 Hz) | 0.95 (d, 6 Hz)[e] | 6.11 (br, 4H) |
| | | 1.86 (m, 4H) | |
| $(1,2\text{-}Me_2C_5H_3)_2Zr$[32] | −1.79 (br, 1H) | 0.43 (d, 7 Hz)[e] | 5.29 (d, 4H, 3 Hz) |
| | −1.42 (d, 7 Hz, 2H) | 0.97 (d, 6 Hz)[e] | 5.86 (t, 2H, 3 Hz) |
| | | 1.88 (m, 7 Hz)[e] | 1.74 (s, 4Cp−Me) |
| $(C_5H_5)_2Hf$[30] | −2.27 (t, 6 Hz, 1H) | 0.26 (d, 12H, 7 Hz) | 5.48 (s, 10H) |
| | −1.40 (d, 6 Hz, 2H) | 0.92 (d, 7 Hz)[e] | |
| | | 1.80 (m, 4H, 7 Hz) | |

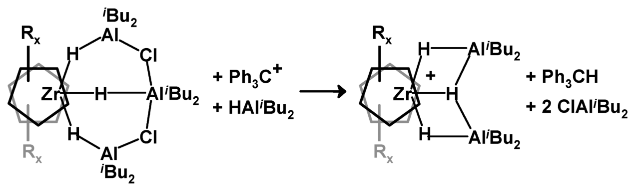
[a] With references to the preparation of the respective zirconocene dichloride starting material. [b] $C_5-H$ unless otherwise noted. [c] Resolved diastereotopic splitting by 0.11 ppm. [d] Diasterotopic splitting not resolved. [e] Not sufficiently resolved for integration. [f] Peak obscured by other signals, chemical shift determined from gCOSY.

bridge give rise to a $Zr-H_2$ doublet at lower field than their $Zr-H$ triplet.[14] This observation sets the unbridged hydride cations apart from their neutral trihydride precursors, for all of which the $Zr-H_2$ doublet had been found at higher fields than the $Zr-H$ triplet.[4] This signal crossover upon conversion of each of the unbridged neutral trihydride precursors to its cationic counterpart appears to be connected with the net loss of the centrally positioned $[Cl_2Al^iBu_2]^-$ unit in the course of this reaction (Scheme 5).

Attempts to isolate the ion pairs described above yielded in general only oily materials. For the $[B(C_6F_5)_4]^-$ salt of the doubly Cp-bridged cation $[(Me_2Si)_2(C_5H_3)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$, however, a few colorless crystals were obtained from benzene-$d_6$ solution. A crystallographic determination yielded the structure shown in Figure 4. Once again, the positions of the hydrides were obtained from the difference map and are entirely in accord with the NMR assignments given above. This structure is of better quality than that of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ shown in Figure 3. The heavy-atom geometry of its $\{Zr(\mu\text{-}H)_3(Al^iBu_2)_2\}$ core is closely similar to that of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$, thus attesting to the unexpectedly pervasive tendency of zirconocene-based reaction systems to form alkylaluminum-complexed hydride cations of this kind.

Attempts to make the corresponding titanocene derivative failed; addition of $HAl^iBu_2$ to $Cp_2TiCl_2$ resulted in $H_2$ evolution and formation of a lavender solution, which does not exhibit any

### Scheme 5




$C_5H$ resonances, thus indicating the presence of a Ti(III) species. Reaction of $Cp_2HfCl_2$ with $HAl^iBu_2$ and $[Ph_3C][B(C_6F_5)_4]$, however, gave the cation $[Cp_2Hf(\mu\text{-}H)_3(Al^iBu_2)_2]^+$, as shown by an $^1H$ NMR spectrum closely resembling that of its unbridged zirconocene hydride congeners (see Table 1). For the product of a reaction of $(SBI)HfCl_2$ with $Al^iBu_3$ and $[Ph_3C][B(C_6F_5)_4]$, NMR spectral features have been described,[9d] which resemble those described above for its Zr analogue; the product of this reaction might thus also be a cation of the type described here.

**3. Interconversion Reactions of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ with Other Cationic Complexes.** The cationic complex $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ described above appears to reversibly interconvert with other zirconocene cations, some of which have been observed in zirconocene-based precatalyst systems. A first case in point concerns the blue-green coloration observed when $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ is formed according to Scheme 3. That this coloration might be due to some side or sequential reaction product, rather than to the hydride cation itself, is suggested by the observation that the intensity of this coloration depends on the reaction conditions.

When $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ is prepared, as described above in the presence of 5 equiv of $HAl^iBu_2$, the reaction mixture gives rise to an absorption band at 614 nm. Absorbance at this wavelength increases, when only a stoichiometric 4 equiv of $HAl^iBu_2$ is used and even more so by use of substoichiometric amounts of $HAl^iBu_2$ (Figure 5). In the presence of 10 equiv of $HAl^iBu_2$, on the other hand, any absorption at 614 nm is minimal. When $ClAl^iBu_2$ is added to such a solution, absorption at 614 nm is retained even in the presence of 10 equiv of $HAl^iBu_2$.

Upon addition of $ClAl^iBu_2$ to a solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$, we observe a new set of signals by $^1H$ NMR. These signals are particularly clear-cut when only 1 equiv of $HAl^iBu_2$ and 2 equiv $ClAl^iBu_2$ are used in the generation of the cation. In these spectra, signals due to complex-bound {Al-$^i$Bu} groups, at 1.88 and at 0.27 ppm, are cleanly separated from signals due to other {$Al^iBu$} species in solution. Comparison of their integrals with those of the zirconocene ligand signals at 6.26 and 5.18 ppm (d, $J$ = 3 Hz, $C_5H$) clearly indicates the presence of only one {$Al^iBu_2$} group per zirconocene unit (see the Supporting Information). This stoichiometry and the reversible appearance and disappearance of these signals upon addition of $ClAl^iBu_2$ or $HAl^iBu_2$, respectively, led us to attribute this set of signals to a $ClAl^iBu_2$-complexed zirconocene chloride cation, $[(SBI)Zr(\mu\text{-}Cl)_2Al^iBu_2]^+$, formed from $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ in an equilibrium according to Scheme 6.[15] Apparently, two Zr—Cl—Al bridges are sufficient to satisfy the coordination requirements of the Zr center in such a complex in distinction to Zr—H—Al bridges, three of which appear to be required to complete the coordination of the Zr center, most likely due to the more electron-deficient nature of Zr—H—Al as compared to Zr—Cl—Al bridges.

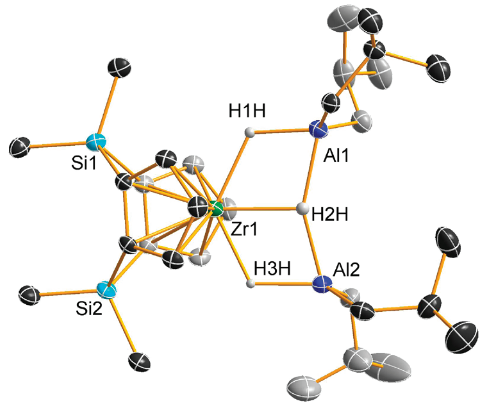



**Figure 4.** Structure of the cation $[(Me_2Si)_2(C_5H_3)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ in crystals of its $[B(C_6F_5)_4]^-$ salt (thermal ellipsoids drawn at 50% probability, hydride positions taken from the difference Fourier map; other H atoms omitted).

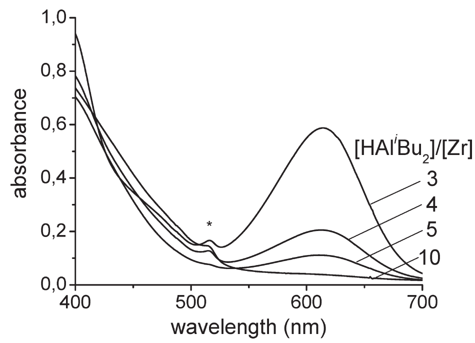
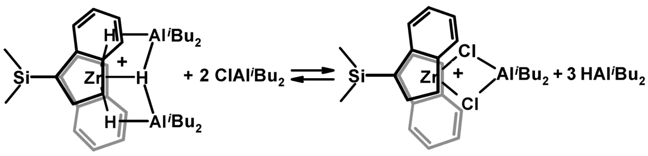



**Figure 5.** UV/vis absorption spectra of toluene solutions containing 0.56 mM $(SBI)ZrCl_2$ in the presence of 3, 4, 5, or 10 equiv of $HAl^iBu_2$, after addition of 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ (path length 1 cm; *artifact due to change of gratings).

### Scheme 6




A related question would concern the degree to which {$CH_3Al$} instead of {ClAl} species could participate in similar equilibria. Addition of relatively small amounts of $AlMe_3$ to a solution of the cation $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ in benzene-$d_6$ causes the appearance of additional signals in the vicinity of those of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$. When only $^1/_3$ equiv of $AlMe_3$ per Zr is added (i.e., [AlMe]/[Zr] = 1), we observe next to the doublet at −2.25 ppm a pair of doublets centered at −2.05 ppm (Figure 6B). This signal can be assigned to a cation similar to $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$, in which one of the Al-bound isobutyl groups is replaced by a methyl group (Scheme 7),[16] such that the complex's lateral hydride positions are rendered inequivalent.[17]

Addition of $AlMe_3$ at somewhat higher $[AlMe_3]/[Zr]$ ratios causes a coalescence of these signals, first to two broad features

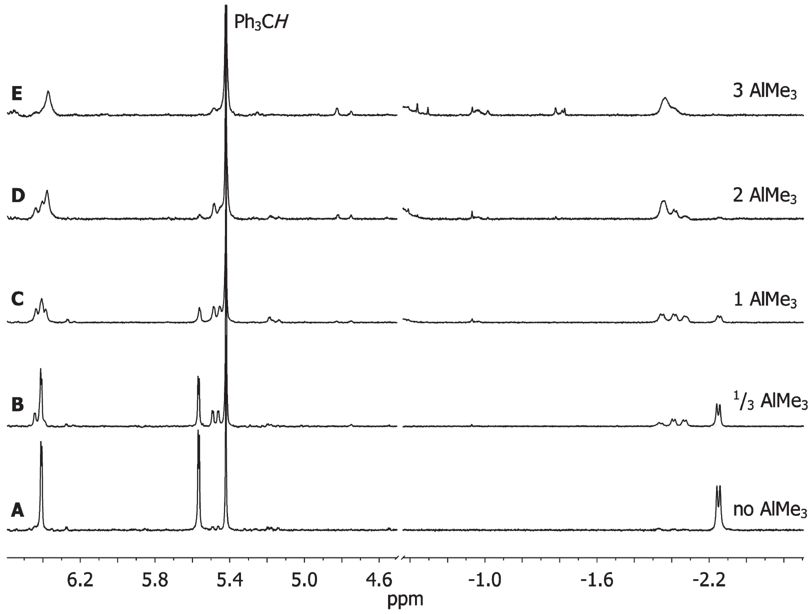
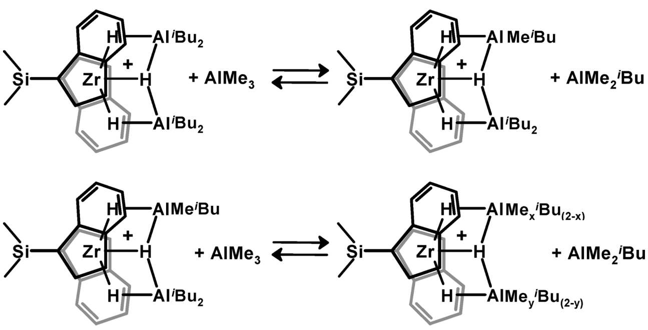



**Figure 6.** $^1$H NMR spectra of a 3 mM solution of $[(\mathrm{SBI})\mathrm{Zr}(\mu\text{-H})_3(\mathrm{Al}^i\mathrm{Bu}_2)_2]^+$ in benzene-$d_6$, obtained by reaction of (SBI)ZrCl$_2$ with 5 equiv of HAl$^i$Bu$_2$ and 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$], before (A) and after addition of $^1/_3$ (B), 1 (C), 2 (D), or 3 (E) equiv of AlMe$_3$ relative to Zr.

Scheme 7




centered at −1.95 ppm and then to one very broad signal ($\nu_{1/2}$ = 29 Hz), likewise centered at −1.95 ppm (Figure 6C−E). These observations are undoubtedly due to the formation of increasing fractions of related cations, in which isobutyl residues at both Al centers are exchanged by Me groups (Scheme 7). The broadening of the Zr-hydride signals of these mixed-alkyl aluminum species, henceforth referred to as $[(\mathrm{SBI})\mathrm{Zr}(\mu\text{-H})_3(\mathrm{AlR}_2)_2]^+$, is probably due to the statistical nature of this exchange.[16]

A purely {AlMe$_2$}-complexed cation, $[(\mathrm{SBI})\mathrm{Zr}(\mu\text{-H})_3(\mathrm{AlMe}_2)_2]^+$, is accessible by reaction of (SBI)ZrCl$_2$ with 1 equiv of [Ph$_3$C]-[B(C$_6$F$_5$)$_4$] in the presence of excess HAlMe$_2$. Its hydride signals (−0.17 and −2.10 ppm) are found close to those seen in Figure 5E and are sharper than these, in accord with the assignment of the latter to Me-rich mixed-alkyl aluminum complexed cations $[(\mathrm{SBI})\mathrm{Zr}(\mu\text{-H})_3(\mathrm{AlR}_2)_2]^+$. $^1$H NMR data for this and several other {Me$_2$Al}-complexed zirconocene hydride cations (Table 2) reveal shifts of the respective hydride signals, which greatly vary without apparent rationale when compared to those of the respective {$^i$Bu$_2$Al}-complexed cations. Sensitivity of the Zr−H signals to the nature of the Al-bound R groups in cations of the type $[(\mathrm{SBI})\mathrm{Zr}(\mu\text{-H})_3(\mathrm{AlR}_2)_2]^+$ is apparent also from the observation that addition of an aluminum alkyl with longer alkyl chains, such as trioctylaluminum, causes a strong broadening of the hydride signal and its shift, in this case to higher fields (−2.4 ppm).[18] (SBI)ZrCl$_2$-based precatalysts activated by excess methylalumoxane (MAO), to which HAl$^i$Bu$_2$ has been added, have been reported to give rise to a set of signals, including a broad Zr−*H*$_2$ resonance at ca. −2 ppm, which were assigned at that time to species of the generic type (SBI)ZrH$_2$·2AlR$_2$X.[9c] These signals are now seen to be identical to those assigned above to mostly dimethylaluminum-complexed hydride cations $[(\mathrm{SBI})\mathrm{Zr}(\mu\text{-H})_3(\mathrm{AlR}_2)_2]^+$ (cf., Figure 6E).[19] We can thus conclude that the zirconocene hydride species produced in MAO-activated reaction

**Table 2. $^1$H NMR Data of {Me$_2$Al}-Complexed Zirconocene Hydride Cations ([(F$_5$C$_6$)$_4$B]$^-$ Salts in Benzene-$d_6$ Solution, 25 °C, $\delta$ in ppm, 300 MHz)[a]**

| complex | Zr*H*$_3$ | ligand[b] |
|---|---|---|
| *rac*-Me$_2$Si(indenyl)$_2$ Zr = (SBI)Zr | −2.06 (d, 2H, 4 Hz) | 5.40 (d, 2H, 2.7 Hz) |
| | −0.17 (br, 1H) | 6.29 (d, 2H, 2 Hz) |
| | | 0.62 (s, (C*H*$_3$)$_2$Si) |
| *rac*-C$_2$H$_4$(indenyl)$_2$Zr | −1.45 (d, 2H, 9 Hz) | 5.49 (d, 2H, 3 Hz) |
| | −1.00 (br, 1H) | 5.60 (d, 2H, 2 Hz) |
| *rac*-C$_2$H$_4$(4,5,6,7-tetrahydroindenyl)$_2$Zr | −0.94 (br, 2H)[c] | 5.70 (d, 2H, 3 Hz) |
| | | 5.15 (d, 2H, 3 Hz) |
| Me$_2$Si(C$_5$H$_4$)$_2$Zr | −2.93 (d, 2H, 7 Hz) | 5.13 (pt, 4H, 2 Hz) |
| | −1.61 (t, 1H, 10 Hz) | 5.91 (pt, 4H, 2 Hz) |
| | | 0.21 (s, (C*H*$_3$)$_2$Si) |

[a] Signals of complex-bound {Al(CH$_3$)$_2$} groups not resolved from those of free HAl(CH$_3$)$_2$. [b] C$_5$−*H* unless otherwise noted. [c] Central hydride resonance not resolved, probably due to overlap with Al(CH$_3$)$_2$ signals.

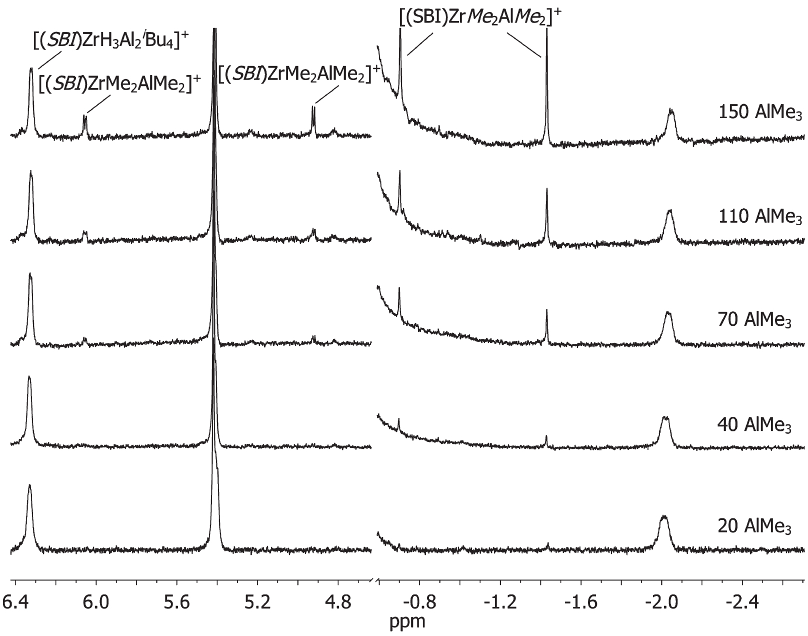
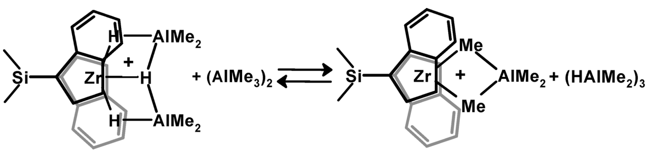



**Figure 7.** $^1$H NMR spectra of a 3 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ with 3.5 equiv of free $HAl^iBu_2$ in benzene-$d_6$, upon addition of 20−150 equiv of $AlMe_3$ relative to Zr.

**Scheme 8**




systems upon addition of $HAl^iBu_2$ are likewise cations of the type $[(SBI)Zr(\mu\text{-}H)_3(AlR_2)_2]^+$.[20]

Upon addition of $AlMe_3$ in yet higher concentrations to solutions containing cations of the type $[(SBI)Zr(\mu\text{-}H)_3(AlR_2)_2]^+$ we observe, in addition to the signals due to these cations, another set of signals comprising characteristic $Zr(\mu\text{-}Me)_2Al$ and $AlMe_2$ signals at −1.43 and −0.71 ppm (Figure 7), which indicate formation of cations of the type $[(SBI)Zr(\mu\text{-}Me)_2AlR_2]^+$.[21] These cations thus appear to arise from the alkylaluminum-complexed zirconocene hydride cations, $[(SBI)Zr(\mu\text{-}H)_3(AlR_2)_2]^+$, by an equilibrium reaction of the type represented in Scheme 8.[19]

On the basis of the $^1$H NMR spectra of reaction systems containing $HAl^iBu_2$ in an initial ratio of $[HAl^iBu_2]/[Zr]_{tot}$ = 7.5 and $AlMe_3$ at ratios of $AlMe_3$ to Zr of 70 to 110:1, we estimate an equilibrium constant on the order of $10^{-2}$ for the reaction shown in Scheme 8 (see the Supporting Information).[22] In solutions containing $HAl^iBu_2$ and $AlMe_3$ in comparable concentrations, the hydride cation $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ would thus be by far the dominant species.

## CONCLUSIONS

The studies described above have brought to light a hitherto unreported family of zirconocene hydride cations stabilized by adduct formation with two $HAlR_2$ units, so as to attain the $ZrH_3$ coordination geometry observed before for related neutral zirconocene hydride species. These cationic hydride complexes are subject to ligand exchange equilibria in the presence of chloroaluminum or methylaluminum compounds. In the first instance, the $\{Zr(\mu\text{-}H)_3(AlR_2)_2\}^+$ arrangement is replaced by the previously unreported doubly Cl-bridged entity $\{Zr(\mu\text{-}Cl)_2AlR_2\}^+$, while exposure to excess $MeAlR_2$ gives rise to species containing a $\{Zr(\mu\text{-}Me)_2AlR_2\}^+$ geometry, which have previously been observed in zirconocene-based olefin-polymerization catalysts.[21]

In equilibria of this kind, hydride-bridged cations are strongly preferred over dimethyl-bridged zirconocene cations. This indicates that the former are likely to arise in typical MAO-activated zirconocene-based olefin-polymerization catalysts, whenever these acquire any hydride units.

## ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Full experimental data; selected distances and angles for the cations. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for crystals containing the $[B(C_6F_5)_4]^-$ salts of the cations $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ (SMB10) and $[(Me_2Si)_2(C_5H_3)_2\text{-}Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ (SMB04) have been deposited with the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; copies can be obtained on request, free of charge, by quoting the publication reference and deposition numbers 778255 and 776421, respectively.

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(3) To make reaction stoichiometries more clearly apparent, diisobutylaluminum hydride (as well as all other alkylaluminum species mentioned) is written as a monomer throughout most of this Article (see, however, ref 22), 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.

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(14) For complexes containing an interannular ethanediyl bridge, no uniform ordering of their doublet and triplet signals is apparent.

(15) The same species, $[(SBI)Zr(\mu\text{-}Cl)_2Al^iBu_2]^+$, was formed when $(SBI)ZrCl_2$ was allowed to react with $Et_3SiH$, $[Ph_3C][B(C_6F_5)_4]$, and $ClAl^iBu_2$ in ratios of 1:150:1:1. Reaction of $(SBI)ZrCl_2$ with $Et_3SiH$ and $[Ph_3C][B(C_6F_5)_4]$, without any added chloroaluminum reagent, gave an insoluble green solid, presumably the $[B(C_6F_5)_4]^-$ salt of the dimeric dication $[\{(SBI)Zr\}_2(\mu\text{-}Cl)_2]^{2+}$, which has previously been structurally characterized: 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. Reaction of this solid with 5 equiv of $ClAl^iBu_2$ in benzene-$d_6$ gave a dark blue solution, which displayed the $^1$H NMR signals of $[(SBI)Zr(\mu\text{-}Cl)_2Al^iBu_2]^+$ (Supporting Information), thus providing further support for the identity of this species. A reaction of $(SBI)ZrMe_2$ with $[Ph_3C][B(C_6F_5)_4]$, $AlMe_3$, and $AlCl_3$ in ratios of 1:1:6:1 gave the related cation $[(SBI)Zr(\mu\text{-}Cl)_2AlMe_2]^+$, the ligand $C_5H$ signals of which appear at 6.35 and 5.29 ppm, that is, at somewhat lower fields than those of $[(SBI)Zr(\mu\text{-}Cl)_2Al^iBu_2]^+$ (6.26 and 5.18 ppm).

(16) Exchange between terminal Me groups of the cation $[(SBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$ and terminal isobutyl groups of $Al_2(\mu\text{-}Me)_2{}^iBu_4$ has been shown to occur to an extent close to statistical expectation: Babushkin, D. E.; Brintzinger, H. H. *Chem.-Eur. J.* **2007**, *13*, 5294.

(17) Reaction of the dimethyl complex $(SBI)ZrMe_2$ with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$, so as to yield the ion pair $[(SBI)ZrMe^+\cdots(F_5C_6)_4B^-]$, and subsequently with 4 equiv of $HAl^iBu_2$, gives rise to the same pair of doublets at −2.05 ppm, undoubtedly due to the presence of one {MeAl} unit per zirconocene in this reaction system.

(18) If $AlMe_3$ is added to a reaction system containing trioctyl aluminum, Zr−H signals due to $\{Al(octyl)_2\}$- and $\{AlMe_2\}$-complexed hydride cations appear with comparable intensities.

(19) In the presence of the large (40−110-fold) excess of added $AlMe_3$, both cations can be considered to contain mostly Me groups in their terminal Al-alkyl positions.

(20) This assignment is supported by the observation of a gCOSY cross-peak in MAO-activated $(SBI)ZrCl_2$ solution containing $HAl^iBu_2$, connecting the broad $ZrH_2$ signal at −2.01 ppm to another Zr$H$ resonance at 0.60 ppm, largely hidden under the low-field tail of the MAO signal.

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(22) Integration of the Al−$H$, Al−$CH_3$, and $(CH_3)_2$Si signals allows one to determine the equilibrium concentrations of the four species involved in this reaction. In accord with Scheme 8, the dimensionless equilibrium constant $K_{eq}$ is calculated using the expression:

$$K_{eq} = \frac{[(SBI)Zr(\mu\text{-}Me)_2AlMe_2]^+ \cdot [(HAlMe_2)_3]}{[(SBI)Zr(\mu\text{-}H)_3(AlMe_2)_2]^+ \cdot [(AlMe_3)_2]}$$

(See the Supporting Information.) Quantification of this equilibrium requires that $HAlMe_2$ and $AlMe_3$ are treated, according to their actual nuclearities, as trimers and dimers, respectively (cf., ref 3). Therefore, this notation is used here, in deviation from the rest of this Article.

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