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Bulky Aluminum Alkyl Scavengers in Olefin Polymerization with Group 4 Catalysts

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The study of olefin polymerization using cationic, transition-metal complexes has been facilitated through the design and study of discrete activators that provide well-defined ion pairs.[1] Typically an aluminum alkyl scavenger is used with these activators and the catalyst precursor to avoid adventitious catalyst deactivation, at least in a commercial setting.[2] As is now known, aluminum alkyls ($AlMe_3$, Al^iBu_3, etc.) are often reactive toward these activators or the ion pairs formed from them.[3] In addition, they can reversibly inhibit catalysts or act as chain transfer agents, thus modifying intrinsic behavior.[4] We have reported over the past few years that $MeAl(OAr)_2$ (**1**: Ar = 2,6-di-*tert*-butyl-4-methylphenyl),[5] is a "non-interacting" scavenger; it does not react readily with common activators and ion pairs derived from them.[6,7]

We noted that an excess of **1** was needed to remove impurities from monomer and solvent, compared to more reactive aluminum alkyls (for an impurity level of, for example, 50 μM H_2O, 250–500 μM **1** vs 50 μM of $AlMe_3$ would be required). We attributed this to slower reaction of **1** with H_2O to produce CH_4, the expected hydrolysis byproduct of $MeAlX_2$ compounds.[8] We now report that the reaction of **1** with H_2O is slow, and that, although CH_4 is formed, the primary product of hydrolysis is 2,6-di-*tert*-butyl-4-methylphenol (BHT).

The reaction between H_2O and **1** in toluene solution was complicated by the low solubility of H_2O and the more rapid nature of the hydrolysis reaction in this solvent. Both CH_4 and BHT were formed, but we were unable to control/monitor the extent of reaction. In THF-d_8, binding of H_2O to **1** could be observed and the kinetics of hydrolysis monitored by ^1H NMR spectroscopy.[9]

Addition of 1.0 equiv of H_2O to a THF-d_8 solution of **1** below −40 °C provides the aquo complex **2** (eq 1). The NMR spectroscopic data (see Supporting Information), in particular the ^1H resonance due to the aquo protons at δ 9.71 and the upfield shift of the Al−Me resonance to δ −0.49, are consistent with spectra of aquo complexes of hindered trialkyl- and triaryl-aluminum compounds.[8]

The molecular structure of complex **2** is depicted in eq 1;[10] this is the first structurally characterized aquo complex of an aluminum alkyl. Notable features of this structure include strong H-bonding between the coordinated H_2O and the two THF molecules with H(3OA)−O(4) and H(3OB)−O(5) distances of 1.79(4) and 1.68(6) Å, respectively and shortened Al−O distances for the phenoxy groups [av 1.718(3) Å] compared with the Al−O(3) distance of 1.863(3) Å for the formally dative bond involving coordinated H_2O. The geometry about Al is similar to that observed in HAl(OAr)$_2$·OEt$_2$,[11] while the H-bonding between H_2O and the THF molecules
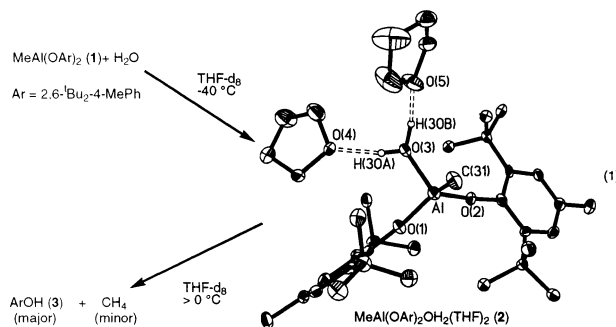
is similar to that observed in $Mes_3Ga(OH_2)\cdot THF_2$[12a] and $(Ph_3-SiO)_3Al(OH_2)\cdot THF_2$.[12b]

Crystals of **2** are unstable at 25 °C, losing THF over a period of several hours under N_2. In THF-d_8 solution, **2** is unstable above 0 °C, and ^1H NMR spectra reveal formation of BHT (1.5 equiv per equiv of **2**), CH_4 (0.10 equiv) and oddly enough, compound **1** (0.20 equiv).[13] In addition, a broad signal grows in at δ −0.78 due to an Al−Me group (0.70 equiv); this resonance resembles that of methylaluminoxane in this solvent,[14] suggesting a similar oligomeric structure for this product.

The decomposition of **2** follows 1st order kinetics with $k_{obs} = 3.0 \times 10^{-4}$ s^{-1} at 5 °C. That BHT is the sole 1° product while CH_4 and additional BHT are formed in subsequent steps, was revealed by monitoring the decomposition of the analogous MeOH adduct which liberated 1 equiv of BHT (and no CH_4) under these conditions (see Supporting Information).[15]

Proton transfer to OAr and loss of BHT is more facile than loss of CH_4, despite the driving force for forming an Al−O bond at the expense of a weaker Al−C bond. Similar conclusions may be inferred from the hydrolyses of donor-stabilized $^tBu_2Al[N(Me)-CH_2CH_2NMe_2]$[16a] or $[^tBu_2Al(\mu-OC_6H_4O)-Al^tBu_2]_n$ in the presence of 2,6-lutidine;[16b] results of this type have been interpreted as arising from the reduced basicity of the Al−C bonds in such compounds.[17] However, in the controlled hydrolysis of the alane, $[HAl(OAr)_2]$, H_2 is exclusively formed.[11b] We suspect the difference in chemoselectivity observed in the hydrolysis of Al−R vs Al−H in these hindered compounds may reflect factors other than differences in basicity.

As BHT is the major hydrolysis product formed from **1**, C_2H_4 polymerization experiments using $[Cp_2ZrMe][MeB(C_6F_5)_3]$ [**4**, generated in situ from Cp_2ZrMe_2 and $B(C_6F_5)_3$] where solvent and monomer were pretreated with excess **1**, must have been conducted in the presence of significant quantities of BHT (i.e. ~150 μM BHT for an impurity level of 100 μM, expressed as H_2O).[6a] The implication is that this phenol is not very reactive toward metallocenium ions! To investigate this hypothesis, we examined the reaction of **4** [generated in situ from Cp_2ZrMe_2 and $B(C_6F_5)_3$,] with

BHT in bromobenzene-d_5 (BB-d_5) solution in which the product of this reaction (**5**) is soluble. As illustrated in eq 2, the novel, phenoxide complex **5** and CH_4 are slowly formed at 25 °C ($t_{1/2} \sim$ 2 h at $[4]_o = [BHT]_o = 0.045$ M).
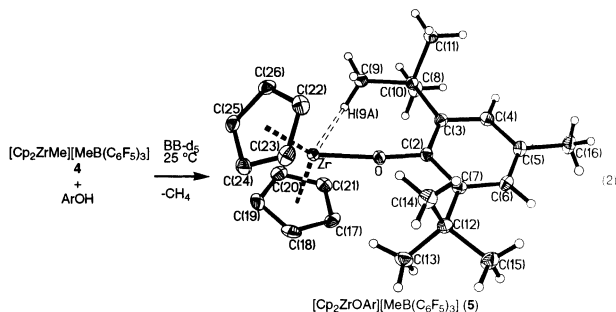
The molecular structure of **5** appears in eq 2.[18] The structure of **5** consists of separated ions in contrast to many structures featuring the $[Me(B(C_6F_5)_3]$ anion.[1] In BB-d_5 solution, there also appears to be limited interaction of the counteranion with Zr as judged from the ^1H and ^{19}F NMR spectra (see Supporting Information) which are characteristic of "free" $[MeB(C_6F_5)_3]$ in this solvent.[19] Details of this structure will be reported elsewhere.

The reaction of **4** with BHT exhibits second-order kinetics at $[4]_o = [BHT]_o = 0.045$ M with an observed rate constant of 2.8×10^{-3} M^{-1} s^{-1} at 25 °C (see Supporting Information). This corresponds to a rate that is about 10^7 times slower than the apparent rate of ethylene insertion (in toluene at 25 °C),[6a] at typical concentrations in a reactor (i.e. $[BHT] \leq 1$ mM, $[C_2H_4] \geq 100$ mM).

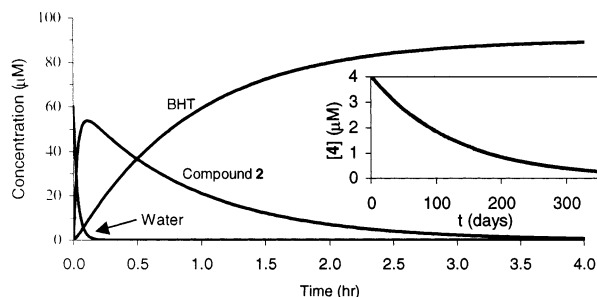**Figure 1.** Simulated scavenging of H_2O by $MeAl(BHT)_2$ (**1**). Initial concentrations are 60 μM H_2O, and 600 μM **1**. Inset: Decomposition of $[Cp_2ZrMe][MeB(C_6F_5)_3]$ (**4**: $[Zr]_o = 4$ μM) by reaction with BHT.

This is illustrated in Figure 1 where the disappearance of **2** and formation of BHT is simulated from the kinetic data while the rate of decomposition of **4** through reaction with BHT is also shown (inset) to illustrate the dramatically different time scales! Further, the deliberate addition of BHT (ca. 250 equiv with respect to **4**) during ethylene polymerization initiated by complex **4** at 25 °C and 28 psi had no effect on the rate of polymerization (see Supporting Information).

It is clear from these results that **1** is useful as a scavenger, provided that the active catalyst (or cocatalyst) is not reactive toward BHT. This certainly seems to be the case for a number of group 4 catalysts or Lewis acidic cocatalysts under mild conditions.[6]

Supporting Information Available: Experimental details for the syntheses of compounds **1**−**5**, polymerization procedures, and X-ray crystallographic, refinement and metrical data for compounds **2** and **5** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org

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(9) The product distribution is similar in THF vs that in aromatic solvents.
(10) Structure of compound **2** with 30% thermal ellipsoids depicted. Only H atoms of interest are shown. Single crystals of **2** were obtained by layering a concentrated THF solution with hexane at low temperature. Crystallographic data (100 K): Monoclinic, space group Cc, $a = 15.2211(13)$ Å, $b = 16.7155(14)$ Å, $c = 15.1522(13)$ Å, $\beta = 98.436(2)°$, $V = 3813.4(6)$ Å^3, $Z = 4$, $R_F = 0.0611$, $R_{wF} = 0.1104$ for 6493 unique reflections with $I > 2\sigma(I)$. Selected bond lengths (Å) and angles (deg) with estimated standard deviation in parentheses: Al−O(3) = 1.863(3); Al−O(2) = 1.715(3); Al−O(1) = 1.721(3); Al−C(31) = 1.953(5); Al−O(1)−C(1) = 169.6(2); Al−O(2)−C(16) = 171.3(2); O(3)−Al−C(31) = 102.0(2).
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(18) Structure of **5** with 50% thermal ellipsoids depicted. The $[MeB(C_6F_5)_3]$ anion and Cp−H atoms are not shown. Single crystals of **5** were grown by layering a concentrated solution in CH_2Cl_2 with hexane. Crystallographic data (100 K): Monoclinic, space group $P2_1/n$, $a = 10.9075(5)$ Å, $b = 30.7926(15)$ Å, $c = 11.7696(6)$ Å, $\beta = 97.8040(10)°$, $V = 3916.4(3)$ Å^3, $Z = 4$, $R_F = 0.0279$, $R_{wF} = 0.0708$ for 8937 unique reflections with $I > 2\sigma(I)$.
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