Reaction of Trimethylaluminum with [(^{t}Bu)Al(μ_3-O)]$_6$: Hybrid *tert*-Butylmethylalumoxanes as Cocatalysts for Olefin Polymerization

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The reaction of trimethylaluminum with the hexameric *tert*-butylalumoxane, [(^{t}Bu)Al(μ_3-O)]$_6$, has been investigated. Reaction of [(^{t}Bu)Al(μ_3-O)]$_6$ with 1 equiv of $AlMe_3$ results in the formation of two isomers (**A** and **B**) of the hybrid *tert*-butylmethylalumoxane, [Al_7(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$]. The structures of compounds **A** and **B**, as determined by NMR spectroscopy and mass spectrometry, consist of [Al_6(μ_3-O)$_6$(^{t}Bu)$_5$Me] alumoxane cages, formed via *tert*-butyl/methyl exchange, in which one of the edges of the Al_6O_6 cage is complexed to the (^{t}Bu)AlMe$_2$ formed during alkyl exchange. The difference between the isomers results from the geometric relationship of the cage Al-Me group and the opened edge. The activity of [Al_7(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$], for the [$Me_2C(Cp)(Flu)$]ZrBz$_2$-catalyzed polymerization of 1,5-hexadiene, is significantly increased in comparison to [(^{t}Bu)Al(μ_3-O)]$_6$. The effect of additional equivalents of $AlMe_3$ on the cocatalytic activity of [Al_7(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] suggests that a maximum activity is obtained at a [(^{t}Bu)Al(μ_3-O)]$_6$ to $AlMe_3$ ratio of 1:6. Under conditions of equal Al:Zr ratio the [(^{t}Bu)Al(μ_3-O)]$_6$($AlMe_3$)$_6$ system has a higher activity than a representative sample of commercial methylalumoxane (MAO). ^{1}H NMR suggests that the reaction of [(^{t}Bu)Al(μ_3-O)]$_6$ with 6 equiv of $AlMe_3$ yields (^{t}Bu)AlMe$_2$ as the only *tert*-butyl-containing species and a proposed $AlMe_3$ “free” form of MAO. Whereas the activity of [Al_7(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] and MAO shows slight inhibition by the addition of Al(^{i}Bu)$_3$, the activity of the [(^{t}Bu)Al(μ_3-O)]$_6$/($AlMe_3$)$_6$ system is unaffected. The reaction of $Cp_2Zr(CD_3)_2$ with [Al_7(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] demonstrates that methyl exchange does not occur between a metallocene and the alkyls of the alumoxane cage, but does occur with the complexed (^{t}Bu)AlMe$_2$.

Introduction

Alumoxanes are species having two or more aluminum atoms bonded together by an oxygen atom bridge.[2] Although the simplest alumoxane compounds are those containing two aluminum atoms bridged by a single oxygen,[3] the term alumoxanes is most commonly used to denote oligomeric species derived from the hydrolysis of aluminum compounds, in particular trialkyl compounds.[4] Alumoxanes have been demonstrated to be active catalysts and cocatalysts for a number of processes,[5] including the transition metal catalyzed polymerization of olefins;[6] however, it is as a consequence of the pioneering work of Kaminsky and co-workers[7] that attention has been focused on the extremely high activity of methyl alumoxane (MAO) as a cocatalyst for the polymerization of ethylene and propylene using a group 4 metallocene catalysts.[8,9] Commercial MAO solutions are prepared by the reaction of water with a controlled excess of $AlMe_3$ such that the resulting product, often called a “MAO solution,” contains $AlMe_3$ in addition to a mixture of alumoxanes.[10]

The cocatalytic activity for MAO involves the abstraction of a ligand from the metallocene (e.g., Me$^-$ from Cp_2ZrMe_2), forming a “cation-like” metal center, i.e., eq 1.[11]

$$Cp_2ZrMe_2 + MAO \rightarrow [Cp_2ZrMe]^+ + [MAO(Me)]^- \quad (1)$$

Since compounds with coordinatively unsaturated non-

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[2] The term “alumoxane” is the generally accepted name, but alternative terms may be found in the literature, such as aluminoxane, alkylalumoxane, poly(alkylalumoxane), poly(alkylaluminum oxide), and poly(hydrocarbylaluminum oxide).

[3] See for example: (a) Kushi, Y.; Fernando, Q. *J. Chem. Soc., Chem. Commun.* **1969**, 555. (b) Wynne, K. Y. *Inorg. Chem.* **1985**, *24*, 1339. (c) Gurian, P.; Cheatham, L. K.; Ziller, J. W.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1991**, 1449.

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[5] See for example: (a) Colclough, R. O. *J. Polym. Sci.* **1959**, *34*, 178. (b) Vandenberg, E. J. *J. Polym. Sci.* **1960**, *47*, 489. (c) Saegusa, T.; Fujii, Y.; Fujii, H.; Furukawa, J. *Makromol. Chem.* **1962**, *55*, 232. (d) Ishida, S. I. *J. Polym. Sci.* **1962**, *62*, 1. (e) Longiave. C.; Castelli, R. *J. Polym. Sci.* **1963**, *4C*, 387.

[6] Manyik, R. M.; Walker, W. E.; Wilson, T. P.; Hurley, G. F. U.S. Patent, 3,242,099, 1966.

[7] See for example: (a) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (c) Kaminsky, W.; Miri, M.; Sinn, H.; Woldt, R. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 417.

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[9] Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255.

[10] Barron, A. R. *Organometallics* **1995**, *14*, 3581.

[11] See for example: (a) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112. (b) Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 7968. (c) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875, and references therein.

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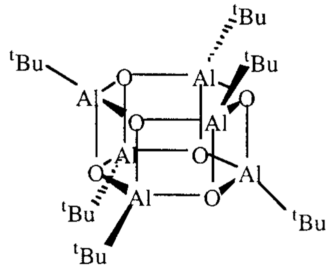
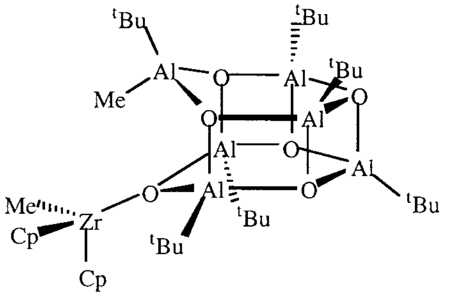
octet three-coordinate aluminum centers are strong Lewis acids, and compounds with aluminum in a four-coordinate, tetrahedral, environment are not usually thought of as Lewis acids, it was assumed that a three-coordinate aluminum center must be present in the catalytically active species of MAO.

Our isolation and structural characterization of the nonfluxional alumoxane compounds $[(^{t}Bu)_2Al\{\mu\text{-}OAl(^{t}Bu)_2\}]_2$ and $[(^{t}Bu)Al(\mu_3\text{-}O)]_n$ (n = 6, 7, 8, 9, 12)[12,13] allowed for an investigation of the mode of activity observed for alumoxanes as cocatalysts for the zirconocene polymerization of olefins.[14] The Lewis acidic compound $[(^{t}Bu)_2Al\{\mu\text{-}OAl(^{t}Bu)_2\}]_2$, which contains two three-coordinate aluminum centers, shows no reaction with Cp_2ZrMe_2 and no catalytic activity toward ethylene polymerization. In contrast, the closed-cage "octet" compound $[(^{t}Bu)Al(\mu_3\text{-}O)]_6$ (**I**) reacts to give the complex $[Cp_2ZrMe][(^{t}Bu)_6Al_6O_6Me]$ (**II**), which is active as a catalyst for the polymerization of ethylene.[14] These results led to our proposing that the cocatalytic activity of alkyl alumoxanes is a consequence of their "*latent Lewis acidity*".[14] We have defined latent Lewis acidity as the ability of a electron precise molecule to undergo heterolytic bond cleavage to generate a Lewis acidic site. For a given bond type the relative magnitude of the latent Lewis acidity is related to the relative strain present in the cage.[15]



(I)



(II)

Our studies have previously focused exclusively on the chemistry of *tert*-butyl alumoxanes due to their relative ease of synthesis, separation, and characterization.[12−14,16,17] However, the factors that allowed us to isolate these compounds offer disadvantages with respect to their activity. First, the observed activity of a series of alumoxane cage structures is often the reverse of the proposed activity due to intramolecular steric hindrance during the opening of the cage.[14,17] Second, the steric bulk of the *tert*-butyl groups limits the activity with metallocenes more sterically hindered than Cp_2ZrMe_2, presumably by restricting the approach of the cage to the metal center.[18] These disadvantages are also present for other sterically hindered alkyl substituents.[19] Thus, it would be desirable to study methylalumoxanes directly. One route to the study of individual methylalumoxane compounds has been investigated by Roesky and co-workers, who have reported the formation of alkali metal salts of MAO.[20] An alternative approach is the subject of the present research described herein.

Results and Discussion

Reaction of $[(^{t}Bu)Al(\mu_3\text{-}O)]_6$ with 1 equiv of $AlMe_3$. The hexameric alumoxane $[(^{t}Bu)Al(\mu_3\text{-}O)]_6$ (**I**)[12] reacts immediately and exothermically, in C_6D_6, at room temperature with a 1 molar equiv of $AlMe_3$. The ^1H NMR spectrum of the reaction mixture (Figure 1a) exhibits multiple environments for both $Al-C(CH_3)_3$ and $Al-CH_3$ groups. No unreacted $[(^{t}Bu)Al(\mu_3\text{-}O)]_6$ or $AlMe_3$ is observed. An equal number of *tert*-butyl resonances were observed in the ^{13}C NMR spectrum, although individual resonances could not be discerned in the $Al-CH_3$ region due to the presence of severe quadrupole broadening. The relationship between various resonances in the ^1H and ^{13}C NMR spectra is determined by $^1H-^{13}C$ HETCOR. After 2 days no additional resonances are observed in either the ^1H or ^{13}C NMR spectrum; however, the relative intensities have changed. For example, in the ^1H NMR spectrum (see Figure 1b), the absolute intensity of the *tert*-butyl resonances at δ 1.21, 1.20, 1.17, 1.13, 1.08, and 1.07 and the methyl resonances at δ −0.08, −0.13, and −0.29 decrease. In contrast, the remaining resonances increase with respect to the internal standard. Irrespective of time of reaction, the relative ratios of the two sets of peaks remain constant (9:9:9:9:9:9:3:3:3 and 18:18:18:6:3), indicating the presence of two distinct species, each with a ᵗBu:Me ratio of 6:3. On the basis of the ^1H NMR peak integration, the reaction mixture appears to consist of two compounds. Given the reaction stoichiometry and charge balance, we propose the NMR data are consistent with the presence of two geometric isomers of a compound with the formula $[Al_7(\mu_3\text{-}O)_6(^{t}Bu)_6Me_3]$. Removal of all volatiles leads to a white solid whose NMR is identical to the isomer mixture prior to removal of the solvent. Elemental analysis of this solid is consistent

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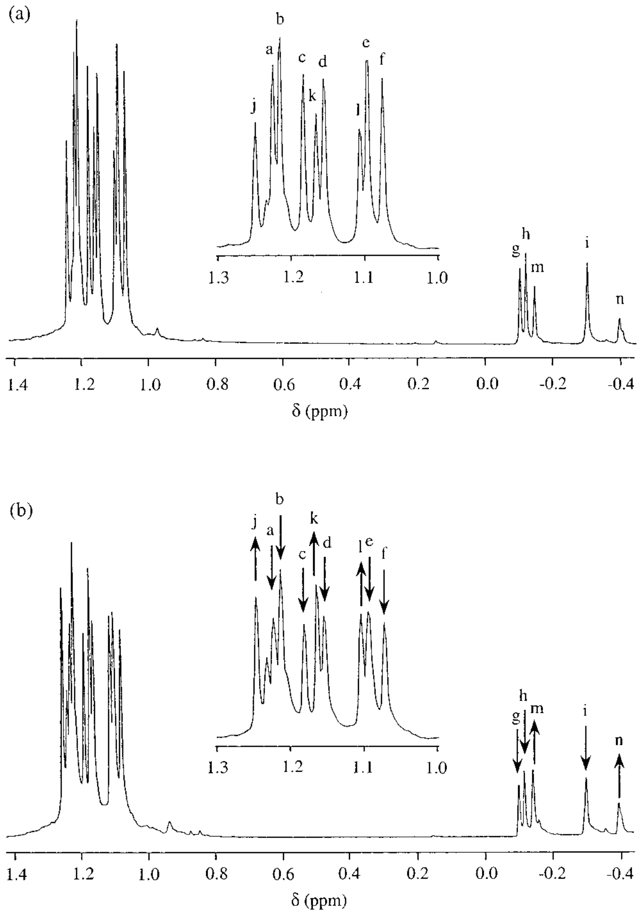

Figure 1. ^1H NMR spectrum of the hybrid alumoxane compounds *ortho*-[$Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3$] (**A**) and *para*-[$Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3$] (**B**), formed from the reaction between [$(^tBu)Al(\mu_3\text{-}O)]_6$ and $AlMe_3$ immediately upon mixing (a) and after 2 days (b).

with an empirical formula of [$Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3$]. In addition, use of EI mass spectrometry allows for observation of a parent ion (*m*/*z* 672) and fragmentation species [e.g., *m*/*z* 616 ($M^+ - CH_2C{=}CMe_2$)] consistent with this formulation.[21] The observation of a reaction of an alumoxane with $AlMe_3$ contrasts with studies suggesting no reaction occurs between MAO and $AlMe_3$.[22]

Using $^1H-^{13}C$ HETCOR and $^1H-^1H$ NOE experiments[23] and comparison with structurally characterized compounds,[12-14] we propose that the structures of the two isomers of [$Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3$] are as shown in Figure 2. Full NMR assignments are given in Table 1. The observation of six separate *tert*-butyl and three separate methyl groups in isomer **A** is consistent with the structure drawn in Figure 2a. From Figure 2b, isomer **B** would also be expected to have nine different resonances; however, we propose that the methyl groups associated with the (^tBu)$AlMe_2$ group are exchanging rapidly on the NMR time scale, resulting in a pseudo mirror plane. The line width of the methyl resonance is temperature dependent; however, no decoalescence is observed at low temperature. The absence of any such exchange for isomer **A** is expected on the basis of the steric interaction between various alkyl groups. Thus, in isomer **A** the "Al(^tBu)Me" moiety is oriented such that $Me_{(h)}$ is adjacent to an Al(^tBu) moiety and $^tBu_{(d)}$ is adjacent to an Al(Me) group. However, in isomer **B** both $Me_{(m)}$ and $^tBu_{(k)}$ in the "Al(^tBu)Me" moiety are adjacent to *tert*-butyl groups, resulting in a significant increase in steric hindrance.

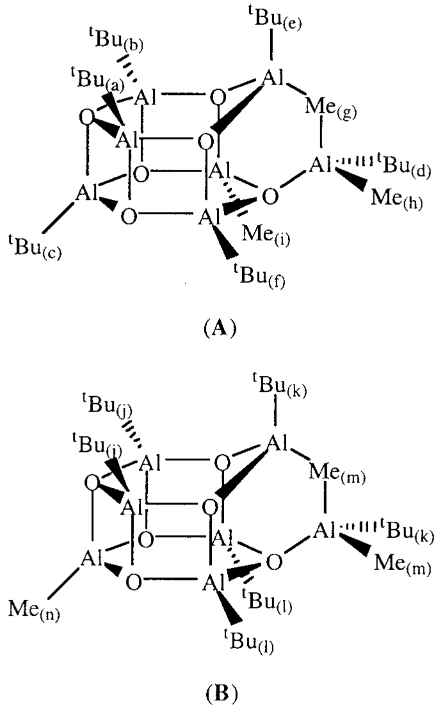

Figure 2. Schematic representation of the structures of *ortho*-[$Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3$] (**A**) and *para*-[$Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3$] (**B**).

Table 1. ^1H and ^{13}C NMR Spectral Assignment for [$Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3$][a]

	^1H NMR[b]		^{13}C NMR[b]	
isomer	δ (ppm, 17 °C)[d]	integration	δ (ppm, 17 °C)[d]	assignment[c]
A	1.21 (1.26)	9H	30.2 (30.33)	$^tBu_{(a)}$
	1.20 (1.28)	9H	30.2 (30.2)	$^tBu_{(b)}$
	1.17 (1.25)	9H	29.5 (29.7)	$^tBu_{(c)}$
	1.13 (1.21)	9H	30.3 (30.3)	$^tBu_{(d)}$
	1.08 (1.11)	9H	30.6 (30.5)	$^tBu_{(e)}$
	1.07 (1.08)	9H	28.8 (28.6)	$^tBu_{(f)}$
	−0.08 (−0.14)	3H	*e*	$Me_{(g)}$
	−0.13 (−0.15)	3H	*e*	$Me_{(h)}$
	−0.29 (−0.26)	3H	*e*	$Me_{(i)}$
B	1.23 (1.29)	18H	30.5 (30.5)	$^tBu_{(j)}$
	1.15 (1.20)	18H	30.7 (30.6)	$^tBu_{(k)}$
	1.09 (1.14)	18H	29.1 (29.1)	$^tBu_{(l)}$
	−0.14 (−0.17)	6H	*e*	$Me_{(m)}$
	−0.38 (−0.36)	3H	*e*	$Me_{(n)}$

[a] All spectra recorded in C_7D_8 solution. [b] ^1H measured at 250 MHz with internal reference to residual ^1H in C_7D_8 (δ 2.09 ppm). ^{13}C measured at 62.6 MHz with internal reference to ^{13}C of CD_3 group in C_7D_8 (δ 137.86 ppm). [c] For assignment see Figure 2. [d] Values given in parentheses measured at −49 °C. [e] Not determined due to severe broadening.

On the basis of the ^1H NMR integration the ratio of **A**:**B** is approximately 3:1. No changes in intensity are observed with changes in temperature (see Table 1), but as noted above, the relative ratio changes over 2 days at room temperature to give an **A**:**B** ratio ~7:3. This suggest the slow equilibrium between the isomers. The

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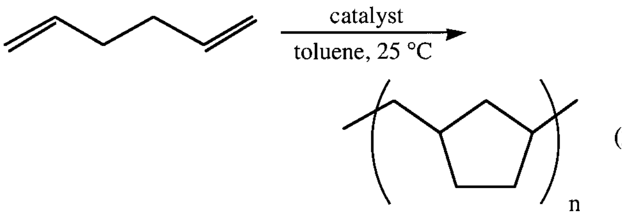
(21) van Poppel, L. G. Personal communication.

(22) Eilersten, J. L.; Rytter, E.; Ystenes, M. In *Proceedings of the International Symposium on Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer, Berlin, 1999; p 136.

(23) The following methyl and *tert*-butyl groups showed positive NOE effects: $Me_{(h)}$-$^tBu_{(d)}$, $Me_{(h)}$-$^tBu_{(f)}$, $Me_{(i)}$-$^tBu_{(d)}$, $Me_{(m)}$-$^tBu_{(l)}$, and $Me_{(m)}$-$^tBu_{(k)}$, see Figure 2.

formation of **A** and **B** is sufficiently rapid that we have been unable to observe any intermediates. However, on the basis of literature precedent we propose that their formation occurs via the following reaction steps: (a) reversible complexation of $AlMe_3$ via cage opening,[14,18] (b) alkyl exchange,[24] and (c) complexation of $(^tBu)AlMe_2$.

Comparison of $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ with MAO as Cocatalysts for the Metallocene Polymerization of 1,5-Hexadiene. To compare the activity of $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ with both MAO and $[(^tBu)Al(\mu_3\text{-}O)]_6$, we have performed polymerization studies on 1,5-hexadiene (eq 2). The choice of 1,5-hexadiene, rather than gaseous ethylene or propylene, was because the use of a liquid allows for the study of the relative rates of polymerization of a series of catalysts to be compared under identical conditions which are not mass transport limited.[25] The substituted metallocene $[Me_2C(Cp)(Flu)]ZrBz_2$ (**III**)[26] was chosen because its steric bulk precludes any catalytic activity with $[(^tBu)Al(\mu_3\text{-}O)]_6$, while it is active in the presence of MAO. In addition, the presence of a preformed Zr−C bond obviates the need for an alkylation step and allows for the direct comparison of the cocatalysts. The MAO used for comparison with $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ was a commercial sample (Albemarle) from which the "free" $AlMe_3$ had been removed under vacuum. Typical procedures for the polymerization reactions are described in the Experimental Section. Since the exact molecularity of MAO is unknown,[27] the alumoxane:Zr ratio cannot be used as a direct comparison of the cocatalytic activity of MAO to $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ and $[(^tBu)Al(\mu_3\text{-}O)]_6$. Thus, equivalent Al:Zr ratios are used in comparing the relative activities of the different alumoxanes. A summary of polymerization data is given in Table 2. Whereas $[(^tBu)Al(\mu_3\text{-}O)]_6$ is not active as a cocatalyst for the $[Me_2C(Cp)(Flu)]ZrBz_2$-catalyzed polymerization of 1,5-hexadiene, $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ shows significant activity even at low Al:Zr ratios (Table 2). The activity of $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ is, however, only 30−40% that of MAO, but does follow the same trend with respect to the dependence on Al:Zr ratio (Figure 3).



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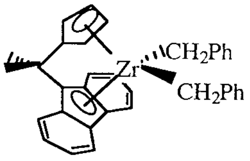

(**III**)

Table 2. Polymerization of 1,5-Hexadiene with $[Me_2C(Cp)(Flu)]ZrBz_2$ Activated by Alumoxane Cocatalysts

cocatalyst (mol, Al)	Al:Zr ratio	polymer yield (g)	activity (kg/g Zr)
MAO			
1.4×10^{-4}	350	0.663	18.2
2.8×10^{-4}	700	0.750	20.1
4.2×10^{-4}	1,050	0.928	25.4
5.6×10^{-4}	1,400	1.075	29.5
1.12×10^{-3}	2,800	1.270	34.8
$[(^tBu)Al(\mu_3\text{-}O)]_6$			
1.2×10^{-4}	300	no polymer	
4.8×10^{-4}	1,200	trace	
$[(^tBu)Al(\mu_3\text{-}O)]_6/AlMe_3$[b]			
1.4×10^{-4}	350	0.099	2.7
$[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$			
1.4×10^{-4}	350	0.254	7.0
2.8×10^{-4}	700	0.412	11.3
4.2×10^{-4}	1,050	0.520	14.3
5.6×10^{-4}	1,400	0.677	18.6
$[(^tBu)Al(\mu_3\text{-}O)]_6/(AlMe_3)_6$			
2.4×10^{-4}	600	1.220	33.4
4.8×10^{-4}	1,200	1.251	34.3
7.2×10^{-4}	1,800	1.291	35.4
9.6×10^{-4}	2,400	1.325	36.3

[a] 4.0×10^{-7} mol $[Me_2C(Cp)(Flu)]ZrBz_2$ used in all catalyst runs (ca. 6.2×10^{-5} mol·L^{-1}). [b] Mixed in a polymerization vessel prior to addition of $[Me_2C(Cp)(Flu)]ZrBz_2$.

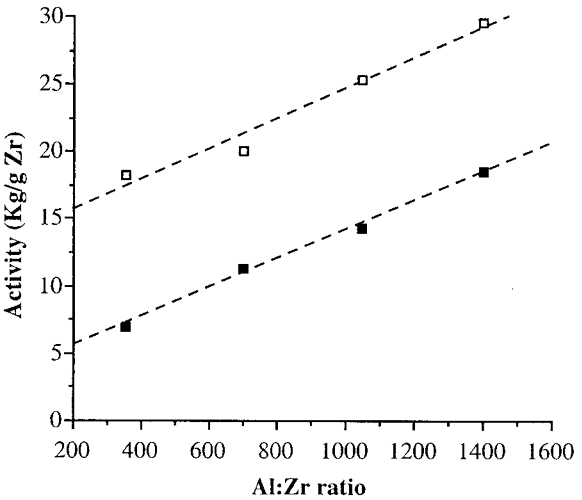

Figure 3. Polymerization activity (kg polymer per g Zr) as a function of Al:Zr ratio for the $[Me_2C(Cp)(Flu)]ZrBz_2$ (4.0×10^{-7} mol) catalyzed polymerization of 1,5-hexadiene: (■) $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$; (□) MAO. The reactions were performed at 25 °C.

It may be concluded from these results that a significant increase in activity of the hexameric alumoxane cage may be obtained by the substitution of one of the *tert*-butyl groups for a methyl group. However, direct comparison of $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ with the commercial MAO solution is difficult because the type and distribution of alumoxanes structures are unknown in the latter.

Optimization of $[(^tBu)Al(\mu_3\text{-}O)]_6$:$AlMe_3$ Ratio. If we assume that the significant increase in activity of $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ in comparison to $[(^tBu)Al(\mu_3\text{-}O)]_6$

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(25) Previous studies involving polymerization of hexa-1,5-diene include: (a) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *11*, 4953. (b) Resconi, L.; Coates, G. W.; Mogstad, A.; Waymouth, R. M. *J. Macromol. Sci. Chem.* **1991**, *A28*, 1225. (c) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91.

(26) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633.

(27) Several studies have recently provided convicing evidence that the average number of aluminum atoms per MAO molecule is between 10 and 18, see: Beard, W. R.; Blevins, D. R.; Imhoff, D. W.; Kneale, B.; Simeral, L. S. In *Polyethylene: New Technology, New Markets*; Institute of Materials: London, 1997.

Table 3. Effect of $AlMe_3$ on the Polymerization of 1,5-Hexadiene with $[Me_2C(Cp)(Flu)]ZrBz_2$ Activated by Alumoxane Cocatalysts[a]

cocatalyst						
$AlMe_3$ (mol, Al)	MAO (mol, Al)	$[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ (mol, Al)	total Al (mol, Al)	Al:Zr ratio	polymer yield (g)	activity (kg/g Zr)
	1.4×10^{-4}		1.4×10^{-4}	350	0.663	18.2
2.0×10^{-5}	1.4×10^{-4}		1.6×10^{-4}	400	0.640	17.5
4.0×10^{-5}	1.4×10^{-4}		1.8×10^{-4}	450	0.601	16.5
6.0×10^{-5}	1.4×10^{-4}		2.0×10^{-4}	500	0.602	16.5
8.0×10^{-5}	1.4×10^{-4}		2.2×10^{-4}	550	0.583	16.0
1.4×10^{-4}	1.4×10^{-4}		2.8×10^{-4}	700	0.511	14.0
2.0×10^{-4}	1.4×10^{-4}		3.4×10^{-4}	850	0.518	14.2
		1.4×10^{-4}	1.4×10^{-4}	350	0.254	7.0
1.0×10^{-5}		1.4×10^{-4}	1.5×10^{-4}	375	0.216	5.9
2.0×10^{-5}		1.4×10^{-4}	1.6×10^{-4}	400	0.322	8.8
3.0×10^{-5}		1.4×10^{-4}	1.7×10^{-4}	425	0.480	13.2
4.0×10^{-5}		1.4×10^{-4}	1.8×10^{-4}	450	0.477	26.8
6.0×10^{-5}		1.4×10^{-4}	2.0×10^{-4}	500	0.958	28.1
8.0×10^{-5}		1.4×10^{-4}	2.2×10^{-4}	550	1.024	31.0
1.4×10^{-4}		1.4×10^{-4}	2.8×10^{-4}	700	1.130	14.0
2.0×10^{-4}		1.4×10^{-4}	3.4×10^{-4}	850	0.899	24.6

[a] 4.0×10^{-7} mol $[Me_2C(Cp)(Flu)]ZrBz_2$ used in all catalyst runs (ca. 6.2×10^{-5} mol·L^{-1}).

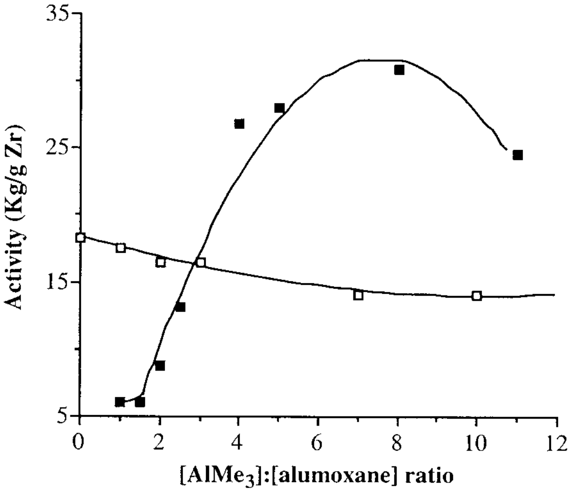

Figure 4. Polymerization activity (kg polymer per g Zr) as a function of $AlMe_3$:alumoxane ratio for the $[Me_2C(Cp)(Flu)]ZrBz_2$ (4.0×10^{-7} mol) catalyzed polymerization of 1,5-hexadiene: (■) $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$; (□) MAO. The reactions were performed at 25 °C, with an alumoxane concentration equivalent to 1.4×10^{-4} mol Al.

is due to the decreased steric hindrance at the alumoxane, then sequential exchange of the *tert*-butyl groups for sterically less hindered methyl groups should result in further improvements in activity.

The polymerization activity as a function of $AlMe_3$:$[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ ratio for the $[Me_2C(Cp)(Flu)]ZrBz_2$-catalyzed polymerization of 1,5-hexadiene was determined; see Table 3. For comparison, independent experiments were performed with MAO as the cocatalyst. All reactions were performed at 25 °C, with the relative concentration of alumoxane (1.4×10^{-4} mol Al; ca. 2.17×10^{-2} mol·L^{-1} Al) and $[Me_2C(Cp)(Flu)]ZrBz_2$ (4.0×10^{-7} mol; ca. 6.2×10^{-5} mol·L^{-1}) constant. As can be seen from Figure 4, the activity of MAO decreases with addition of $AlMe_3$. The decrease in activity of the MAO in the presence of excess $AlMe_3$ is presumably due to the competition with $AlMe_3$ to binding Zr−R.[9,28] Tritto et al. have shown the formation of $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ cations,[29] and we have shown that the reaction of Cp_2ZrX_2 (X = Cl, Me) with $Al(^tBu)_3$ yields the Lewis acid−base complex $Cp_2Zr(X)(\mu\text{-}X)Al(^tBu)_3$.[14]

In contrast to the results for MAO, the activity of the $[Me_2C(Cp)(Flu)]ZrBz_2/[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ catalyst is enhanced with increasing $AlMe_3$:$[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ ratio (Figure 4). A maximum activity is reached at an $AlMe_3$:$[(^tBu)Al(\mu_3\text{-}O)]_6$ ratio of between 6 and 8. Upon the basis of the formulation of **A** and **B** we propose that this is a consequence of exchanging all the alumoxane *tert*-butyl groups for methyls. Thus, the reaction products formed from the reaction of $[(^tBu)Al(\mu_3\text{-}O)]_6$ with 6 equiv of $AlMe_3$ were studied by ^1H NMR spectroscopy.

Upon the addition of 6 equiv of $AlMe_3$, all the $[(^tBu)Al(\mu_3\text{-}O)]_6$ immediately reacts to form a mixture of the hexameric *tert*-butylmethylalumoxanes **A** and **B**. In addition to unreacted $AlMe_3$, a new *tert*-butyl resonance is observed at δ 1.09 ppm. This latter resonance increases in intensity with time along with the disappearance of all the resonances associated with **A** and **B**. After 100 min, the methyl region shows a medium-broad peak (δ −0.29 ppm, $W_{1/2} \approx 12$ Hz) superimposed on a very broad resonance (δ −0.23 ppm, $W_{1/2} \approx 60$ Hz). The sharper methyl peak and the remaining *tert*-butyl resonance (δ 1.09 ppm) are due to the formation of $(^tBu)AlMe_2$. This assignment was confirmed by comparison with the ^1H NMR of a genuine sample of $(^tBu)AlMe_2$.[30]

Upon the basis of the foregoing, we propose that the reaction of $[(^tBu)Al(\mu_3\text{-}O)]_6$ with 6 equiv of $AlMe_3$ results in the complete exchange of the alumoxane *tert*-butyl substituents for methyl groups. Unfortunately the broad nature of the alumoxane methyl group ^1H NMR resonance, and the possibility of alkyl exchange with $(^tBu)AlMe_2$, precludes any structural characterization of the resulting methylalumoxane; however, it is clearly an "$AlMe_3$-free" soluble MAO.[31] Unfortunately, unlike $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ we were unable to obtain mass spectrometry data consistent with any simple structure.

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(28) Sacchi, M. C.; Barsties, E.; Tritto, I.; Paolo, L.; Brintzinger, H. H.; Stehling, U. *Macromolecules* **1997**, *30*, 1267.

(29) Tritto, I.; Raffealla, D.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247.

(30) The synthesis and characterization of $(^tBu)AlMe_2$ has been previously reported, see: Jones, A. C.; Jacobs, P. R.; Rushworth, S. A.; Roberts, J. S.; Button, C. C.; Wright, P. J.; Oliver, P. E.; Cockayne, B. *J. Cryst. Growth* **1989**, *96*, 505.

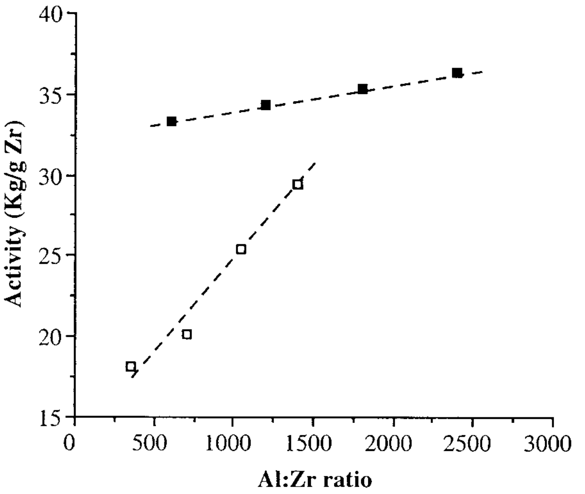

Figure 5. Polymerization activity (kg polymer per g Zr) as a function of Al:Zr ratio for the $[Me_2C(Cp)(Flu)]ZrBz_2$ (4.0×10^{-7} mol) catalyzed polymerization of 1,5-hexadiene: (■) $[(^tBu)Al(\mu_3\text{-}O)]_6/(AlMe_3)_6$; (□) MAO. The reactions were performed at 25 °C.

Since we cannot demonstrate what the structure (or structures) of this species is, we will designate it as "$[(^tBu)Al(\mu_3\text{-}O)]_6/(AlMe_3)_6$".

A comparison of catalytic activity of $[(^tBu)Al(\mu_3\text{-}O)]_6/(AlMe_3)_6$ versus the Al:Zr ratio (Figure 5 and Table 2) indicates that at any given Al:Zr ratio it is more active than MAO and $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$. However, it is interesting to note that whereas the activities of both MAO and $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ show significant dependence on the overall Al:Zr ratio, the activity of $[(^tBu)Al(\mu_3\text{-}O)]_6/(AlMe_3)_6$ shows only a slight effect with increased Al:Zr ratio; for example, less than a 9% increase of activity is observed for a 4-fold increase in the Al:Zr ratio (Figure 5).

What Is the Effect of $Al(^iBu)_3$ on the Activity of Hybrid Alumoxanes? As was noted in the Introduction, commercial MAO solutions contains $AlMe_3$ in addition to a mixture of alumoxanes. The effect of the $AlMe_3$ appears to be 3-fold. First, when halide-containing zirconocenes are employed [e.g., $CpZrCl_2$, $(C_5Me_5)_2ZrCl_2$, etc.], the $AlMe_3$ is a possible reagent for the alkylation of the zirconocene, eq 3.[32]

$$Cp_2ZrCl_2 + AlMe_3 \rightarrow Cp_2Zr(Me)Cl + Me_2AlCl \quad (3)$$

Second, it is commonly observed that the solubility of MAO in common organic solvents such as toluene appears to be negligible in the absence of $AlMe_3$; that is, removal of all volatiles from commercial MAO/$AlMe_3$ solutions results in the formation of an insoluble material. Thus, the $AlMe_3$ is required to provide a homogeneous solution. Third, the $AlMe_3$ is considered to act as a scavenger of impurities in the olefin feedstock, in particular H_2O, O_2, and HCl. Thus, the presence of $AlMe_3$ in commercial MAO solutions appears beneficial; however, the activity of MAO unfortunately decreases with increasing $AlMe_3$ content (see above). Since the purpose of the present study is to prepare enhanced activity alumoxanes, the presence of excessive amounts of $AlMe_3$ as scavenger is counterproductive. It would be desirable to try alternative AlR_3 compounds as scavenger compounds.

To determine the effect of added $Al(^iBu)_3$, aliquots were added to the polymerization vessel prior to the addition of the alumoxane and $[Me_2C(Cp)(Flu)]ZrBz_2$, and the relative polymerization activity was determined. All reactions were performed at 25 °C, with the relative concentrations of the alumoxane (1.4×10^{-4} mol Al) and $[Me_2C(Cp)(Flu)]ZrBz_2$ (4.0×10^{-7} mol) maintained as constant. A comparison was made for MAO, $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$, and "$[(^tBu)Al(\mu_3\text{-}O)]/(AlMe_3)_6$"; see Table 4. As can be seen from Figure 6, addition of $Al(^iBu)_3$ to $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ or MAO results in a slight decrease in activity; however, essentially no effect is observed on "$[(^tBu)Al(\mu_3\text{-}O)]/(AlMe_3)_6$". The data in Figure 6 are presented as the ratio [Al in $Al(^iBu)_3$]:[Al in alumoxane] in order to allow for a comparison with MAO; however, it is worth noting that the $Al(^iBu)_3$ has little effect on the activities of "$[(^tBu)Al(\mu_3\text{-}O)]/(AlMe_3)_6$" even with a 4:1 [$Al(^iBu)_3$]:[alumoxane] ratio.

Methyl Exchange between $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ and $Cp_2Zr(CD_3)_2$. Alkyl exchange between Cp_2ZrMe_2 and AlR_3 has been extensivley studied by the groups of Siedle[33] and Brintzinger.[32] Although, as discussed in the Introduction, the activation of a metallocene by MAO is proposed to involve the abstraction of a ligand from the metallocene (eq 1), it is also accepted that the reactivity of MAO with halide-containing zirconocenes involves the alkylation of the zirconocene. Siedle et al. have reported that methyl exchange is observed between Cp_2ZrMe_2 and commercial MAO solutions ($\Delta G^{\ddagger} = 58$ kJ·mol^{-1}, $\Delta H^{\ddagger} = 46$ kJ·mol^{-1}).[34] However, since these MAO solutions contained free and complexed $AlMe_3$, it is difficult to separate the effect of the MAO from that of $AlMe_3$ ($\Delta G^{\ddagger} = 69$ kJ·mol^{-1}), especially since the latter is known to methylate Cp_2ZrCl_2. We have previously reported that while hydride/methyl metathesis occurs between Cp_2ZrMe_2 and $[HAl(\mu_3\text{-}N^tBu)]_4$, the activation energy is high ($\Delta H^{\ddagger} = 104$ kJ·mol^{-1}).[24] The synthesis of $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ offers an excellent opportunity to investigate the potential for methyl exchange of both a methylalumoxane and complexed trialkylaluminum.

To a toluene-d_8 solution of $[Al_7(\mu_3\text{-}O)_6(^tBu)_6Me_3]$ was added 0.5 equiv of $Cp_2Zr(CD_3)_2$. The ^{1}H NMR spectrum of the reaction mixture shows an immediate decrease in the relative intensities of the peaks we have assigned to $Me_{(m)}$ and $Me_{(h)}$[35] and a lesser decrease in the peak assigned to $Me_{(g)}$. In addition, a new peak at −0.21 ppm, assigned to a zirconocene methyl, is observed. No change in relative intensity is observed for the peaks due to $Me_{(i)}$ or $Me_{(n)}$. After allowing the reaction mixture to stand at room temperature for 3 h the peaks due to $Me_{(m)}$, $Me_{(h)}$, and $Me_{(g)}$ have all decreased further with a concomitant increase in the Zr−Me resonance. Again, no change in relative intensity is observed for the peaks due to $Me_{(i)}$ or $Me_{(n)}$. For clarity these results are

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[31] We have previously noted that removal of $AlMe_3$ from a commercial MAO sample results in it being insoluble in common organic solvents, see: ref 10.

[32] Beck, S.; Brintzinger, H. H. *Inorg. Chim. Acta* **1998**, *270*, 376.

[33] Siedle, A. R.; Newmark, R. A.; Lamanna, W. M. Lyon, P. A. *Organometallics* **1991**, *10*, 400.

[34] Siedle, A. R.; Newmark, R. A.; Lamanna, W. M. Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301.

[35] The resonances for $Me_{(h)}$ and $Me_{(m)}$ are superimposed in toluene-d_8 solution, but separated in benzene-d_6.

Table 4. Effect of Al(^{i}Bu)$_3$ on the Polymerization of 1,5-Hexadiene with [Me$_2$C(Cp)(Flu)]Zr(CH$_2$Ph)$_2$ Activated by Alumoxane Cocatalysts

cocatalyst						
Al(^{i}Bu)$_3$ (mol, Al)	MAO (mol, Al)	[Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] (mol, Al)	[(^{t}Bu)Al(μ_3-O)]$_6$.(AlMe$_3$)$_6$ (mol, Al)	Al:Zr ratio	polymer yield (g)	activity (kg/g Zr)
	1.4×10^{-4}			350	0.663	18.2
2.0×10^{-5}	1.4×10^{-4}			400	0.588	16.1
4.0×10^{-5}	1.4×10^{-4}			450	0.617	16.9
6.0×10^{-5}	1.4×10^{-4}			500	0.572	15.7
8.0×10^{-5}	1.4×10^{-4}			550	0.579	15.9
1.4×10^{-4}	1.4×10^{-4}			700	0.516	14.1
2.0×10^{-4}	1.4×10^{-4}			850	0.389	10.7
		1.4×10^{-4}		350	0.663	18.2
1.0×10^{-5}		1.4×10^{-4}		375	0.259	7.1
2.0×10^{-5}		1.4×10^{-4}		400	0.190	5.2
3.0×10^{-5}		1.4×10^{-4}		425	0.190	5.2
4.0×10^{-5}		1.4×10^{-4}		450	0.165	4.5
			2.4×10^{-4}	600	1.220	33.3
2.0×10^{-5}			2.4×10^{-4}	650	0.997	27.3
4.0×10^{-4}			2.4×10^{-4}	700	1.164	31.9
6.0×10^{-4}			2.4×10^{-4}	750	1.110	30.4
8.0×10^{-4}			2.4×10^{-4}	800	1.213	33.2

[a] 4.0×10^{-7} mol [Me$_2$C(Cp)(Flu)]Zr(CH$_2$Ph)$_2$ used in all catalyst runs (ca. 6.2×10^{-5} mol·L^{-1}).

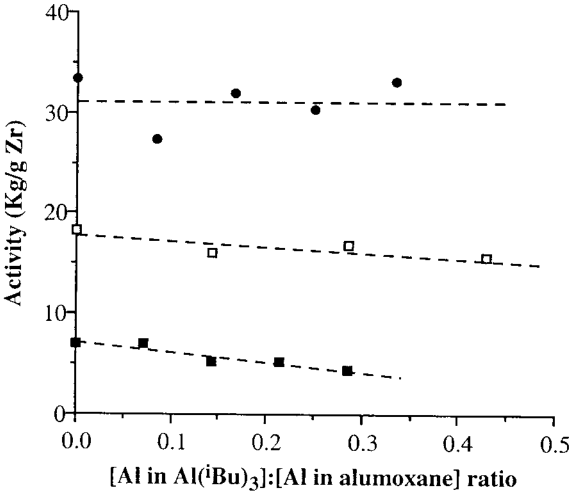

Figure 6. Polymerization activity (kg polymer per g Zr) as a function of Al(^{i}Bu)$_3$:alumoxane ratio for the [Me$_2$C(Cp)(Flu)]ZrBz$_2$ (4.0×10^{-7} mol) catalyzed polymerization of 1,5-hexadiene: (■) [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$]; (□) MAO; [(^{t}Bu)Al(μ_3-O)]$_6$/(AlMe$_3$)$_6$″ (●). The reactions were performed in toluene at 25 °C, with an Al:Zr ratio > 350.

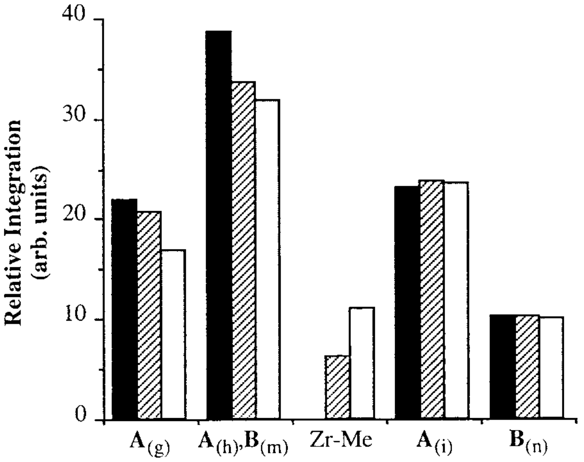

Figure 7. Plot of the relative integrations of the methyl region for the reaction between [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] and Cp$_2$Zr(CD$_3$)$_2$ in C$_6$D$_6$. (black bar) [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$]; (hatched bar) after addition of Cp$_2$Zr(CD$_3$)$_2$; (white bar) after 3 h.

presented in graph form in Figure 7. No significant change is observed in the *tert*-butyl region of the ^{1}H NMR spectra.

The above observations are consistent with the following: (a) rapid methyl exchange occurs between the zirconocene and the complexed (^{t}Bu)AlMe$_2$; (b) no exchange appears to occur between the zirconocene and the methyl groups on the alumoxane. Furthermore, observation that the exchange for the complexed (^{t}Bu)AlMe$_2$ in isomer **B** is initially more rapid than for that in isomer **A** is in agreement with the proposed fluxional nature of isomer **B**. These results suggest that alkyl exchange occurs between the coordinated AlMe$_3$ and zirconocenes, but does not occur with individual MAO methyl groups.

Conclusions

Reaction of [(^{t}Bu)Al(μ_3-O)]$_6$ with 1 equiv of AlMe$_3$ results in the formation of two isomers (**A** and **B**) of the hybrid *tert*-butyl-methylalumoxane, [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$]. The structures of compounds **A** and **B** consist of [Al$_6$(μ_3-O)$_6$(^{t}Bu)$_5$Me] alumoxane cages, formed via *tert*-butyl/methyl exchange, in which one of the edges of the Al$_6$O$_6$ cage is complexed to the (^{t}Bu)AlMe$_2$ formed during alkyl exchange. The difference between the isomers results from the geometric relationship of the cage Al−Me group and the opened edge. The activity of [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$], for the [Me$_2$C(Cp)(Flu)]ZrBz$_2$-catalyzed polymerization of 1,5-hexadiene, is significantly increased in comparison to [(^{t}Bu)Al(μ_3-O)]$_6$, but less than commercial MAO solutions. The activity of [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] may be dramatically increased by the addition of further equivalents of AlMe$_3$, up to a [(^{t}Bu)Al(μ_3-O)]$_6$-to-AlMe$_3$ ratio of 1:6. At this point [(^{t}Bu)Al(μ_3-O)]$_6$/(AlMe$_3$)$_6$ has a slightly higher activity (per aluminum) than a representative sample of commercial MAO. Thus, the following trend is found for the activity of these alumoxanes: "[(^{t}Bu)Al(μ_3-O)]$_6$/(AlMe$_3$)$_6$" > MAO > [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] ≫ [(^{t}Bu)Al(μ_3-O)]$_6$.[36]

The reaction of Cp$_2$Zr(CD$_3$)$_2$ with [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] demonstrates that methyl exchange is unlikely to occur between a metallocene and the alkyls of the alumoxane cage, but does occur with the complexed (^{t}Bu)AlMe$_2$. This latter observation suggests that the alkylation of Cp$_2$ZrCl$_2$ to give Cp$_2$ZrMe$_2$ and/or Cp$_2$Zr(Me)Cl is due not to the methylalumoxanes in commercial MAO solutions but the AlMe$_3$ that is present.

Experimental Section

All synthetic procedures were performed under purified nitrogen using standard Schlenk techniques or in an argon atmosphere VAC glovebox. [(^{t}Bu)Al(μ_3-O)]$_6$, [(^{t}Bu)$_2$Al(μ-OH)]$_3$, and [Me$_2$C(Cp)(Flu)]ZrBz$_2$ were prepared as previously reported.[12,13,25] MAO solution (30% in toluene) and AlMe$_3$ were generously donated by Albemarle Corporation. 1,5-Hexadiene (Aldrich) was used as received. Solvents were distilled and degassed prior to use. Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY.

NMR spectra were obtained on Bruker AC-250 MHz and Avance 200 MHz spectrometers, ^{1}H NMR chemical shifts are referenced to the residual ^{1}H signal in C$_6$D$_6$ (δ 7.16), ^{13}C NMR shifts are referenced to C$_6$D$_6$ (δ 128). The ^{1}H−^{13}C NMR chemical shift correlation experiment was performed using the standard Bruker pulse program XHCORRD. Selected parameters, include 90° and 180° proton pulses = 25.7 and 51.4 μs, 90° and 180° ^{13}C pulses = 5.6 and 11.2 μs, optimized for J(C−H) = 125 Hz, relaxation delay = 3 s, and 64 scans per increment (128 increments). The 2D ^{1}H−^{1}H NOE experiment was performed using the standard Bruker pulse program NOESY. Selected parameters, include 90° proton pulse = 11.7 μs, two dummy scans, increment = 0.001 85 s (128 increments with 32 scans per increment), mixing time = 0.5 s (which was varied by ±4% to suppress zero quantum J-cross-peaks), and relaxation delay = 3 s.

Preparation of [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$]. To a toluene (35 mL) solution of [(^{t}Bu)Al(μ_3-O)]$_6$ (0.5 g, 0.83 mmol) was added AlMe$_3$ (0.83 mmol, 1.08 mL of a 0.77 M solution in toluene). The solution was then stirred at room temperature for 1 h. The resulting solution was used directly in polymerization studies (2.3 × 10^{-2} mol·L^{-1} in alumoxane, i.e., 0.16 mol·L^{-1} in Al). ^{1}H and ^{13}C NMR characterization of a sample prepared in toluene-d_8 is given in Table 1. Removal of all volatiles in vacuo resulted in the isolation of a white solid. The ^{1}H and ^{13}C NMR (toluene-d_8) of this solid is identical to the isomer mixture prior to removal of the solvent. Attempts to recrystallize resulted in a similar mixture of isomers **A** and **B**. Anal. Calcd for C$_{27}$H$_{63}$Al$_7$O$_6$: C, 48.2; H, 9.44. Found: C, 48.3 ±0.4; H, 9.50 ±0.08. MS (EI, %): m/z 672 (M$^+$, 5), 616 (M$^+$ − CH$_2$C=CMe$_2$, 10), 114 [(^{t}Bu)AlMe$_2$, 100], 57 (^{t}Bu, 100).

Preparation of [(^{t}Bu)Al(μ_3-O)]$_6$/(AlMe$_3$)$_6$. To a toluene (50 mL) solution of [(^{t}Bu)Al(μ_3-O)]$_6$ (0.5 g, 0.83 mmol) was added AlMe$_3$ (4.98 mmol, 6.5 mL, 0.77 M in toluene). The solution was then heated to 75 °C for 100 min. The resulting solution was used directly in polymerization studies (1.47 × 10^{-2} mol·L^{-1} in alumoxane, i.e., 0.176 mol·L^{-1} in Al). ^{1}H and ^{13}C NMR characterizations were performed on samples prepared in C$_6$D$_6$ and toluene-d_8. Removal of the volatiles resulted in the formation of a colorless oil.

Polymerization Procedure. In an argon atmosphere glovebox toluene (4 mL) and 1,5-hexadiene (2.0 mL) were placed into a 30 mL glass serum bottle along with a magnetic stir bar. To this was added a weighed quantity of the alumoxane activator (see Table 1), and [Me$_2$C(Cp)(Flu)]ZrBz$_2$ (0.04 mL of 0.01 M toluene solution, 4.0 × 10^{-7} mol) was added. The serum bottle was sealed and removed from the glovebox. After stirring at room temperature for 24 h, the serum bottle was opened and an excess of MeOH added. The polymer produced was separated and washed with MeOH (2 × 10 mL) and HCl$_{aq}$ (2 × 5 mL). After drying under vacuum, the mass was determined. The poly-1,5-hexadiene was characterized by ^{1}H NMR and TG/DTA in comparison to a reference sample. A summary of the various alumoxane activators employed along is given in Table 2.

Investigations of the Influence of AlMe$_3$ on Polymerization Activity. Polymerization reactions were carried out in the manner described above, except a weighed quantity of AlMe$_3$ (see Table 2) was added prior to the alumoxane (1.4 × 10^{-4} mol Al). The [Me$_2$C(Cp)(Flu)]ZrBz$_2$ (0.04 mL of 0.01 M toluene solution, 4.0 × 10^{-7} mol) was added after the alumoxane and the AlMe$_3$ had been allowed to react for 1−10 min at room temperature. A summary of the various alumoxane activators employed along with the quantities of AlMe$_3$ is given in Table 3.

Investigations of the Influence of Al(^{i}Bu)$_3$ on Polymerization Activity. Polymerization reactions were carried out in the manner described above, except a weighed quantity of Al(^{i}Bu)$_3$ (see Table 3) was added prior to the alumoxane (see Table 3). The [Me$_2$C(Cp)(Flu)]ZrBz$_2$ (0.04 mL of 0.01 M toluene solution, 4.0 × 10^{-7} mol) was added after the alumoxane and the Al(^{i}Bu)$_3$ had been allowed to react for 1−10 min at room temperature. A summary of the various alumoxane activators employed along with the quantities of Al(^{i}Bu)$_3$ is given in Table 4.

Reaction of [Al$_7$(μ_3-O)$_6$(^{t}Bu)$_6$Me$_3$] with Cp$_2$Zr(CD$_3$)$_2$. In a 5 mm NMR tube solutions of AlMe$_3$ (3.0 × 10^{-5} mol, 0.3 mL, 0.1 M in C$_7$D$_8$) and [(^{t}Bu)Al(μ_3-O)]$_6$ (3.0 × 10^{-5} mol, 0.3 mL, 0.1 M in C$_7$D$_8$) were allowed to react for 3 h, after which time a solution of Cp$_2$Zr(CD$_3$)$_2$ (1.5 × 10^{-5} mol, 0.15 mL, 0.1 M in C$_7$D$_8$) was added. ^{1}H NMR spectra were obtained immediately and after 3 h. To verify catalytic activity, 1,5-hexadiene was added (0.15 mL, 1.26 × 10^{-3} mol).

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(36) We note that the activity of commercial MAO is highly dependent on the source, age, and the relative content of both AlMe$_3$ and insoluble gel. The samples used herein were freshly prepared by Albemarle Corporation and used within two weeks of receipt.