Reactions of Olefin Polymerization Activators with Complexed Pentamethylcyclopentadienyl Ligands: Abstraction of Tetramethylfulvalene

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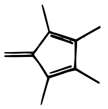
Trialkylaluminum and triarylborane compounds are commonly used as activators for generating cationic alkylmetallocenes which are effective olefin polymerization catalysts.[1] For example, $(AlR_3)_x$ and related compounds function as Lewis acids and can provide alkyl initiating sites in the conversion of complexes such as Cp_2MCl_2 to species such as $[Cp_2MR][R_3AlCl]$ (M = Ti, Zr, Hf; "Cp_2" = separate or linked cyclopentadienyl ligands with various degrees of alkylation) and the powerful Lewis acid, $B(C_6F_5)_3$, has been used to abstract alkyl ligands from Cp_2MR_2 complexes to form catalytically active $[Cp_2MR][RB(C_6F_5)_3]$ complexes.[1] In the past it has been assumed that the Cp_2 bis(cyclopentadienyl) ligand sets function as inert spectator ligands which provide solubility, stability, and the proper steric environment for catalysis. We now report that in certain cases the frequently used C_5Me_5 ligand is not inert to triarylborane and trialkylaluminum activators.

This discovery was made in a study of the reactivity of the sterically crowded complexes $(C_5Me_5)_3Sm$[2] and $(C_5Me_5)_3U$.[3] These compounds initiate the catalytic polymerization of ethylene to high molecular weight,[3] and the reaction chemistry of $(C_5Me_5)_3Sm$[4] suggested that the polymerization could occur through an η^1-C_5Me_5 intermediate. To provide more information on the existence of an η^1-C_5Me_5 species, $(C_5Me_5)_3Sm$ was reacted with $B(C_6F_5)_3$ and Al_2Me_6 to determine if a C_5Me_5 ligand could be abstracted like an alkyl ligand to form an $[\eta^1\text{-}(C_5Me_5)B(C_6F_5)_3]^-$ anion or a $Sm(\mu\text{-}\eta^1\text{-}C_5Me_5)(\mu\text{-}Me)AlMe_2$ bridging unit,[5] respectively.

A reaction does occur between $(C_5Me_5)_3Sm$ and $B(C_6F_5)_3$ upon mixing in toluene,[7] but as shown in eq 1, the isolated products do not retain all of the C_5Me_5 ligands intact. Tetramethylfulvalene (TMF) was identified as one product by ^1H NMR spectroscopy and the samarium product was identified as $[(C_5Me_5)_2Sm][\eta^3\text{-}HB(C_6F_5)_3]$, **1**, by multinuclear NMR spectroscopy, elemental analysis,[7] and single-crystal X-ray diffraction[8] (Figure 1). The samarium atom in **1** is ligated by two C_5Me_5 rings, two fluorine atoms from different arene rings, and the hydride. In contrast, in the related complex $[(C_5Me_5)_2ZrH][\eta^2\text{-}HB(C_6F_5)_3]$,[9] no hydride coordination is observed and two fluorine atoms from the same ring are coordinated to zirconium.

$$(C_5Me_5)_3Sm + B(C_6F_5)_3 \dashrightarrow \underset{\mathbf{1}}{[(C_5Me_5)_2Sm][\eta^3\text{-}HB(C_6F_5)_3]} +$$



(1)

Further confirmation of the composition of **1** was obtained from the independent synthesis of **1** via eq 2. $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$[12] reacts instantly with $B(C_6F_5)_3$ in toluene to give a product whose ^1H NMR spectrum is identical to that of **1**.[13]

$$[(C_5Me_5)_2Sm(\mu\text{-}H)]_2 + 2\,B(C_6F_5)_3 \dashrightarrow 2\,\underset{\mathbf{1}}{[(C_5Me_5)_2Sm][\eta^3\text{-}HB(C_6F_5)_3]} \qquad (2)$$

It is interesting to note that eq 1 is the reverse of the synthesis of $(C_5Me_5)_3Sm$ from tetramethylfulvalene and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$.[3] Equation 1 can be viewed as a Lewis acid assisted β-hydrogen elimination from a putative $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$ unit which shows no tendency to β-hydrogen eliminate to give $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$. The most closely related reactions in the literature are the internal metalations of $(C_5Me_5)^-$ in complexes highly reactive in σ-bond metathesis. In these cases, formation of a formally dianionic $(C_5Me_4CH_2)^{2-}$ ligand results.[10,14]

$(C_5Me_5)_3Sm$ also reacts with Al_2Me_6. In this case, an η^1-C_5Me_5 ligand is found in the product,[15] but single-crystal X-ray diffraction[16] shows that it has completely left the coordination

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(1) For reviews and leading references only, see: Brintzinger, H. H.; Fischer, D. F.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217. Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. Ewen, J. A.; Elder, M. J. U.S. Pat. Appl. 1989, 41907; *Chem. Abstr.* **1991**, *115*, 136998g. Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. Herzog. T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988.

(2) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7423.

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(4) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 12635.

(5) For example, $(C_5Me_5)_2SmMe(THF)$ reacts with Al_2Me_6 to form $(C_5Me_5)_2Sm[(\mu\text{-}Me)_2AlMe_2]_2Sm(C_5Me_5)_2$.[6]

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(7) In an argon-filled glovebox, addition of $(C_5Me_5)_3Sm$ (0.150 g, 0.270 mmol) in toluene (5 mL) to a solution of $B(C_6F_5)_3$ (0.138 g, 0.270 mmol) in toluene (5 mL) caused an immediate brown to red color change. The solvent and tetramethylfulvalene (identified by ^1H NMR spectroscopy) were removed by rotary evaporation to afford $(C_5Me_5)_2Sm[\mu\text{-}HB(C_6F_5)_3]$ as a red powder (0.246 g, 98% yield). ^1H NMR (C_6D_6): δ −0.63 ($C_5\mathit{Me}_5$). ^{13}C NMR (C_6D_6): δ 119.7 (C_5Me_5), 21.38 ($C_5\mathit{Me}_5$). ^{19}F NMR (C_6D_6): δ −156.9, −162.4. ^{11}B NMR (C_6D_6): δ −7.30 (unresolved multiplet). IR (KBr): 2914 m, 2290 m, 2104 w, 1644 m, 1516 s, 1462 s, 1377 w, 1273 m, 1100 s, 959 s, 802 w, 731 w, 646 w cm^{-1}. Magnetic susceptibility $\chi_{m(298K)} = 1.0 \times 10^{-3}$ cgsu, $\mu_{eff} = 1.6\ \mu_B$. Anal. Calcd for $SmC_{35}H_{31}F_{15}B$: Sm 16.12; C 48.90; H, 3.32. Found: Sm, 16.20; C, 49.04; H 3.47.

(8) Compound **1** crystallizes from toluene in space group $P\bar{1}$ with a = 14.554(2) Å, b = 15.765(2) Å, c = 17.066(2) Å, V = 3855.5(7) $Å^3$, and $D_{calcd} = 1.688$ g/cm^3 for $Z = 4$. Least-squares refinement of the model based on 13 593 reflections converged to a final wR2 = 0.0726. The $(C_5Me_5)_2Sm$ part of complex **1** has structural parameters typical of formally nine-coordinate $(C_5Me_5)_2Sm$-containing complexes (Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79−94). Comparison of the 2.45(5) Å Sm−H and the 1.18(5) Å B−H distance with other data in the literature is complicated by the large error limits involved in these and the other measurements. The B−H distance equals 1.06(6) Å in the anion of $[(C_5Me_5)_2ZrH][HB(C_6F_5)_3]$.[9] Sm−H distances are 2.05(11) and 2.11(9) Å in $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)_2$,[10] 1.80(15) and 2.75(15) Å in $[(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}H)]_2$ (Bulychev, B. M.; Gun'ko, Y. K.; Soloveichik, G. L.; Belsky, V. K. *J. Organomet. Chem.* **1992**, *424*, 289). Sm−H−B distances are 2.480(9) and 2.660(9) Å in the Sm^{2+} complex $\{[(C_6H_5CH_2)_2C_2B_9H_9]Sm(DME)_2\}_2$ (Xie, Z.; Liu, Z.; Chiu, K.; Xue, F.; Mak, T. C. W. *Organometallics* **1997**, *16*, 2460). Sm^{2+} is 0.191 Å larger than Sm^{3+}.[11] The 2.537(2) and 2.546(2) Å Sm−F distances have lengths consistent with dative bonds in comparison to other Sm−F bond distances: 2.244(6) Å in $[(C_5H_4CMe_3)_2Sm(\mu\text{-}F)]_3$ (Schumann, H.; Keitsch, M. R.; Winterfeld, J. Demtschuk, J. *J. Organomet. Chem.* **1996**, *525*, 279) and 2.302(3) Å in $\{[C_5H_3(SiMe_3)_2]_2Sm(\mu\text{-}F)\}_2$ (Xie, Z.; Liu, Z.; Xue, F.; Mak, T. C. W. *J. Organomet. Chem.* **1997**, *539*, 127).

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(12) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.

(13) Addition of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$12 (0.050 g, 0.06 mmol) in toluene (5 mL) to a solution of $B(C_6F_5)_3$ (0.061 g, 0.12 mmol) in toluene (5 mL) in an argon-filled glovebox caused an immediate color change from orange to red. Rotary evaporation of the solvent left a red powder (0.110 g, 98%) whose ^1H NMR spectrum (C_6D_6) was identical to that of **1**.

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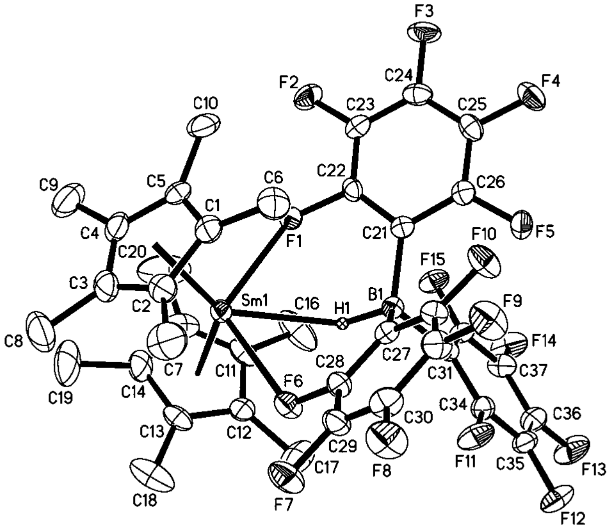

Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm][\eta^3\text{-}HB(C_6F_5)_3]$, **1**, with ellipsoids drawn at the 50% probability level. Bond distances (Å) and angles (deg) include the following: Sm(1)−H(1), 2.45(5); B(1)−H(1), 1.18(5); Sm(1)−F(1), 2.537(2); Sm(1)−F(6), 2.546(2); Sm−C(C_5Me_5) av, 2.69(3); Cnt(1)−Sm(1)−Cnt(2), 136.4; C(22)−F(1)-Sm(1), 134.0(2); C(28)−F(6)−Sm(1), 117.1(2).

sphere of samarium and is attached to only aluminum as shown in eq 3 and Figure 2. The structure of **2** is closely related to that

$$2(C_5Me_5)_3Sm + Al_2Me_6 \text{--->} \underset{\mathbf{2}}{(C_5Me_5)_2Sm[(\mu\text{-}Me)_2Al(C_5Me_5)Me]_2Sm(C_5Me_5)_2} \quad (3)$$

of $(C_5Me_5)_2Sm[(\mu\text{-}Me)_2AlMe_2]_2Sm(C_5Me_5)_2$, **5**,[6] except that an η^1-C_5Me_5 ligand is attached to each Al in place of a methyl group in **5**. Equation 3 parallels the formation of **5** from $(C_5Me_5)_2SmMe(THF)$ and Al_2Me_6.[6] Since the C_5Me_5 ligands bound to aluminum in the structure of **2** remain on the same side of the $\overline{\mathrm{SmCAlCSmCAlC}}$ ring, two different η^5-C_5Me_5 environments are present. This arrangement is preserved in solution to at least −60 °C: two singlets are found for these rings. Another singlet is observed for the C_5Me_5 ring attached to Al which is consistent with earlier observations on the fluxional hapticity of cyclopentadienyl groups bound to aluminum.[17] No evidence was found for a monomer−dimer equilibrium as was observed for **5** and related species.[18]

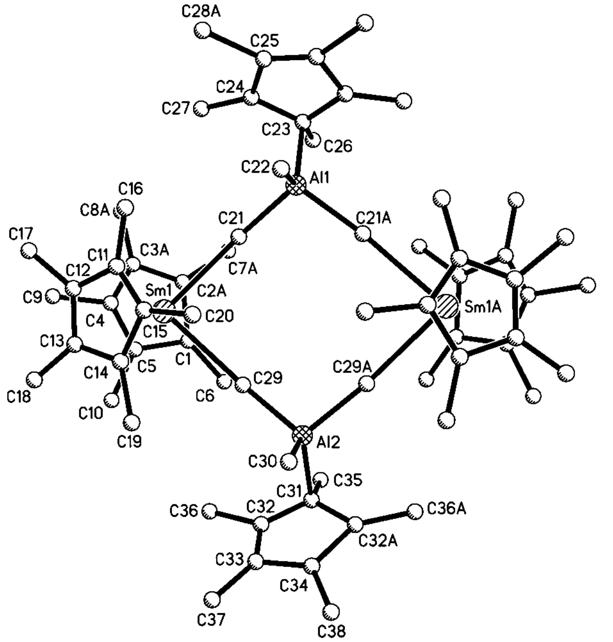

Figure 2. Ball-and-stick plot of $(C_5Me_5)_2Sm[(\mu\text{-}Me)_2Al(C_5Me_5)Me]_2Sm(C_5Me_5)_2$, **2**.

The reactions reported here show that the C_5Me_5 ligand is not necessarily inert in the presence of Lewis acids commonly used as activators in olefin polymerization systems. The conversion in eq 1 of M−C_5Me_5 to M−H, a potential initiating site for olefin polymerization,[19] and the abstraction of C_5Me_5 in eq 3 to form a bridged complex of the cationic $[(C_5Me_5)_2Sm]^+$ moiety both lead to units which can be effective in polymerization.

Although these examples were observed with $(C_5Me_5)_3Sm$, which has previously been shown to have unusual chemistry,[4] they show that under the proper conditions, the C_5Me_5 ligand can react with Lewis acids. Since the special chemistry of $(C_5Me_5)_3Sm$ appears to arise from the steric crowding of this ligand set, similar steric crowding (and reactivity) could be available via other ligand sets.

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Supporting Information Available: Tables of atomic coordinates, atomic displacement parameters, and bond distances and angles (49 pages). See any current masthead page for ordering information and Web access instructions.

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(15) In the glovebox, addition of $(C_5Me_5)_3Sm$ (0.100 g, 0.180 mmol) in toluene (5 mL) to a solution of Al_2Me_6 (0.013 g, 0.180 mmol) in toluene (5 mL) caused an immediate brown to orange color change. The solvent was removed by rotary evaporation, and recrystallization from toluene afforded $(C_5Me_5)_2Sm[\mu\text{-}Me_2Al(C_5Me_5)(Me)]_2Sm(C_5Me_5)_2$ (0.110 g, 97% yield). ^1H NMR (300 MHz, 25 °C, C_6D_6): δ 0.96 (15H, C_5Me_5), 0.61 (15H, C_5Me_5), −0.30 (15H, C_5Me_5), −1.07 (3H, Me), −13.7 (3H, μ-Me). ^{13}C NMR (300 MHz, 25 °C, C_6D_6): δ 119.3 (C_5Me_5), 119.2 (C_5Me_5), 113.3 (C_5Me_5), 20.44 (C_5Me_5), 20.04 (C_5Me_5), 10.33 (C_5Me_5). IR (KBr): 2909 s, 1443 m, 1382 w, 1178 w, 1022 m, 944 s, 796 m, 649 m cm^{-1}. Magnetic susceptibility $\chi_{m(298K)} = 3.88 \times 10^{-4}$ cgsu, $\mu_{eff} = 1.0\ \mu_B$. Anal. Calcd for $SmC_{33}H_{54}Al$: Sm, 23.97; C, 63.12; H, 8.61. Found: Sm, 24.20; C, 62.79; H, 8.47.

(16) Compound **2** crystallizes from toluene in space group *Cmca* with $a = 24.590(3)$ Å, $b = 15.832(4)$ Å, $c = 32.648$ (4) Å, $V = 12709(4)$ Å^3, and $D_{calcd} = 1.313$ g/cm^3 for $Z = 8$. The quality of the data were sufficient to establish atomic connectivity but not to report detailed bond distances and angles.

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