

# *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sup>+</sup>: An Alkyl Zirconocenium Cation Stabilized by Steric Shielding against Interaction with Ancillary Ligands

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The sterically shielded cation *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sup>+</sup>, generated by reaction of *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sub>2</sub> with methylalumoxane (MAO) or with dimethylanilinium or trityl perfluorotetraphenylborate, differs from other, more open zirconocene methyl cations in that it does not form the symmetric AlMe<sub>3</sub> adduct *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Zr( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub><sup>+</sup>. Instead, the unsymmetric ternary adduct *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe( $\mu$ -Me)AlMe<sub>3</sub>-NMe<sub>2</sub>Ph<sup>+</sup> is formed in the presence of dimethylaniline and trimethylaluminum. UV/vis and <sup>1</sup>H NMR characteristics of hydrocarbon solutions containing *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sup>+</sup>⋯B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> or *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sup>+</sup>⋯MAOMe<sup>-</sup> indicate that cation–anion association in these ion pairs is unusually weak.

## Introduction

Mechanistic considerations on olefin polymerization catalysis by methylalumoxane (MAO)-activated zirconocene dichlorides, Cp<sup>x</sup><sub>2</sub>ZrCl<sub>2</sub>, with Cp<sup>x</sup> being a variety of substituted, annelated, and/or bridged cyclopentadienyl ligands,<sup>1</sup> ascribe a central role to an alkyl zirconocenium cation of the type Cp<sup>x</sup><sub>2</sub>Zr–R<sup>+</sup>. By analogy to carbenium or, more significantly, to silylenium cations,<sup>2</sup> one might expect, however, that “free” species of this kind are of such high energy that their formation will generally be circumvented.<sup>3</sup> Generation and characterization of such a “free” alkyl zirconocenium cation might be facilitated if the cationic metal center is efficiently shielded from otherwise prevalent stabilizing interactions with ancillary ligands or counteranions.

Among the many substituted, annelated, and/or bridged zirconocene complexes made available for studies on their catalytic properties,<sup>1</sup> one of the most sterically shielded yet easily accessible representatives is the di-*tert*-butyl-substituted complex *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub>.<sup>4,5</sup> In a previous communication, we have reported that interactions of the anion B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>

with the methyl zirconocenium cation *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sup>+</sup>, derived from this zirconocene complex, are weaker than those with other, more open methyl zirconocenium cations, as indicated by an exceptionally high rate of symmetrization.<sup>3a</sup> Here, we wish to report on further properties of this highly shielded cation.

## Results and Discussion

To characterize the nature of cationic species formed from the highly shielded zirconocene complexes *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrX<sub>2</sub> (**1**, X = Cl; **2**, X = Me), activation reactions with various cation-forming reagents were investigated by means of UV/vis and NMR methods (see Experimental Section).

Upon addition of MAO to a toluene solution of **1**, the UV/vis absorption bands at 318 and 384 nm are first shifted to shorter wavelengths (Figure 1, left), with maximum absorption increases at ca. 310 and 352 nm. As with other zirconocene systems studied,<sup>8</sup> this hypsochromic shift is attributable to formation of a monomethyl species, *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Zr(Cl)Me, due to Cl vs Me exchange with the AlMe<sub>3</sub> content of

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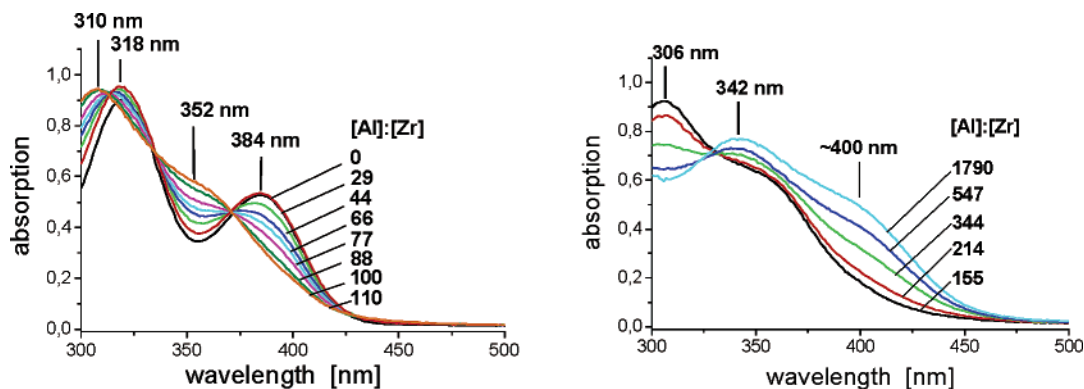
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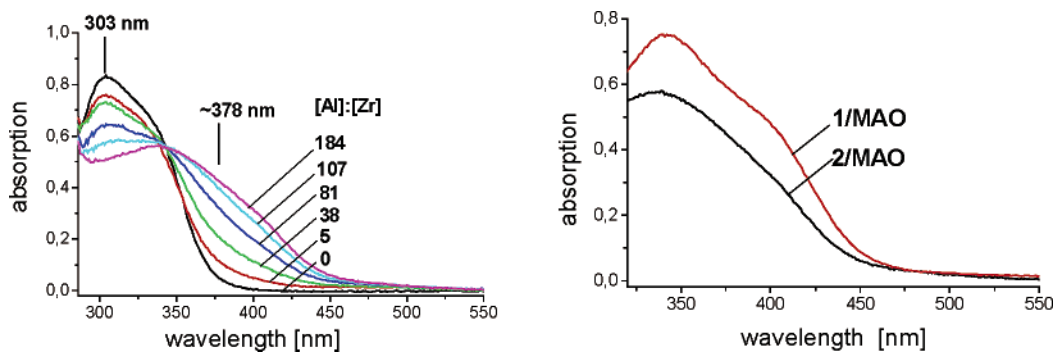
(5) Similar degrees of shielding might be expected for other *tert*-butyl-substituted zirconocene complexes such as *rac*-Me<sub>2</sub>C(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub><sup>6</sup> and *rac*-R<sub>2</sub>C(3-*t*-Bu-Ind)<sub>2</sub>ZrCl<sub>2</sub> (R = H, Me).<sup>7</sup>

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**Figure 1.** Successive reactions of *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> (**1**) with increasing excesses of MAO.



**Figure 2.** Reaction of *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sub>2</sub> (**2**) with increasing excesses of MAO (left) and final absorption spectra for the systems **1**/MAO ([Al]:[Zr] ≈ 1800) and **2**/MAO ([Al]:[Zr] ≈ 180) (right).

MAO, which occurs without any side or consecutive reactions up to a ratio of [Al]:[Zr] = 110, as indicated by isosbestic points at 313, 333, and 371 nm. At higher ratios of [Al] to [Zr], 110–155, a transition range without isosbestic points indicates that methyl transfer is going to completion together with the onset of a second reaction step.

Further additions of MAO then cause a bathochromic shift with maximal absorption increase at ca. 400 nm. In the range [Al]:[Zr] = 155–1800, this second reaction step appears to proceed again without any side or consecutive reactions, as documented by an isosbestic point at 331 nm (Figure 1, right). At higher [Al]:[Zr] ratios, no further spectral changes are apparent.

These observations set the reaction system **1**/MAO apart from all other MAO-activated zirconocene systems studied so far: in all other cases, increasing MAO additions had been found to cause two consecutive bathochromic shifts,<sup>8,9</sup> associated with the formation first of contact ion pairs of the type Cp<sup>x</sup><sub>2</sub>ZrMe<sup>+</sup>⋯MAOX<sup>-</sup> (type **IV**,<sup>10</sup> with X = Me, Cl) and then of AlMe<sub>3</sub>-containing, heterobinuclear cations in outer-sphere association with MAO-derived anions, [Cp<sup>x</sup><sub>2</sub>Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>MAOX<sup>-</sup> (type **III**).<sup>10,11</sup> In the present case, only one of these cationic species is formed. The size of the

bathochromic shift of Δλ ~50 nm suggests, by analogy to numerous related reaction systems studied before,<sup>8,9</sup> that only the contact ion pair *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sup>+</sup>⋯MAOX<sup>-</sup> is formed in the reaction system **1**/MAO. The AlMe<sub>3</sub> adduct [*rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>MAOX<sup>-</sup> appears to be inaccessible, probably for steric reasons.

To corroborate this finding, we have also investigated by UV/vis spectroscopy the reaction of MAO with the dimethyl complex *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sub>2</sub> (**2**). Addition of MAO to a toluene solution of **2** causes a bathochromic shift of the lowest energy absorption band from 303 nm to higher wavelengths with maximal absorption increase at ca. 380 nm (Figure 2, left), which is completed at a ratio of [Al]:[Zr] ≈ 180. As for the system **1**/MAO, an isosbestic point at 343 nm and the absence of any further changes at higher [Al]:[Zr] ratios indicate again that only a single reaction takes place.

Direct comparison of the final spectra for **1**/MAO and **2**/MAO shows practically identical absorption maxima at ca. 380 nm and also similar shapes of the absorption bands (Figure 2, right). The nature of X = Cl, Me in *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sup>+</sup>⋯MAOX<sup>-</sup>, according to its origin from either **1** or **2**, thus appears to have little influence on its lowest energy UV/vis absorption band. It is remarkable, however, that complete abstraction of Cl<sup>-</sup> from **1** requires about 10 times higher MAO concentrations than abstraction of Me<sup>-</sup> from **2**.

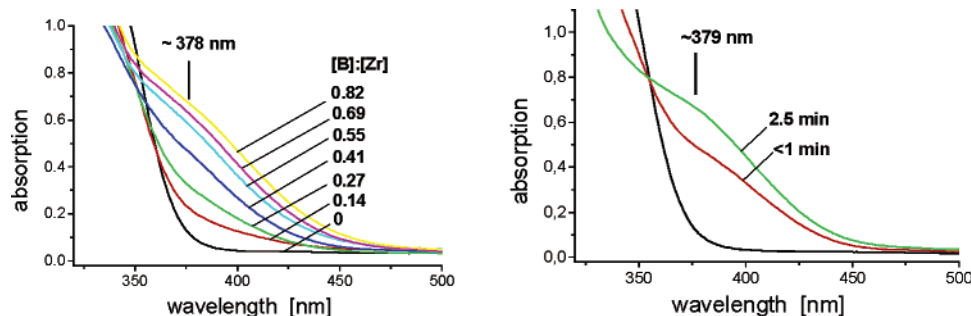
Closely related species as by reaction with MAO are generally formed by reaction of a zirconocene dimethyl complex with 1 equiv of dimethylanilinium perfluorotetraphenylborate.<sup>12,13</sup> As expected, stepwise additions of

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**Figure 3.** Stepwise (left) and immediate addition (right) of 1 equiv of  $\text{PhNMe}_2\text{H}^+(\text{C}_6\text{F}_5)_4\text{B}^-$  to a toluene solution of  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{ZrMe}_2$ .

**Table 1.**  $^1\text{H}$  NMR Signals in Reaction Mixtures of  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{ZrMe}_2$  with ca. 1 Equiv of  $\text{PhNMe}_2\text{H}^+(\text{C}_6\text{F}_5)_4\text{B}^-$  (A), with ca. 1 Equiv of  $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$  (B), and with ca. 1 Equiv of  $\text{PhNMe}_2\text{H}^+(\text{C}_6\text{F}_5)_4\text{B}^-$  and 12 Equiv of  $\text{Al}_2\text{Me}_6$  (C), in  $\text{C}_6\text{D}_6$  at 293 K (250 MHz)<sup>a</sup>

assignt	A			B			C		
	$\vartheta$ (ppm)	$\Delta\nu_{1/2}$ (Hz)		$\vartheta$ (ppm)	$\Delta\nu_{1/2}$ (Hz)		$\vartheta$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	
2-Me-4- <i>t</i> -Bu-C <sub>5</sub> H <sub>2</sub> ( <b>3</b> )	6.00	11	s, <sup>b</sup> 2H	6.01	2.1	d, <sup>c</sup> 2H	6.33	1.8	d, <sup>c</sup> 1H
2-Me-4- <i>t</i> -Bu-C <sub>5</sub> H <sub>2</sub> ( <b>5</b> )	5.09	6	s, <sup>b</sup> 2H	5.09	1.8	d, <sup>c</sup> 2H	5.86	1.8	d, <sup>c</sup> 1H
2-CH <sub>3</sub> -4- <i>t</i> -Bu-C <sub>5</sub> H <sub>2</sub>	1.45	3.3	s, 6H	1.46	1.8	s, 6H	5.19	1.5	d, <sup>c</sup> 1H
2-Me-4-C(CH <sub>3</sub> ) <sub>3</sub> C <sub>5</sub> H <sub>2</sub>	0.85	3.7	s, 18H	0.84	1.8	s, 18H	4.98	1.5	d, <sup>c</sup> 1H
Zr(CH <sub>3</sub> )	0.29	3	s, 3H	0.29	2	s, 3H	0.80	1.9	s, 9H
Zr( $\mu$ -CH <sub>3</sub> )Al(CH <sub>3</sub> ) <sub>2</sub>							0.28	1.7	s, 3H
							-0.67	1.8	s, 3H
							-0.76	1.8	s, 3H
							-1.05	1.9	s, 3H
(CH <sub>3</sub> ) <sub>2</sub> Si	0.04	3.2	s, 6H	0.04	1.5	s 6H	0.10	1.5	s, 3H
							0.25	1.5	s, 3H
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>									
<i>m</i>	7.23	nd	t, 2H				6.96	nd	t, 2H
<i>p</i>	6.79	nd	t, 1H				6.85	nd	t, 1H
<i>o</i>	6.62	nd	d, 2H				6.66	nd	d, 2H
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	2.50 <sup>d</sup>	0.7	s, 6H				2.20	3.0	s, 6H
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CCH <sub>3</sub>				7.00–7.12	nd	m, 15H			
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CCH <sub>3</sub>				2.03	0.6	s, 3H			
CH <sub>4</sub>	0.15	0.4	s				0.15	0.3	s
C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> N–AlMe <sub>3</sub> <sup>e</sup>							2.23 <sup>f</sup>	1.6	s

<sup>a</sup> For  $^1\text{H}$  NMR spectra of reaction systems **B** and **C**, see the Supporting Information. <sup>b</sup> Apparent  $\Delta\nu_{1/2}$  values include unresolved doublet splitting of 2.4 Hz. <sup>c</sup>  $^4J_{\text{HH}} = 2.4$  Hz. <sup>d</sup> Position and  $^1J_{\text{CH}} = 135$  Hz as for  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$  in  $\text{C}_6\text{D}_6$ . <sup>e</sup> Signals of the  $\text{AlMe}_3$  adduct of dimethylaniline indicate the presence of excess borate activator in these solutions.<sup>14</sup> <sup>f</sup> Position and  $^1J_{\text{CH}} = 139.5$  Hz, as for  $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{N}-\text{AlMe}_3$  in  $\text{C}_6\text{D}_6$ .

increasing portions of a 1.5 M toluene solution of  $\text{PhNMe}_2\text{H}^+(\text{C}_6\text{F}_5)_4\text{B}^-$  to a 0.73 mM solution of **2** lead to the appearance of a similar broad shoulder at ca. 378 nm, as observed with MAO, which is completed after addition of 0.82 equiv of this activator reagent (Figure 3, left).<sup>14,15</sup> When 1 equiv of the dimethylanilinium borate is added to a toluene solution of **2** all at once, the same absorption band, as observed for stepwise addition, appears and goes to full height over the course of 2–3 min (Figure 3, right).

The close similarity of the spectrum of the borate-activated species with that obtained by activation with

a large excess of MAO indicates that the same cation is indeed contained in the ion pairs  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{ZrMe}^+\cdots\text{B}(\text{C}_6\text{F}_5)_4^-$  and  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{ZrMe}^+\cdots\text{MAOX}^-$  and that its electronic properties are not significantly affected by its association with different anions.

The nature of ion pairs containing the cation  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{ZrMe}^+$  was further investigated by  $^1\text{H}$  NMR spectroscopy. Upon addition of 1 equiv of the dimethylanilinium borate activator to a toluene solution of complex **2** at 20 °C,<sup>14</sup> the  $^1\text{H}$  NMR spectrum of the resulting reaction mixture shows, in addition to the signals of free methane and dimethylaniline,<sup>16</sup> only one signal set for each substituent group of the zirconocene cation formed, in accord with a complex structure of time-averaged  $C_2$  symmetry (Table 1).<sup>3a</sup>

$^1\text{H}$  NMR signals superimposable to those discussed above are observed when the zirconocenium cation is produced by reaction of complex **2** with trityl perfluoro-

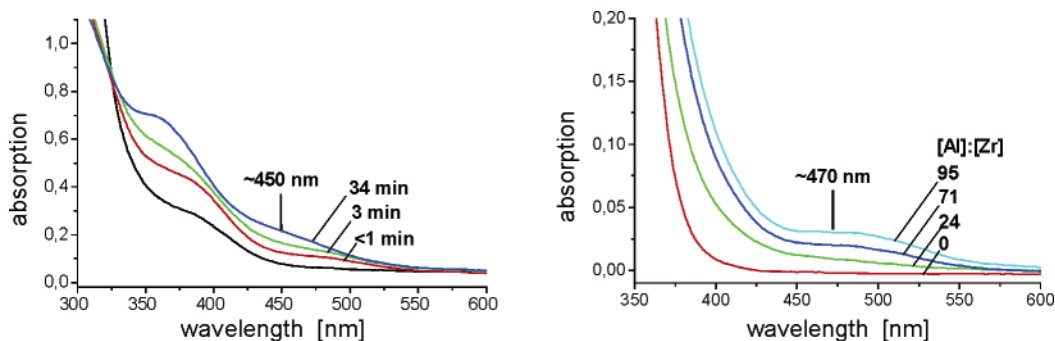
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(14) For activations by dimethylanilinium or trityl perfluorotetraphenylborate, concentrations of complex **2** were chosen to be higher by a factor of 2 than those used in other studies, to minimize possible losses of these highly reactive species by solvent impurities. Nevertheless, some deviation from the expected stoichiometry indicates that a small fraction of Zr–methyl units had been lost and, hence, that the borate activators are generally present in slight excess in these solutions.

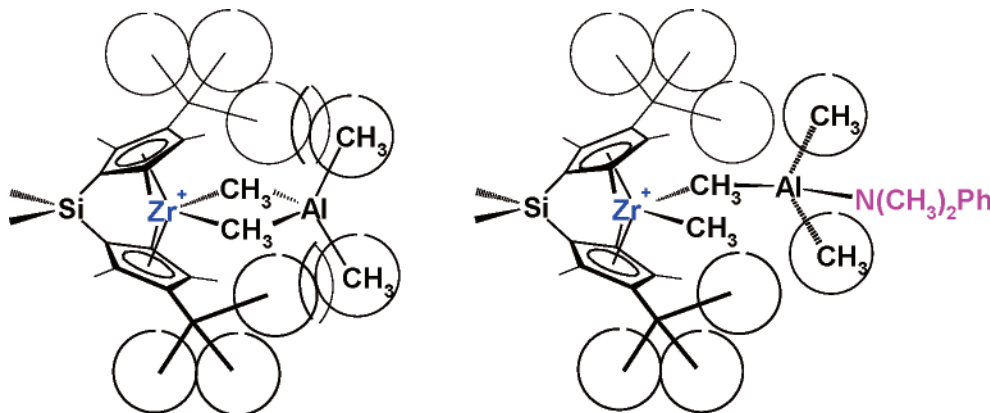
(15) These UV/vis as well as  $^1\text{H}$  NMR data document that homobimetallic intermediates with a Zr–( $\mu$ -Me)–Zr bridge, observed in related reaction systems,<sup>10,11</sup> are not formed in the present system, presumably due to the steric demands of the ligand substituents.

(16) These solutions contain free dimethylaniline, as indicated by a  $\text{CH}_3$  singlet at 2.50 ppm, with  $^1J_{\text{CH}} = 135$  Hz and a line width of only 0.7 Hz, values which are identical with those of dimethylaniline in  $\text{C}_6\text{D}_6$ , while dimethylaniline coordinated to the Zr-bound  $\text{AlMe}_3$  unit gives rise to a singlet at 2.20 ppm with  $^1J_{\text{CH}} = 139.5$  Hz and a line width of 3.0 Hz.



**Figure 4.** Spectral changes caused by addition of 9.2 equiv of trimethylaluminum to a solution containing the products of a reaction of complex **2** with 1.2 equiv of dimethylanilinium perfluorotetraphenylborate (left) and by addition of MAO to a solution containing complex **2** and 42 equiv of dimethylaniline (right).

**Chart 1. Unfavorable Symmetric  $\text{Al}(\text{CH}_3)_3$  Adduct with Two  $\mu\text{-CH}_3$  Bridges (Left) and Dimethylaniline-Stabilized Unsymmetric  $\text{AlMe}_3$  Adduct with Only One  $\mu\text{-CH}_3$  Bridge (Right)**



rotetraphenylborate (Table 1). Cooling of this reaction system in toluene- $d_8$  solution to temperatures below 0 °C causes a slight broadening of these signals, in particular those of the C<sub>5</sub> ring protons, but signal separation was not apparent down to ca. 223 K, at which temperature these signals became unobservable.

These NMR data, as well as the UV/vis data presented above, thus provide no indication for direct coordinative cation–anion interactions. They would rather indicate an unusually weak interaction between  $\text{B}(\text{C}_6\text{F}_5)_4^-$  anions and  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{-ZrMe}^+$  cations in these solutions, possibly approaching an outer-sphere electrostatic association.

As discussed above, the efficient steric shielding of the Zr center in this di-*tert*-butyl-substituted cation precludes the formation of the otherwise prevalent cationic  $\text{AlMe}_3$  adduct. Surprisingly enough, however, addition of ca. 10 equiv of trimethylaluminum to a reaction mixture of complex **2** with 1 equiv of the dimethylanilinium borate causes, over the course of several minutes, the generation of a long-wavelength shoulder at ca. 445 nm in addition to an absorption increase at ca. 380 nm. An isosbestic point at 324 nm indicates again the absence of side or consecutive reactions (Figure 4, left).

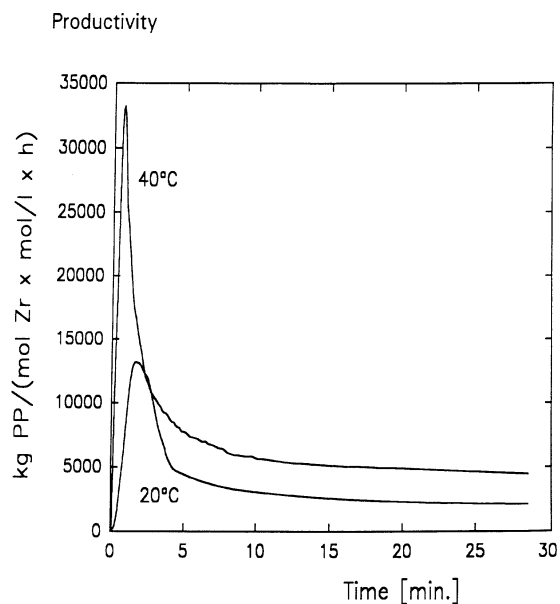
The nature of the product of this reaction is revealed by its  $^1\text{H}$  NMR spectrum: the presence of an  $\text{AlMe}_3$  adduct with an unsymmetric structure is indicated by a double set of signals for all ligand positions, except for the methyl groups in position 2 of the C<sub>5</sub> ring ligands and the methyl groups of the dimethylaniline. The signals of the latter are now found at 2.20 ppm, i.e., at

significantly higher fields than the singlet of free dimethylaniline at 2.50 ppm (Table 1). This shift undoubtedly arises from coordination of the N ligand atom to the Al center of the  $\text{AlMe}_3$  adduct, since this binding causes, at the same time, a substantial diastereotopic splitting of the terminal  $\text{Al-CH}_3$  signals. The persistence of this splitting at room temperature indicates a stable mutual attachment of the components of the ternary adduct  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{-Zr}(\text{Me})(\mu\text{-Me})\text{AlMe}_2\text{-NMe}_2\text{Ph}^+$  (Chart 1).<sup>17,19</sup>

We have further tried to assess whether a similar ternary adduct is also stabilized by the presence of dimethylaniline in solutions in which the cation  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{-ZrMe}^+$  is generated by reaction of **2** with excess MAO. Addition of increasing amounts of MAO to a toluene solution containing complex **2** and ca. 40 equiv of dimethylaniline does indeed give rise to a weak but distinct absorption band at ca. 470 nm: i.e., in a region close to the absorption increase caused by formation of the ternary adduct  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{-Zr}(\text{Me})(\mu\text{-Me})\text{AlMe}_2\text{-NMe}_2\text{Ph}^+$ . Further additions of MAO to [Al]:[Zr] ratios above 100 cause a shift back to ca. 380 nm, however, indicating that the ion pair  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{-ZrMe}^+\cdots\text{MAOMe}^-$  finally prevails in these solutions again. Obviously, the Lewis acidic centers present in excess MAO deplete these solutions of the dimethylaniline required to form the ternary adduct  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{-Zr}(\text{Me})(\mu\text{-Me})\text{AlMe}_2\text{-NMe}_2\text{Ph}^+$ .

The results presented above leave little doubt that the bulky *tert*-butyl substituents shield the cation  $\text{rac-Me}_2\text{Si}(2\text{-Me-4-}t\text{-Bu-C}_5\text{H}_2)_2\text{-ZrMe}^+$  sufficiently to prevent





**Figure 5.** Productivity of the catalyst system *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub>/MAO for the polymerization of propene at *p* = 2 atm, at 20 and 40 °C.

formation of a symmetric AlMe<sub>3</sub> adduct, in which a rigid four-membered ring with two methyl bridges would force the terminal Al–methyl groups to collide with the *tert*-butyl ring substituents. In a dimethylaniline-stabilized adduct with only one bridging methyl group, however, the Zr and Al centers are farther apart from each other and are conformationally free to arrange their ligands in less repulsive orientations, such that this adduct gains surprising stability (Scheme 1).

The structural proposal for the unsymmetric AlMe<sub>3</sub> adduct (Scheme 1) is closely related to the solid-state structure of the ion pair *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>-ZrMe<sup>+</sup>⋯(μ-Me)-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup>, in which one bridging methyl group is found at a Zr–C distance of 255 pm from the zirconium center.<sup>3a</sup> It can thus be reasonably assumed that a “slim” substrate, such as an α-olefin, will have a substantial competitive advantage over larger neutral or anionic ligand entities in its approach to the Zr center of a cationic catalyst species. In MAO-activated catalyst systems derived from complex **1** or **2**, an olefin would have to compete for a coordination site at the metal center only with a very weakly bound counteranion, rather than with an AlMe<sub>3</sub> unit. An unusually high initial activity observed for propene polymerization with the catalyst system **1**/MAO (Figure 5) attests to this notion. The unusually rapid activity decay observed for this catalyst system, on the other hand, is most likely due to the lack of protection against catalyst deactivation, which AlMe<sub>3</sub> adduct formation normally exerts in more open zirconocene catalyst systems. It remains to be established to which degree related anion and AlMe<sub>3</sub><sup>-</sup> exclusion effects pertain also to other, sterically crowded metallocene catalyst systems.<sup>20,21</sup>

## Experimental Section

Toluene-*d*<sub>8</sub> and benzene-*d*<sub>6</sub> were dried over molecular sieves (4 Å) prior to use. All operations were carried out in a glovebox under dry nitrogen (99.999%). For UV/vis measurements, a MAO solution in toluene (1.8 M in Al, AlMe<sub>3</sub> content ca. 30%) was used, which was obtained as a gift from Crompton (Bergkamen). Samples of dimethylanilinium and tritylperfluorotetraphenyl borates and of perfluorotriphenylborane were obtained as gifts from BASSELL GmbH. Complex **1** was synthesized according to ref 4 and converted to complex **2** by reaction with 5–6 equiv of methylmagnesium chloride in diethyl ether/THF.<sup>3a</sup>

UV/vis spectra were measured in a Schlenk vessel under an argon atmosphere by use of an immersion probe with 10 mm path length and light-conducting connections to a Carey 50 spectrometer.<sup>9</sup> To 15 mL of a 0.4–1.0 mM solution of complex **1** or **2** in toluene were added small volumes of MAO solution or of a 1.5 M stock solution of the respective boron-containing reagent through a double-septum closure. The data thus obtained were corrected for changes in background absorption by use of the standard software provided with the spectrometer and for dilution by addition of reagent solutions by use of software contained in the program package Microcal Origin 5.0.

<sup>1</sup>H NMR spectra were recorded in standard 5 mm NMR tubes on a Bruker AMX 250 MHz spectrometer. Typical operating conditions for <sup>1</sup>H NMR measurements: spectral width 5 kHz; spectrum accumulation frequency 0.03–0.2 Hz; number of transients 32–200. For the determination of <sup>1</sup>H chemical shifts, residual solvent peaks were taken as 2.09 ppm (CHD<sub>2</sub> group of deuterated toluene) and 7.15 ppm (deuterated benzene).

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**Supporting Information Available:** Figures giving <sup>1</sup>H NMR spectra of reaction systems **B** and **C**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) No such adduct is formed when trimethylaluminum is added to a solution of *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrMe<sup>+</sup>⋯B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>, obtained by reaction of complex **2** with trityl perfluorotetraphenylborate, as expected from the lack of dimethylaniline. In this case, the large number of unassigned signals indicates some decomposition reaction, probably under transfer of pentafluorophenyl units from the borate anion to a cationic aluminum species.<sup>18</sup>

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(19) Solutions in which the ion pair *rac*-Me<sub>2</sub>Si(2-Me-4-*t*-Bu-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>-ZrMe<sup>+</sup>⋯MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> has been generated by reaction of complex **2** with perfluorotriphenylborane develop, upon reaction with Al<sub>2</sub>Me<sub>6</sub>, an absorption band at 440 nm, similar to that observed in the system **2**/PhMe<sub>2</sub>NH<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>/Al<sub>2</sub>Me<sub>6</sub>. We assume that the cationic AlMe<sub>3</sub> adduct is stabilized in this case by attachment of the rather nucleophilic anion MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> to the Al center.

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