3558 *Organometallics* **2003,** *22,* 3558−3565

# Analysis of Metallocene−Methylalumoxane Methide Transfer Processes in Solution Using a $^{19}$F NMR Spectroscopic Probe

Eric J. Hawrelak and Paul A. Deck*

*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061-0212*

*Received March 7, 2003*

The metallocenes $(C_6F_5C_5H_4)CpZrMe_2$ (**1**, Cp = $C_5H_5$) and $(C_6F_5C_5H_4)_2MMe_2$ (**2a**, M = Zr; **2b**, M = Hf) were treated with $B(C_6F_5)_3$ and, separately, with commercial methylalumoxane (MAO, depleted of excess $Me_3Al$). The ensuing methide transfer reactions were followed by $^{19}$F NMR. Spectra of the "activated" species obtained using MAO and excess $B(C_6F_5)_3$ were strikingly similar, suggesting that similar "cation-like" species are formed using either organo-Lewis acid, and the MAO-activated species were tentatively formulated as $(C_6F_5C_5H_4)CpZrMe^+\ Me[AlMeO]_n^-$ and as $(C_6F_5C_5H_4)_2MMe^+\ Me[AlMeO]_n^-$ (M = Zr, Hf). The relative amount of $L_2MMe_2$ and $[L_2MMe]^+$ species observed in solution was measured as a function of [MAO] and as a function of [M] at constant [MAO]. Results are interpreted in terms of a canonical model in which MAO contains relatively few highly active Lewis acidic sites.

## Introduction

Activation of group 4 metallocene olefin polymerization catalysts using methylalumoxane (MAO) is often described as a Lewis acid−base equilibrium (eqs 1 and 2, L = $\eta^5$-$C_5H_5$ or similar ligand; M = Ti, Zr, or Hf).[1] Using $^{13}$C labeling techniques, Siedle showed that methyl groups exchange among MAO and Zr sites, suggesting that the methide abstraction process (eq 1) is reversible.[2] However, if eq 1 represents a true equilibrium, one would expect to find a constant reaction quotient ($Q \equiv K_{eq}$). Marks and co-workers observed such behavior using well-defined organo-Lewis acids (triarylboranes) as MAO models,[3] and they determined the corresponding equilibrium constants using $^1$H NMR analysis in the slow exchange regime.

$$\underset{\textbf{M}}{L_2MMe_2} + \underset{\textbf{A}}{[AlMeO]_n} \rightleftharpoons \underset{\textbf{C}}{L_2MMe^+Me[AlMeO]_n^-} \qquad (1)$$

$$Q = \frac{[\textbf{C}]}{[\textbf{M}][\textbf{A}]} \qquad (2)$$

Metallocene activation with MAO is apparently more complicated.[4] Commercial alumoxanes are ill-characterized mixtures of organoaluminum complexes with varying Lewis acidities.[5−10] Experimental and theoretical studies suggest that particular alumoxane compositions may be either "active" or "dormant".[11−14] The structure of the alumoxane may also aggregate or somehow change upon contact with the metallocene, revealing "latent" Lewis acidic sites.[15,16] Excess $Me_3Al$ present in commercial MAO solution may also play important roles besides adventitious contaminant scavenging, possibly in stabilizing the active catalyst by forming Zr−Al heterobimetallic complexes.[17−22] Finally, most catalytic reactions use metallocene dichlorides, whereas much of the model chemistry has revolved around metallocene dimethyls. The various alkylation, ligand abstraction, and cation stabilization roles of $Me_3Al$ and MAO are difficult to uncouple.

Important quantitative aspects of metallocene activation by MAO also remain poorly understood. Some

---

(1) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434.

(2) Siedle, A. R.; Lamanna, W. M.; Newmark, R. A.; Schroepfer, J. N. *J. Mol. Catal. A Chem.* **1998**, *128*, 257−271.

(3) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772−1784.

(4) Pédoutour, J. N.; Radhakrishnan, K.; Cramail, H.; Deffieux, A. *Macromol. Rapid Commun.* **2001**, *22*, 1095−1123.

(5) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390−392.

(6) Sinn, H. *Macromol. Symp.* **1995**, *97*, 27−52.

(7) Imhoff, D. W.; Simeral, L. S.; Blevins, D. R.; Beard, W. R. *ACS Symp. Ser.* **2000**, *749*, 177−191.

(8) Watanabi, M.; McMahon, C. N.; Harlan, C. J.; Barron, A. R. *Organometallics* **2001**, *20*, 460−467.

(9) Barron, A. R. In *Preparation, Properties, and Technology of Metallocene-Based Polyolefins*; Sheirs, J., Kaminsky, W., Eds.; Wiley: New York, 1999; p 33.

(10) Bryant, P. L.; Harwell, C. R.; Mrse, A. A.; Emery, E. F.; Gan, Z. H.; Caldwell, T.; Reyes, A. P.; Kuhns, P.; Hoyt, D. W.; Simeral, L. S.; Hall, R. W.; Butler, L. G. *J. Am. Chem. Soc.* **2001**, *123*, 12009−12017.

(11) Babushkin, D. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **2002**, *124*, 12869−12873.

(12) Zurek, E.; Ziegler, T. *Organometallics* **2002**, *21*, 83−92.

(13) Zhitao, X.; Vanka, K.; Firman, T.; Michalak, A.; Zurek, E.; Zhu, C.; Ziegler, T. *Organometallics* **2002**, *21*, 2444−2453.

(14) Xu, Z.; Vanka, K.; Firman, T.; Michalak, A.; Zurek, E.; Zhu, C.; Ziegler, T. *Organometallics* **2002**, *21*, 2444−2453.

(15) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465−6474.

(16) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5514−5518.

(17) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634−1637.

(18) Tritto, I.; Li, S. X.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1995**, *28*, 5358−5362.

(19) Tritto, I.; Sacchi, M. C.; Locatelli, P.; Li, S. X. *Macromol. Chem. Phys.* **1996**, *197*, 1537−1544.

(20) Eilertsen, J. L.; Rytter, E.; Ystenes, M. *Vib. Spectrosc.* **2000**, *24*, 257−264.

(21) Rytter, E.; Stovneng, J. A.; Eilertsen, J. L.; Ystenes, M. *Organometallics* **2001**, *20*, 4466−4468.

(22) Babushkin, D. E.; Semikolenova, N. V.; Panchenko, V. N.; Sobolev, A. P.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **1997**, *198*, 3845−3854.

10.1021/om030171n CCC: $25.00
Publication on Web 07/24/2003

useful qualitative trends have been established by examining metallocene/MAO mixtures in solution using NMR spectroscopy.[2,18,23−25] Nuclei such as $^{13}$C, $^{91}$Zr, $^{27}$Al, and $^{11}$B enjoy excellent dispersion but suffer from low sensitivity,[10,26] whereas the reverse is true of $^{1}$H. Interference from alumoxanes at high Al:Zr ratios and exchange broadening have presented problems in both $^{1}$H and $^{13}$C NMR studies of activated metallocenes. Isotopic enrichment of methyl groups offers convenient improvement in $^{13}$C NMR signal intensity, but scrambling of the methyl groups into unenriched MAO (e.g., commercial samples) presents an important source of error in quantitative work.

Qualitatively, however, the dispersion of $^{13}$C is useful in identifying several different species. Using CPMAS NMR techniques, Marks and co-workers showed that the residue remaining after evaporating the solvent from metallocene/MAO solutions is entirely (i.e., [**C**]/[**M**] > 10) activated using an Al:Zr ratio of only 12:1.[27] This result provided some of the earliest evidence that the large Al:Zr ratios used to optimize empirical polymerization activities were not actually required to generate the active "cation-like" intermediates.

Tritto and co-workers analyzed mixtures of $Cp_2Zr(^{13}CH_3)_2$ with either MAO or $B(C_6F_5)_3$ using solution $^{13}$C NMR spectroscopy and assigned well-resolved signals to $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ and $[Cp_2ZrMe]^+$.[28,29] In both cation-like species, the $\delta(^{13}C)$ values for the Zr−Me and Cp ligand were nearly the same whether the counteranion was $MeB(C_6F_5)_3$ or MeMAO. They then examined the distribution of cation-like species varying temperature, concentration, and reactant stoichiometry (Al:Zr ratio). In their study, the dimer $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ was present in significant and varying amounts, and their discussion focused mainly on the effect of concentrations and conditions on monomer−dimer equilibria, confirming earlier reports that dimer formation increased with overall zirconium concentration.[30]

Babushkin and co-workers obtained comparable results using both $^{13}$C NMR and $^{1}$H NMR spectroscopy.[31] On the basis of careful analysis of $\delta_H(C_5H_5)$ as a function of Al:Zr ratio (holding [Al] constant to rule out medium effects), they concluded that MAO may contain a distribution of aluminum acids with varying competence for methide abstraction and that different portions of that distribution are sampled at different values of Al:Zr.

Deffieux and Cramail followed the alkylation and activation of *rac*-$[C_2H_4(Ind)_2]ZrX_2$ (X = Cl, $CH_3$) using solution UV−vis spectroscopy.[4,32] The intense ligand-to-metal charge transfer (LMCT) bands enable reliable relative concentration estimates at low metallocene concentrations, even though the absorptions of different species are not fully resolved. Although their conclusions are qualitative (major species are assigned to broad Al:Zr regimes), they observe complete conversion of *rac*-$[C_2H_4(Ind)_2]ZrMe_2$ to a cationic species in toluene solution when Al:Zr > 150. Mäkelä and co-workers obtained similar results with a series of 2-trialkylsiloxy-substituted bis(indenyl) and bis(tetrahydroindenyl) complexes of zirconium.[33] One particularly interesting aspect of the UV−vis studies is their apparent sensitivity to the presence of chloride, trimethylaluminum, and other species that could be present in practical polymerizations. For example, Cramail and Deffieux observed different species in the activation of $L_2ZrX_2$ type complexes depending on X (Cl or Me),[34] whereas Weiser and Brintzinger observed a common species regardless of the X ligands.[35] Heterobimetallic species derived from $Me_3Al$ such as $[Ind_2Zr(\mu\text{-}Me_2)AlMe_2]^+$, which may increase catalyst lifetimes,[17,21,36] are generally observed when using MAO as the activator but sometimes not when using other alkylalumoxanes.[37] However, with only a few exceptions the UV−vis technique has been limited to conjugated systems such as indenyl complexes (or M = Ti[38]) to avoid interference from MAO in the region 280−330 nm.

Taken together, the complexity of existing spectroscopic and polymerization data convinces us that the development of new approaches to the study of metallocene−alumoxane reactions is warranted. In particular, *quantitative* data arising from analyses *in solution* are still rather scarce. We now report[39] that $C_6F_5$ substituents on the metallocene ancillary ligands provide strong yet well-resolved $^{19}$F NMR signals corresponding to **M** and **C** (eq 1). We use the relative integrated intensities of these signals to probe this activation model (eq 1) as a function of MAO and metallocene concentrations.

## Results and Discussion

**Precursor Synthesis.** We prepared the $C_6F_5$-substituted metallocenes **1**, **2a** (M = Zr), and **2b** (M = Hf) by standard methods (Scheme 1). Hydrocarbon suspensions of $CH_3Li$ avoid substitution at the *para* positions of the $C_6F_5$ groups, which can be a troublesome side-reaction when ethereal solvents are used. Furthermore, the methylation reactions and subsequent product isolation must be carried out in the dark. Although the

---

(23) Tritto, I.; Li, S. X.; Sacchi, M. C.; Zannoni, G. *Macromolecules* **1993**, *26*, 7111−7115.

(24) Nekhaeva, L. A.; Bondarenko, G. N.; Rykov, S. V.; Nekhaev, A. I.; Krenstel, B. A.; Mar'in, V. P.; Vyshinskaya, L. I.; Khrapova, I. M.; Polonski, A. V.; Korneev, N. N. *J. Organomet. Chem.* **1991**, *406*, 139−146.

(25) Zhang, Z. Y.; Duan, X. F.; Zheng, Y.; Wang, J.; Tu, G. Z.; Hong, S. L. *J. Appl. Polym. Sci.* **2000**, *77*, 890−897.

(26) Komon, Z. J. A.; Rogers, J. S.; Bazan, G. C. *Organometallics* **2002**, *21*, 3189−3195.

(27) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112−1114.

(28) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247−1252.

(29) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1999**, *32*, 264−269.

(30) Beck, S.; Prosenc, M. H.; Brintzinger, H. H.; Goretzki, R.; Herfert, N.; Fink, G. *J. Mol. Catal. A Chem.* **1996**, *111*, 67−79.

(31) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2000**, *201*, 558−567.

(32) Pédeutour, J. N.; Cramail, H.; Deffieux, A. *J. Mol. Catal. A Chem.* **2001**, *174*, 81−87.

(33) Mäkelä, N. I.; Knuuttila, H. R.; Linnolahti, M.; Pakkanen, T. A.; Leskelä, M. A. *Macromolecules* **2002**, *35*, 3395−3401.

(34) Pédeutour, J. N.; Cramail, H.; Deffieux, A. *J. Mol. Catal. A Chem.* **2001**, *176*, 87−94.

(35) Wieser, U.; Brintzinger, H. H. *Organomet. Catal. Olefin Polym.* **2001**, 3−13.

(36) Reddy, S. S.; Shashidhar, G.; Sivaram, S. *Macromolecules* **1993**, *26*, 1180.

(37) Wang, Q.; Song, L.; Zhao, Y.; Feng, L. *Macromol. Rapid Comm.* **2001**, *22*, 1030−1034.

(38) Long, W. P.; Breslow, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 1953−1957.

(39) Preliminary data was presented orally: Deck, P. A.; Thornberry, M. P.; Hawrelak, E. J. *Book of Abstracts*, 220th National Meeting of the American Chemical Society, Washington, DC, Aug 20−24, 2000, Abstract INOR 192.

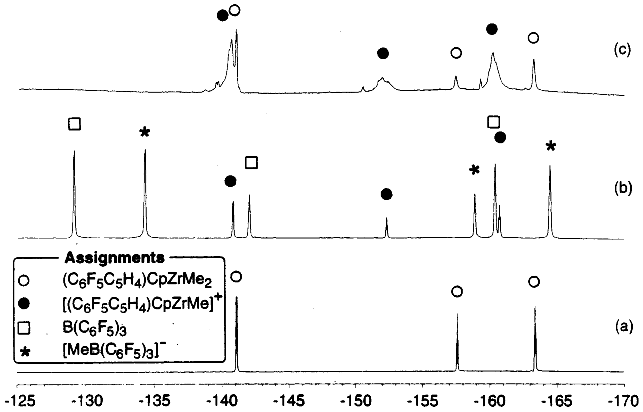
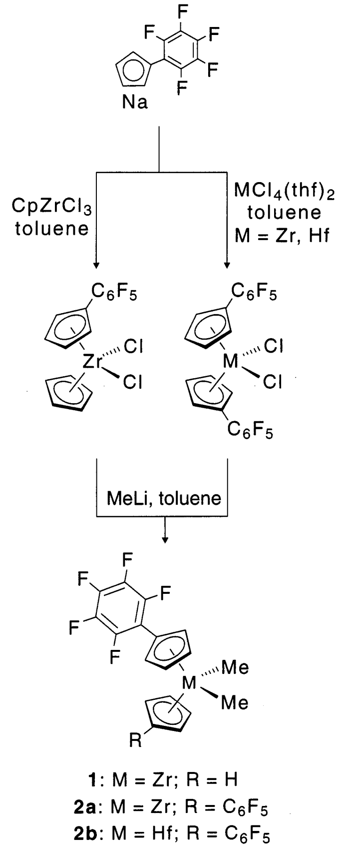


**Figure 1.** $^{19}$F NMR spectra in $C_6D_6$: (a) **1**; (b) **1** + excess $B(C_6F_5)_3$; (c) **1** + MAO.

**Scheme 1**



products, when purified, are not especially photosensitive, methylation reactions carried out under ambient light slowly deposit intractable black solids and give poor yields. The cause of this photodecomposition remains unknown at present, although the possibility of intramolecular CF activation in these complexes has provided us a new line of inquiry.

**Spectroscopic Assignment of Activated Metallocenes.** Figure 1a shows the $^{19}$F NMR spectrum of the arylated zirconocene dimethyl complex (**1**). Upon treatment with a slight excess of the well-defined activator $B(C_6F_5)_3$, **1** is completely converted (eq 3) to the corresponding "cation-like" species **3**.[40-42] The $^{19}$F NMR spectrum of **3** (Figure 1b) shows the expected downfield shifts in each of the three $C_6F_5$ signals as the metallocene becomes more electron-deficient. The conversion of **2a**/**2b** to **4a**/**4b** (eq 4) is analogous. An isolated analytical sample of **4a** shows the expected equally integrating sharp Zr−Me (0.19 ppm) and broadened B−Me (0.34 ppm) signals in the $^1$H NMR spectrum and the 2:3 ratio of $C_6F_5$ groups in the $^{19}$F NMR spectrum.[40]

$$\mathbf{1} + B(C_6F_5)_3 \rightleftharpoons [(C_6F_5C_5H_4)CpZrMe]^+[MeB(C_6F_5)_3]^- \ (\mathbf{3}) \quad (3)$$

$$\mathbf{2a/2b} + B(C_6F_5)_3 \rightleftharpoons [(C_6F_5C_5H_4)_2MMe]^+[MeB(C_6F_5)_3]^- \ (\mathbf{4a},\ M = Zr;\ \mathbf{4b},\ M = Hf) \quad (4)$$

Interestingly, when metallocene **1** in $C_6D_6$ is treated with about 0.5 equiv of $B(C_6F_5)_3$, signals assigned to the metallocene dimethyl (**1**) and the monomeric cation (**3**) are observed in the $^1$H and $^{19}$F NMR spectra along with signals assigned to a methyl-bridged dinuclear complex (eq 5). The concentration ratio of the monometallic contact ion pair **3** to the dinuclear species was 3:1 at $[Zr]_{total}$ = 30 mM. Starting with similar concentrations of $Cp_2ZrMe_2$, Beck and Brintzinger found that treatment with 0.5 equiv of $B(C_6F_5)_3$ led to a mixture that was much richer in the dinuclear cationic species.[30] This trend extends to the disubstituted metallocene (**2a**). When a 30 mM solution of **2a** was treated with 0.5 equiv of $B(C_6F_5)_3$, only unreacted **2a** and the monometallic contact ion pair **4a** were observed. *$C_6F_5$ substituents strongly attenuate the tendency to form these dinuclear cationic species*: the monometallic cation is more Lewis acidic, but the neutral dimethyl complex is also less Lewis basic, and on balance the reaction shown in eq 5 lies more toward the left.

$$L_2ZrMe_2 + [L_2ZrMe]^+[MeB(C_6F_5)_3]^- \rightleftharpoons [L_2ZrMe\}_2(\mu\text{-}Me)]^+[CH_3B(C_6F_5)_3]^- \quad (5)$$

When **1** is treated instead with MAO, the $^{19}$F chemical shifts observed (Figure 1c) for the putative zirconocenium aluminate (**5**) are nearly identical to those observed in the "well-defined" monometallic species (**3**). From this observation, we infer that **1** reacts with MAO according to eq 6. We further infer that the cationic portions of **3** and **5** are structurally analogous, within the sensitivity of this $^{19}$F NMR probe. Similarly, **2a** and **2b** react with MAO to afford **6a** and **6b**, respectively (eq 7), and the $^{19}$F NMR spectra of **4a**/**4b** (cationic portion) and **6a**/**6b** are respectively coincident. Spectra are provided in the Supporting Information.

$$\mathbf{1} + MAO \rightleftharpoons [(C_6F_5C_5H_4)CpZrMe]^+[MeMAO]^- \ (\mathbf{5}) \quad (6)$$

$$\mathbf{2a/2b} + MAO \rightleftharpoons [(C_6F_5C_5H_4)_2MMe]^+[MeMAO]^- \ (\mathbf{6a},\ M = Zr;\ \mathbf{6b},\ M = Hf) \quad (7)$$

---

(40) Yang, X. M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625.

(41) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031.

(42) Siedle, A. R.; Newmark, R. A. *J. Organomet. Chem.* **1995**, *497*, 119−125.

Broadening in the $^{19}$F NMR spectra of **5**, **6a**, and **6b** is attributed to two phenomena. First, there is a distribution of aluminate "counterion" structures, because MAO is, after all, a mixture of compounds. In some spectra, features appear to emerge from these broad bands. Potentially, reactions of **1** and **2a**/**2b** with well-defined aluminum activators could enable us to further assign these bands; these studies are underway. Importantly, the spectra do not have any signals corresponding to $\mu$-Me-bridged dimeric cations. Well-known fluxional processes can also contribute to line broadening.[3,40,43] Such broadening can be seen in the signals assigned to **1** in Figure 1c and is attributed to the dynamic nature of the abstraction equilibrium (eq 6). In an EXSY experiment,[44] strong off-diagonal signals correlated respective signals assigned to **1** and **5**, indicating chemical exchange in eq 6.

When a large excess of $Me_3Al$ was added to a solution of the MAO-activated metallocenium complex (**6a**), no change was observed in the $^{19}$F NMR spectrum. If $Me_3Al$ adducts represented only part of an equilibrating mixture, then we would expect to see the band shape assigned to **6a** to change with $[Me_3Al]$.[17,28,31,45] Nevertheless, our "$Me_3Al$-depleted" MAO sample almost certainly contains some residual $Me_3Al$.[7,46−48] Therefore we concede that the possibility remains that $Me_3Al$ adducts account for all of our activated species (**5**, **6**) *and* that the $^{19}$F chemical shift is completely insensitive to the adduct formation. Addition of $Me_3Al$ to a solution of the $B(C_6F_5)_3$-activated model compound **4a** resulted in rapid decomposition, probably due to methyl−aryl exchange between Al and B centers.[49−51] Additional study of the reactions of $C_6F_5$-substituted metallocenes with simple aluminum alkyls and aluminum alkyl halides is underway in our laboratories.

**Concentration Studies.** Titration of a toluene solution of either **1** or **2a**/**2b** with MAO at 25 °C led to a monotonic decrease in the intensity of the signals assigned to **1** or **2a**/**2b** and a corresponding increase in the signals assigned to **5** and **6a**/**6b**, respectively. In our samples, the starting concentrations ($[\mathbf{1}]_o$ $[\mathbf{2}]_o$, and $[MAO]_o$) were known, and the equilibrium ratios $[\mathbf{1}]$:$[\mathbf{5}]$ and $[\mathbf{2}]$:$[\mathbf{6}]$ were obtained from integration of the well-resolved *para* regions of the $^{19}$F NMR spectra. These data enabled us to calculate a reaction quotient ($Q$) according to eq 2. Importantly, if $Q$ were constant with respect to $[metallocene]_o$, $[MAO]_o$, and time, we could infer that $Q$ is an equilibrium constant.

While $[\mathbf{M}]_o$ was fixed at a nominal concentration of 10 mM, we determined $Q$ at the widest range of MAO concentrations that would still allow us to integrate signals assigned to both forms of the metallocene (**M** and **C**). The results (Figure 2) give rise to three general findings. First, $Q$ is within the range $0.1 < Q < 50$. Tritto and co-workers observed (using $^{13}$C NMR) a reaction quotient of 4.0 for methide abstraction from $Cp_2TiCH_3Cl$ (eq 8) at −20 °C.[52] Here it should be noted that our calculation of [MAO] uses a formula weight of 58 g mol$^{-1}$, corresponding to the arbitrary [AlMeO] "repeat unit," and then simply [MAO] = [Al]. Actual number-averaged molecular weights of MAO samples are typically 400 or higher and are subject to complex ligand disproportionation pathways as samples age.[7,48]

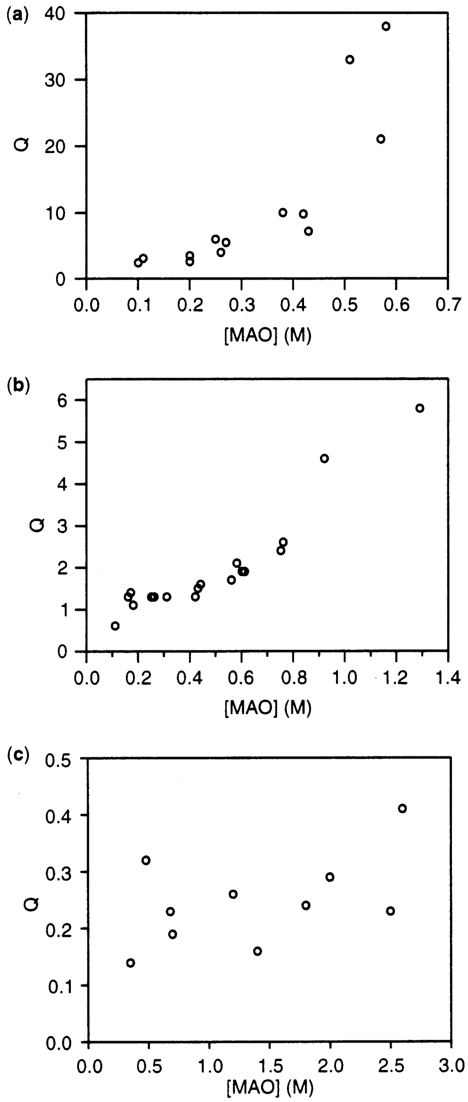


**Figure 2.** Plot of $Q$ (calculated by eq 2) vs [MAO]: (a) **1** + MAO; (b) **2a** + MAO; (c) **2b** + MAO.

$$Cp_2TiMe_2 + MAO{\cdot}AlMe_2Cl \rightarrow [Cp_2TiCl]^+[MAO{\cdot}AlMe_3]^- \quad (8)$$

Using 58 g mol$^{-1}$ as the formula weight for MAO allows direct comparison of $Q$ to practical Al:Zr ratios. Useful catalyst concentrations are micromolar or even less (i.e., $[\mathbf{C}] \approx [\mathbf{M}]_o \approx 10^{-6}$ M). On the basis of typical amounts of MAO reported to optimize catalytic activity, a large "excess" of MAO (e.g., $[\mathbf{A}] \approx 1000\ [\mathbf{M}]_o \approx 10^{-3}$ M) is required to keep the catalyst mostly in its active form (e.g., $[\mathbf{C}]/[\mathbf{M}] \approx 10$). These quantities lead to a very rough estimate of about $10^4$ for Q. In polymerization

---

(43) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301−308.

(44) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935−967.

(45) Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1998**, *199*, 1451−1457.

(46) Resconi, L.; Bossi, S. *Macromolecules* **1990**, *23*, 4489−4491.

(47) Barron, A. R. *Organometallics* **1995**, *14*, 3581−3583.

(48) Imhoff, D. W.; Simeral, L. S.; Sangokoya, S. A.; Peel, J. H. *Organometallics* **1998**, *17*, 1941−1945.

(49) Klosin, J.; Roof, G. R.; Chen, E. Y. X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684−4686.

(50) Lee, C. H.; Lee, S. J.; Park, J. W.; Kim, K. H.; Lee, B. Y.; Oh, J. S. *J. Mol. Catal. A Chem.* **1998**, *132*, 231−239.

(51) Kim, J. S.; Wojcinski, L. M.; Liu, S. S.; Sworen, J. C.; Sen, A. *J. Am. Chem. Soc.* **2000**, *122*, 5668−5669.

reactions, especially when large volumes of solvent are used, one can never be sure how much alumoxane is consumed scavenging impurities or "reactivating" dormant species. Some silica-supported metallocene catalysts are reported to be fully activated at Al:Zr ratios well below 100, and as we recalled earlier, Marks found complete activation at Al:Zr < 15.[53−55]

The second general finding arising from Figure 2 is that a comparison of the reaction quotients for **1** ($Q \approx 3.5$) and **2a** ($Q \approx 1.3$) at a fixed alumoxane concentration ([MAO] ≈ 0.2 M) is consistent with our prior observations that $C_6F_5$ substituents are strongly electron-withdrawing,[56−60] destablizing the "cation-like" form (**C**) more in the case of **2a**. Comparison of the reaction quotients for **2a** and **2b** at a fixed alumoxane concentration ([MAO] ≈ 0.2 M) is consistent with Marks's observation that abstraction of methide from hafnocene dimethyl is less exothermic than abstraction from zirconocene dimethyl.[3]

Our third finding is that *Q increases* with increasing [MAO] (Figure 2) for metallocenes **1** and **2a**. MAO is arguably more polar than the reaction solvent (toluene), and aggregation of MAO around the ion-paired species as a diffuse "solvent effect" would stabilize **C** relative to **M** with increasing [MAO].[61,62] However, we expected a "solvent effect" to be more gradual and to influence methide abstraction from the three metallocenes similarly. However, Figure 2 shows that the *Q* varies dramatically with [MAO] and that the effect of [MAO] on *Q* is more pronounced for **1** (a factor of 10 over 0.1 M < [MAO] < 0.6 M, Figure 2a) than for **2a** (a factor of 5 over 0.1 M < [MAO] < 1.3 M, Figure 2b). The value of *Q*, within experimental error, is constant for **2b** over the range 0.1 < [MAO] < 3.0 M (Figure 2c). The spectra obtained for the hafnium complex **2b** showed low concentrations of **6b**, even when [MAO] was close to saturation. There is significant error in the determination of *Q* for **2b**. However, this result suggests that rational metallocene design can allow us to probe the limits of the methide-abstraction capability of MAO. Methide abstraction from **2b** is not discussed further.

We investigated the possibility that more than one MAO "molecule" may be required to abstract a methyl group from a metallocene or that MAO forms discreet aggregates with the activated "cationic" form of the metallocene (**C**). Babushkin and Brintzinger recently characterized a metallocene−alumoxane complex using pulsed-field-gradient NMR techniques to estimate hydrodynamic radii and concluded that each metallocene is associated with an alumoxane species having, on average, about 50 aluminum atoms. Still it is not known if all of those aluminum atoms are part of a single covalent framework or if several smaller alumoxane fragments might be aggregated. We attempted to model our data by introducing the number of MAO molecules required as a parameter (eq 9). Varying the aggregation number (0 < **a** < 2.0) made *Q* constant with [MAO] at high [MAO] but not at low [MAO]. In an earlier version of this paper, a reviewer pointed out that we might lose a more significant fraction of [MAO] to reaction with adventitious moisture at low [MAO]. However $CH_4$ signals ($\delta_H = 0.15$ ppm) are not observed in the $^1$H NMR spectra of these mixtures, suggesting that in situ hydrolysis of MAO is negligible. We conclude that we cannot rule out the possibility that multiple Al sites are involved in the abstraction process, but that theory just does not fit our data *better* than interacting with only one reactive Al site at a time (**a** = 0).

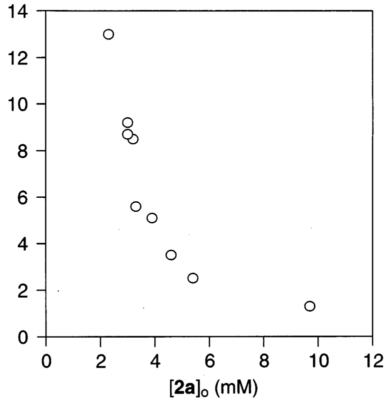


**Figure 3.** Plot of *Q* (calculated by eq 2) vs [**2a**].

$$\mathrm{Cp'_2MMe_2} + (\mathbf{a}+1)[\mathrm{AlMeO}]_n \rightleftharpoons \mathrm{Cp'_2MMe^+Me[AlMeO]_n^-{\cdot}\mathbf{a}[AlMeO]_n} \quad (9)$$

To rule out medium effects, we next conducted a separate series of experiments in which we held $[\mathrm{MAO}]_o$ at a fixed value (0.35 M) and varied the initial metallocene concentration, $[\mathbf{2a}]_o$, from about 2−10 mM (limited by our ability to obtain reasonable integrals). *Q* was calculated according to eq 2, and the results are plotted in Figure 3. In concert with Babushkin's finding,[31] we observed a decrease in *Q* with increasing $[\mathbf{1}]_o$. Moreover, we found that the concentration of the "cation-like" species, [**C**], is roughly constant for all experiments, suggesting that even after the first aliquot of metallocene is added (Al:Zr = 70:1), all of the "active" aluminum sites are already titrated.

**Temperature Effects.** A solution of **2a** (nominally 30 mM with Al:Zr ≈ 35) was analyzed using $^{19}$F NMR spectroscopy at several temperatures ranging from 50 to −80 °C. Between 50 and −40 °C, the percent of metallocene in the cation-like form (**6a**) was constant (within ±10%). Below −40 °C, a decrease in the apparent concentration of **6a** was noted, but we disregarded these data because significant gelation of the sample had also occurred. Tritto and co-workers had reported a dramatic decrease in the "proportion" of cationic

---

(52) Tritto, I.; Sacchi, M. C.; Sanxi, L. *Macromol. Rapid Commun.* **1994**, *15*, 217−223.

(53) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347−1376.

(54) Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377−1390.

(55) Jezequel, M.; Dufaud, V.; Ruiz-Garcia, M. J.; Carrillo-Hermosilla, F.; Neugebauer, U.; Niccolai, G. P.; Lefebvre, F.; Bayard, F.; Corker, J.; Fiddy, S.; Evans, J.; Broyer, J. P.; Malinge, J.; Basset, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 3520−3540.

(56) Deck, P. A.; Jackson, W. F.; Fronczek, F. R. *Organometallics* **1996**, *15*, 5287−5291.

(57) Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 327−333.

(58) Thornberry, M. P.; Slebodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 5352−5369.

(59) Thornberry, M. P.; Slebodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2001**, *20*, 920−926.

(60) Maldanis, R. J.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **2000**, *599*, 107−111.

(61) Vizzini, J. C.; Chien, J. C. W.; Babu, G. N.; Newmark, R. A. *J. Polym. Sci. Polym. Chem.* **1994**, *32*, 2049−2056.

(62) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128−6129.

products when $Cp_2ZrMe_2$ was combined with 10 equiv of MAO and the temperature lowered from 25 °C to −78 °C,[28] corroborating an earlier study using a mixture of $Cp_2Ti^{13}CH_3Cl$ and 10 equiv of MAO.[23] Their total aluminum concentrations were 0.7 M, whereas ours were marginally higher (1.0 M). In their earlier report they also noted that solutions of MAO are “quite viscous, especially at very low temperatures”.

We now propose a model to account for our observations. First, MAO comprises aluminum sites having a distribution of Lewis acidities, and the number of acidic sites that are “competent” to abstract methide from the metallocene is relatively small. Thus, when a fixed amount of MAO reacts with a small amount of **1**, there are enough “competent” sites to generate an appreciable fraction of cationic metallocene. However, additional **1** does not generate much additional cationic metallocene, because the most reactive alumoxane sites are already consumed (titrated). Thus, the apparent $Q$ is described by a function that is approximately reciprocal in the metallocene concentration (Figure 3). The same concept could also rationalize the data in Figure 2. At low [MAO], there are only enough “competent” Lewis acidic sites to activate a small fraction of the metallocene. As [MAO] increases, the number of “competent” sites and the concentration of cationic metallocene also increase proportionally. The effect on eq 2 is to increase [**C**] in proportion to [**A**], but the concomitant decrease in [**M**] raises $Q$. From Figure 2 it is also clear that the fraction of “competent” sites is metallocene-dependent, such that only alumoxane sites that are more acidic than the corresponding activated metallocenium species are “competent”. The more Lewis basic metallocene **1** samples a different fraction of acidic sites than does **2a**. Metallocene **2b** may be sufficiently electron-deficient to engage in a more even-handed equilibrium with perhaps only a single type of alumoxane Lewis acidic site, rationalizing the nearly constant value of $Q$ observed for **2b** at various MAO concentrations (Figure 2c). The temperature-independence of $Q$ is also consistent with a model in which a small number of highly acidic sites are “titrated” by the metallocene. The “equilibrium constant” for those sites is so high that the change in temperature does not have a measurable effect. Yet, the activation must still be a dynamic equilibrium to have observed off-diagonal signals in the EXSY spectrum. In the latter two aspects, the behavior of $B(C_6F_5)_3$ presents a good model. We concede that our model is speculative and that additional experimentation will be needed to test it further. We are also presently working to understand the complex reaction pathways that occur when a metallocene dichloride is treated with methylalumoxane. Preliminary results are qualitatively consistent with the UV−vis spectroscopic studies cited above.

**Structural Data.** We have not yet been able to obtain crystal structures of any of our $B(C_6F_5)_3$-activated metallocenium complexes. Chiefly we want to know if there are any $F_{ortho}\cdots Zr$ interactions. A crystal structure of **2b** (to be reported elsewhere) shows no F···Zr interactions. However, in related work still underway, we have found that 3-(pentafluorophenyl)indene and (pentafluorophenyl)cyclopentadiene undergo regioselective *ortho* C−F substitution by $NMe_2$ upon treatment with $Ti(NMe_2)_4$, presumably by intramolecular substitution in putative $LTi(NMe_2)_3$ intermediates. A $^{19}F$ NMR spectrum of **4a** at −80 °C showed rapid rotation of the $C_6F_5$ groups, indicating that a $F_{ortho}\cdots Zr$ interaction, if present, is not strong enough to impede that dynamic process. We have also found that **1** and **2a** are active catalysts for homopolymerization of ethylene and copolymerization of ethylene and 1-hexene, whereas strong intramolecular $F_{ortho}\cdots Zr$ coordination might be expected to exert a poisoning effect. The polymerization activity is not as high as $Cp_2ZrCl_2$, but ordinary substituent trends could account for that decrease.[60,63−65] These polymerization data will be reported elsewhere.

## Experimental Section

**General Considerations.** All manipulations were carried out using standard nitrogen-atmosphere techniques. MeLi was purchased from Aldrich as a solution in diethyl ether and dried under high vacuum ($3 \times 10^{-5}$ Torr) at 60 °C. For these procedures, it is important to remove as much ether as possible. MAO was received from Albemarle as a 10% toluene solution, filtered, and dried under high vacuum ($3 \times 10^{-5}$ Torr) for 15 h to remove “free” trimethylaluminum. The same sample of MAO was used for all the experiments described here. $B(C_6F_5)_3$ was obtained as a gift from Albemarle, sublimed (120 °C, $5 \times 10^{-6}$ Torr), recrystallized from hexanes, and found be 99+% pure according to $^{19}F$ NMR spectroscopy. $[(C_6F_5)C_5H_4]_2ZrCl_2$ and $Na[(C_6F_5)C_5H_4]$ were prepared according to our own methods.[56] $CpZrCl_3(DME)$ was prepared according to the method of Lund and Livinghouse.[66] NMR spectra were recorded on a Varian U-400 instrument at 22 °C. $^{19}F$ NMR spectra are referenced to external $C_6F_6$ in $CDCl_3$ at −163.0 ppm. Elemental microanalyses were performed by Oneida Research Services (Whitesboro, NY) or Desert Analytics (Tucson, AZ).

**(Pentafluorophenyl)zirconocene Dichloride.** A mixture of $CpZrCl_3(dme)$ (1.50 g, 4.25 mmol), $Na[(C_6F_5)C_5H_4]$ (1.10 g, 4.33 mmol), and toluene (400 mL) was stirred at 110 °C for 2 h. The hot mixture was filtered, and the precipitate was rinsed with an additional 100 mL of hot toluene. The yellow filtrate was cooled to 25 °C, and the resulting crystalline product was collected on a filter, washed with hexanes, and dried under vacuum to afford 1.47 g (3.21 mmol, 76%) of a yellow crystalline solid. $^1H$ NMR ($C_6D_6$): $\delta$ 6.45 (m, 2 H), 5.89 (s, 5 H), 5.75 (m, 2 H). $^{19}F$ NMR ($C_6D_6$): $\delta$ −140.06 (m, 2 F), −155.18 (t, $^3J$ = 22 Hz, 1 F), −163.14 (m, 2 F). Anal. Calcd for $C_{16}H_9Cl_2F_5Zr$: C, 41.93; H, 1.98. Found: C, 42.05; H, 1.89.

**(Pentafluorophenyl)zirconocene Dimethide (1).** A mixture of $[(C_6F_5)C_5H_4]CpZrCl_2$ (500 mg, 1.09 mmol), methyllithium (480 mg, 22 mmol), and toluene (20 mL) was stirred at 25 °C in the dark for 18 h. The solvent was evaporated, and the residue was recrystallized from 20 mL of hexanes to afford 391 mg (0.94 mmol, 86%) of colorless crystals. $^1H$ NMR ($C_6D_6$): $\delta$ 6.29 (m, 2 H), 5.70 (s, 5 H), 5.58 (m, 2 H), −0.27 (s, 6 H). $^{19}F$ NMR ($C_6D_6$): $\delta$ −141.08 (m, 2 F), −157.59 (t, $^3J$ = 22 Hz, 1 F), −163.36 (m, 2 F). Satisfactory elemental analysis could not be obtained in repeated attempts. $^1H$ and $^{19}F$ NMR spectra are included (Figures S1 and S2 in the Supporting Information) as evidence of substantial bulk purity.

**1,1′-Bis(pentafluorophenyl)zirconocene Dimethide (2a).** A mixture of $[(C_6F_5)C_5H_4]_2ZrCl_2$ (1.00 g, 1.60 mmol), methyl-

---

(63) Mohring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29.

(64) Mohring, P. C.; Coville, N. J. *J. Mol. Catal. A Chem.* **1995**, *96*, 181−195.

(65) Mohring, P. C.; Vlachakis, N.; Grimmer, N. E.; Coville, N. J. *J. Organomet. Chem.* **1994**, *483*, 159−166.

(66) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426−2427.

lithium (700 mg, 32 mmol), and toluene (35 mL) was stirred at 25 °C in the dark for 18 h. The solvent was evaporated, and the residue was recrystallized from 35 mL of hexanes to afford 770 mg (1.32 mmol, 82%) of colorless crystals. $^1$H NMR ($C_6D_6$): $\delta$ 6.32 (m, 4 H), 5.60 (m, 4 H), −0.39 (s, 6 H). $^{19}$F NMR ($C_6D_6$): $\delta$ −140.92 (m, 4 F), −156.95 (t, $^3J$ = 24 Hz, 2 F), −163.11 (m, 4 F). Satisfactory elemental analysis could not be obtained in repeated attempts. $^1$H and $^{19}$F NMR spectra are included (Figures S3 and S4 in the Supporting Information) as evidence of substantial bulk purity.

**1,1′-Bis(pentafluorophenyl)hafnocene Dichloride.** A mixture of $HfCl_4(THF)_2$ (1.50 g, 3.23 mmol), sodium (pentafluorophenyl)cyclopentadienide (1.72 g, 6.78 mmol), and toluene (400 mL) was stirrred at 110 °C for 2 h. The hot mixture was filtered, and the filter was washed with 50 mL of additional hot toluene. Cooling the yellow filtrate to 25 °C afforded a crystalline product, which was collected on a filter, washed with hexane, and dried under vcuum to afford 1.51 g (2.12 mmol, 66%) of pure $[(C_6F_5)C_5H_4]_2HfCl_2$. $^1$H NMR ($C_6D_6$): $\delta$ 6.41 (m, 4 H), 5.73 (m, 4 H). $^{19}$F NMR ($C_6D_6$): $\delta$ −140.13 (d, 4 F), −154.76 (t, 2 F), −162.93 (m, 4 F). Anal. Calcd for $C_{22}H_8Cl_2F_{10}Hf$: C, 37.13; H, 1.13. Found: C, 37.79; H, 1.13.

**1,1′-Bis(pentafluorophenyl)hafnocene Dimethide (2b).** A mixture of $[(C_6F_5)C_5H_4]_2HfCl_2$ (1.00 g, 1.41 mmol), methyllithium (620 mg, 28 mmol), and toluene (35 mL) was stirred at 25 °C in the absence of light for 18 h. Toluene was evaporated, and the residue was extracted with 35 mL of warm hexane. The mixture was filtered, and the filtrate was concentrated and cooled to afford 508 mg (0.76 mmol, 54%) of pure **2b**. $^1$H NMR ($C_6D_6$): $\delta$ 6.26 (m, 4 H), 5.53 (m, 4 H), −0.59 (s, 6 H). $^{19}$F NMR ($C_6D_6$): $\delta$ −141.04 (m, 4 F), −156.85 (tt, 2 F), −163.81 (m, 4 F). Anal. Calcd for $C_{24}H_{14}F_{10}Hf$: C, 42.97; H, 2.10. Found: C, 42.78; H, 2.05.

**Solution Observation of "Cation-Like" Species ($C_6F_5C_5H_4$)CpZrMe$^+$MeB($C_6F_5$)$_3^-$ (3) and ($C_6F_5C_5H_4$)$_2$ZrMe$^+$MeB($C_6F_5$)$_3^-$ (4).** In a resealable (J-Young) NMR tube, a solution of **1** and $B(C_6F_5)_3$ (slightly more than 1 equiv) was prepared in $C_6D_6$. NMR spectra showed that conversion to **3** was complete, with no remaining **1** but some unreacted $B(C_6F_5)_3$. Data for **3**: $^1$H NMR ($C_6D_6$): $\delta$ 6.20 (br s, 1 H), 5.85 (br s, 1 H), 5.49 (m, 2 H), 5.48 (s, 5 H), 0.23 (broad, unsymmetrical singlet, 6 H). $^{19}$F NMR ($C_6D_6$): $\delta$ −134.31 (m, 6 F), −140.82 (m, 2 F), −152.30 (t, $^3J$ = 21 Hz, 1 F), −158.89 (m, 3 F), −160.72 (m, 2 F), −164.45 (m, 6 F). The same procedure was used to convert **2a** to **4a**. Data for **4a**: $^1$H NMR ($C_6D_6$): $\delta$ 6.32 (br s, 2 H), 5.95 (br s, 2 H), 5.57 (m, 4 H), 0.33 (br s, 3 H, $BCH_3$), 0.18 (s, $ZrCH_3$). $^{19}$F NMR ($C_6D_6$): $\delta$ −134.54 (m, 6 F), −140.54 (m, 4 F), −151.64 (t, $^3J$ = 21 Hz, 2 F), −158.71 (m, 3 F), −160.53 (m, 4 F), −164.41 (m, 6 F). The same procedure was used to convert **2b** to **4b**, except that toluene-$d_8$ was used, and the NMR spectra were collected at −30 °C; otherwise the signals were too broad to assign. Data for **4b**: $^1$H NMR (toluene-$d_8$): $\delta$ 6.20 (br s, 2 H), 5.78 (m, 2 H), 5.48 (m, 4 H, two coincident Cp-H signals), 0.64 (br s, 3 H, B−$CH_3$), −0.08 (br s, 3 H, Hf−$CH_3$). $^{19}$F NMR (toluene-$d_8$): $\delta$ −134.50 (m, 6 F), −140.00 (m, 4 F), −151.72 (t, $^3J$ = 22 Hz, 2 F), −158.15 (m, 3 H), −160.31 (m, 4 F), −164.02 (m, 6 F).

**Observation of [{[$C_6F_5C_5H_4$)CpZrMe}$_2$($\mu$-Me)]$^+$[$CH_3B$($C_6F_5$)$_3$]$^-$.** In a resealable J-Young NMR tube, a solution of **1** (29 mM) and $B(C_6F_5)_3$ (14 mM) was prepared in $C_6D_6$. $^1$H and $^{19}$F NMR analyses showed unreacted **1** (50% of Zr), mononuclear contact ion pair **3** (30% of Zr), and a new set of signals accounting for 20% of the Zr present. In the $^1$H NMR spectrum most of the signals were obscured by signals arising from **1** and **3**. Only one of the Cp-H signals was well-resolved at 6.42 ppm (2 H). A signal at −1.00 ppm was assigned to the $\mu$-$CH_3$ group (br s, 3 H). On the basis of integration data we conclude that the terminal $CH_3$ signal coincides with the signal arising from the $ZrMe_2$ group of **1** at −0.27 ppm. Other data for the dinuclear complex: $^{19}$F NMR ($C_6D_6$): $\delta$ −132.5 (m, 6 F, *ortho*-CF of $MeBAr_3$ anion), −153.1 (m, 2 F, *para*-CF of cation), −161.0 (m, 4 F, *meta*-CF of cation), −164.2 (m, 3 F, *para*-CF of $MeBAr_3$ anion), −166.8 (m, 6 F, *meta*-CF of $MeBAr_3$ anion). On the basis of integration data we conclude that the remaining signal, assigned to the *ortho*-CF of the cation, is located at −141.1 ppm (4 F), coincident with the *ortho*-CF signal of **1**. To confirm the assignment of the anion associated with the dinuclear cation in the $^{19}$F NMR spectrum, we repeated the experiment reported by Beck et al.,[30] in which a 35 mM solution of $Cp_2ZrMe_2$ was treated with about 0.5 equiv of $B(C_6F_5)_3$, but $^{19}$F NMR data were not reported. Under these conditions we find, as did Beck et al., that the monometallocenium cation (with its associated anion) is the minor product, whereas the major product is the "associated" dinuclear cation $[(Cp_2ZrCH_3)_2(\mu\text{-}CH_3)_2][CH_3B(C_6F_5)_3]$. The three strongest signals in the $^{19}$F NMR spectrum were at −132.4, −164.2, and −166.8 ppm.

**Synthesis of ($C_6F_5C_5H_4$)$_2$ZrMe$^+$MeB($C_6F_5$)$_3^-$ (4).** The following procedure was carried out with minimal exposure to light. A solution of **2** (105 mg, 0.18 mmol) and $B(C_6F_5)_3$ (96 mg, 0.19 mmol) in toluene (15 mL) was stirred for 5 min at 25 °C and then evaporated. The residue was triturated with 10 mL of pentane, and the yellow precipitate was collected on a filter and dried under vacuum to afford 160 mg (0.15 mmol, 81%) of a yellow solid. $^1$H NMR (toluene-$d_8$): $\delta$ 6.37 (br s, 2 H), 5.98 (br s, 2 H), 5.61 (m, 4 H), 0.34 (br s, 3 H), 0.19 (s, 3 H). $^{19}$F NMR (toluene-$d_8$): $\delta$ −135.2 (d, 6 F), −141.5 (d, 4 F), −152.3 (t, 2 F), −159.1 (t, 3 F), −161.1 (m, 4 F), −164.8 (m, 6 F). Anal. Calcd for $C_{42}H_{14}BF_{25}Zr$: C, 46.05; H, 1.29. Found: C, 46.45; H, 0.90. Combining **2** and a slight excess of $B(C_6F_5)_3$ in hexane solution at 25 °C also affords good yields of **4**, which is collected on a filter and dried under vacuum.

**Titration of Dimethyl Complexes with MAO.** All weighings were carried out using an analytical balance (±0.1 mg resolution) in a nitrogen glovebox, using caution to minimize exposure of the samples to ambient light. A typical experiment was conducted as follows. A solution of **1** ($3.99 \times 10^{-2}$ M) in $C_6D_6$ was prepared by dissolving 50 mg of **1** in 3.0 mL of $C_6D_6$ (needed for spectrometer frequency lock and magnetic field shim adjustments). A solution of MAO (0.865 M) in toluene was prepared by dissolving 251 mg of MAO in 5.0 mL of toluene. To each of five J-Young NMR tubes was added 380 mg of the $C_6D_6$ solution of **1**. Assuming that **1** forms an ideal solution in $C_6D_6$ ($\rho$ = 0.95 g mL$^{-1}$), the density of the $C_6D_6$ solution of **1** was 0.97. A 380 mg sample of this solution corresponds to 0.400 mL; therefore, 0.016 mmol of **1** was added. To each of the five NMR tubes, a different amount (e.g., 160, 407, 622, 800, and 950 mg) of the MAO solution in toluene was added. Assuming that MAO forms an ideal solution in toluene, the density of the toluene ($\rho$ = 0.865) solution of MAO was 0.915. The added weights of this solution correspond to 0.18, 0.44, 0.68, 0.87, and 1.04 mL, or 0.16, 0.38, 0.59, 0.75, and 0.87 mmol of MAO, respectively. Then, sufficient toluene was added by weight to each tube to bring the total calculated volume to 1.45 mL. The samples were shaken vigorously, allowed to equilibrate for 5 min, and then subjected to $^{19}$F NMR analysis. Longer equilibration times (up to 2 h in the dark at 25 °C) did not change the spectra noticably. Stacked plots showing the treatment of **2a**/**2b** with $B(C_6F_5)_3$ to generate **4a**/**4b** and with MAO to generate **6a**/**6b** are provided in the Supporting Information (Figures S7, S8).

**$Me_3Al$ Addition Experiments.** In the glovebox, an NMR tube was charged with **2a** (11.9 mg, 20.3 $\mu$mol), $B(C_6F_5)_3$ (12.5 mg, 24.4 $\mu$mol), $C_6D_6$ (∼1.0 mL), and $Me_3Al$ (∼0.5 mL of a 2.0 M solution in toluene, ∼1.0 mmol). NMR spectra ($^1$H and $^{19}$F) showed no signals that could be assigned to **2a**, **4a**, or $B(C_6F_5)_3$. Instead, the $^1$H NMR spectrum showed four strong multiplets at 6.60, 6.33, 5.74, and 5.46 ppm and a set of four weaker, broadened signals at 6.30, 6.16, 5.60, and 5.56 ppm, in addition to a strong singlet at 0.75 ppm, a weaker triplet at 0.12 ppm, and $Me_3Al$ at −0.15 ppm. The $^{19}$F NMR spectrum showed strong signals at −115.9, −122.6, −130.4, −140.5, −140.9,

−152.9, −155.2, −155.5, −156.2, −161.7, −161.8, and −162.8 ppm in addition to a smaller number of weak signals. A second NMR tube was charged with **2a** (13.2 mg, 22.6 $\mu$mol), MAO (80.2 mg, 1.38 mmol), and $C_6D_6$ (~1 mL). $^1$H and $^{19}$F NMR spectra were recorded, showing a mixture of **2a** and **6a**. An identical sample was prepared, but this time a large excess of $Me_3Al$ (~1.0 mmol as a 2.0 M toluene solution, obtained from Aldrich) was added. The $^1$H and $^{19}$F NMR spectra were unchanged except for a large signal assigned to the added $Me_3Al$ in the $^1$H NMR spectrum.

**Variable-Temperature Study.** Small portions of **2a** (10.0 mg, 17 $\mu$mol) and MAO (35 mg, 610 $\mu$mol, Al:Zr = 36) were weighed into an NMR tube in the glovebox. The tube was sealed with a valved, Teflon-sealed cap and interfaced to a high-vacuum line. Toluene-$d_8$ (roughly 0.6 mL) was condensed into the sample. Upon shaking at room temperature, a clear yellow solution was obtained. $^{19}$F NMR analysis revealed the ratio of **2a**:**6a** at the following temperatures: 42:58 at 50 °C, 47:53 at 25 °C, 48:52 at 0 °C, 47:53 at −20 °C, 46:54 at −40 °C, 39:61 at −60 °C, and 27:73 at −80 °C. Cooling the sample to −78 °C for 5 min using a dry ice−2-propanol bath resulted in faint turbidity and significant gelation of the sample.

## Conclusions

$^{19}$F NMR spectroscopy is a useful probe of methide abstraction from metallocenes by MAO. Metallocene dimethides and "cationic" methylmetallocenium species are readily distinguished using chemical shifts assigned to well-defined model compounds, and their relative concentrations are obtained simply by spectral integration. Apparent reaction quotients obtained for methide abstraction are much lower than one might anticipate based on Al:Zr ratios and concentrations actually used in olefin polymerization but at least qualitatively consistent with other spectroscopic studies. The observed effects of [MAO] on $Q$ suggest that a simple equilibrium model (eqs 1 and 2) does not describe the methide abstraction by MAO at the concentrations used in this study. Rather, MAO behaves as though only a small fraction of highly reactive sites are present. Ongoing studies in our laboratory are directed toward understanding metallocene activation in greater depth.

**Acknowledgment.** We thank W. F. Jackson for preliminary experiments. This work was supported by the Petroleum Research Fund (30738-G) and the National Science Foundation (CHE-98-75446).

**Supporting Information Available:** Experimental details, including tables of data obtained from the NMR titration experiments and the equations used to determine $Q$ from measured quantities. This information is available free of charge via the Internet at http://pubs.acs.org.

OM030171N