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An Ethyl Aluminum Oxide (EAO) Complex with μ-η^1:η^2-Ethyl Coordination Derived from a Samarocene Carboxylate and Triethylaluminum

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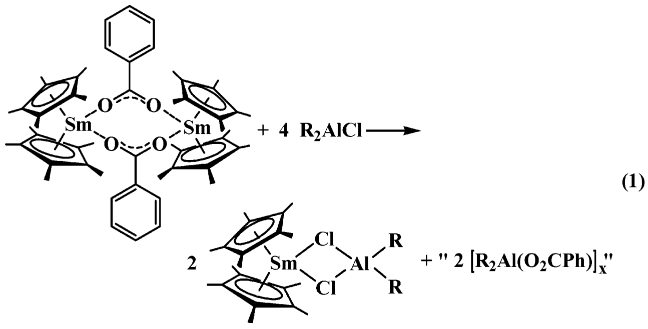
Summary: The samarocene carboxylate $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$ *reacts with* $AlEt_3$ *to form a mixture of metallocene-stabilized ethylaluminum compounds, including an ethyl aluminum oxide (EAO) complex,* $[(C_5Me_5)_2Sm]_2[(\mu\text{-}Et)_4Al_4Et_6O_2]$*, that displays* μ-η^1:η^2*-Et coordination similar to that found in* $[(C_5Me_5)_2Sm(\mu\text{-}Et)(\mu\text{-}Cl)AlEt_2]_2$ *obtained from the reaction between* $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ *and* $AlEt_3$*.*

The reactions of lanthanide carboxylates with alkylaluminum reagents are of interest, since they generate highly efficient catalysts that polymerize isoprene to high *cis*-1,4-polyisoprene, the main component of natural rubber.[1−12] The lanthanide-based catalysts are typically prepared from a carboxylate, $[Ln(O_2CR)_3]_n$, an ethyl aluminum chloride reagent, and an isobutylaluminum compound. Examining this multicomponent catalyst system directly is challenging,[12] and metallocene carboxylates such as $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$ have been used to model the reactions involved in catalyst generation.[13−15] These metallocene derivatives have the advantage that the reactivity of a single carboxylate per metal can be evaluated in well-defined coordination environments in soluble complexes that are often crystalline. We report here that reactions of samarocene carboxylates with alkylaluminum reagents can also provide information about alkyl aluminum oxide chemistry.

Reactions of metallocene carboxylates with dialkyl aluminum chloride reagents, R_2AlCl, have previously been shown to give the dichloro-bridged products $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2AlR_2$ (eq 1; R = Me, Et, ^{i}Bu).[13] We now report that when $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$ is treated with $AlEt_3$, a rare example of a structurally characterizable ethyl aluminum oxide complex results. Given the importance of methylaluminoxane, MAO, in olefin polymerization catalysis[16] and the difficulty in defining the composition of MAO,[17] this "EAO" chemistry provides a new option for studying organoaluminum oxide chemistry. We report here the synthesis of this EAO complex and structural studies of related compounds that contain the unusual μ-η^1: η^2-ethyl bridging that the EAO complex displays.



(1)

A yellow solution of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$[18] in toluene readily reacts with $AlEt_3$ to generate a mixture of products (eq 2) that contains the previously defined tetraalkylaluminate complex $(C_5Me_5)_2Sm(\mu\text{-}Et)_2AlEt_2$ (**1**),[19] as well as the ethyl aluminum oxide $[(C_5Me_5)_2Sm]_2[(\mu\text{-}\eta^1\text{: }\eta^2\text{-}Et)_2(\mu\text{-}\eta^1\text{-}Et)_2Al_4Et_6(\mu_3\text{-}O)_2]$ (**2**), identified by X-ray crystallography (Figure 1).[20] Complex **1** was the expected product on the basis of eq 1: i.e., complete removal of the carboxylate ligand and formation of a $[(C_5Me_5)_2Sm(\mu\text{-}X)_2AlX_2]_n$ ligand redistribution product (X = monoanionic ligand originating from the aluminum reagent).

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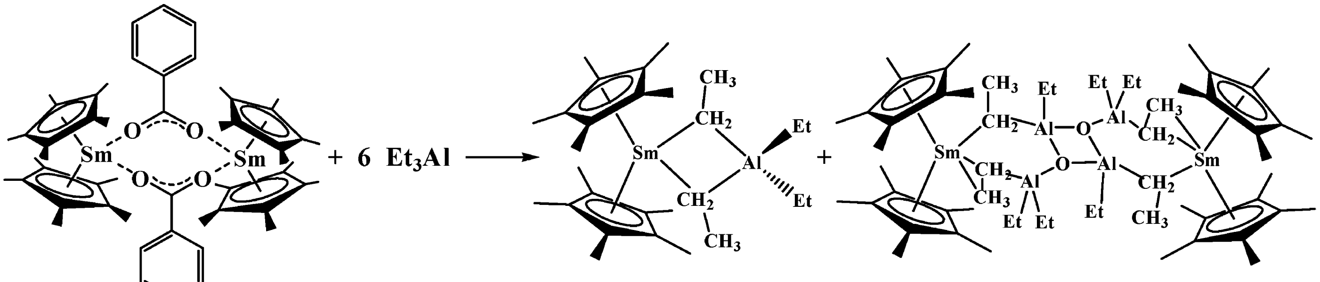

1

2

(2)

Complex **2**, on the other hand, is the first structurally characterized example of an EAO metallocene complex to our knowledge.[21] Since alkylaluminoxanes are hydrolysis products, it was possible that **2** was an errant crystal obtained as an extraneous product of adventitious hydrolysis. However, the reaction has been conducted numerous times under ostensibly air- and water-free conditions, and identical crystals have been isolated and defined by X-ray crystallography.[22] GC-MS of the organic byproducts of eq 2 revealed $PhC(Et)_2(OH)$ and $PhC(Et){=}CHMe$, both of which are consistent with attack of alkylaluminum reagents on carboxylates.[23] Analogous reactions between $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$ and $AlMe_3$ and Al^iBu_3 also form mixtures, but only the analogues of **1**, namely $[(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2]_n$ (n = 1, 2)[24] and $(C_5Me_5)_2Sm(\mu\text{-}^iBu)_2Al^iBu_2$,[25] have been definitively identified in the product mixtures.

Complex **2** is comprised of two trivalent samarium metallocene units, $[(C_5Me_5)_2Sm]^+$, connected by an ethyl aluminum oxide bridge that carries a formal dinegative charge. This symmetric dimeric $[(Al_2Et_5O)_2]^{2-}$ "EAO" unit can be viewed as the adduct of two molecules of $AlEt_3$ with two $(AlEt_2O)^-$ anions. The latter two anions form a diamond-shaped Al_2O_2 core familiar in many types of organoaluminum oxide species.[26]

In addition to containing a new EAO ligand system, **2** displays unusual μ-η^1:η^2-ethyl bonding to the trivalent samarium center. This has previously been observed only in the divalent ytterbium complex $(C_5Me_5)_2Yb(\mu\text{-}\eta^1{:}\eta^2\text{-}Et)AlEt_2(THF)$[27] and the THF adduct of **1**: namely, $(C_5Me_5)_2Sm(THF)(\mu\text{-}\eta^1{:}\eta^2\text{-}Et)AlEt_3$.[13] One ethyl group of each of the $AlEt_3$ components of the EAO dianion is bound in this way in **2**. With this μ-η^1: η^2-ethyl bonding, the EAO dianion has an overall hapticity of 6.

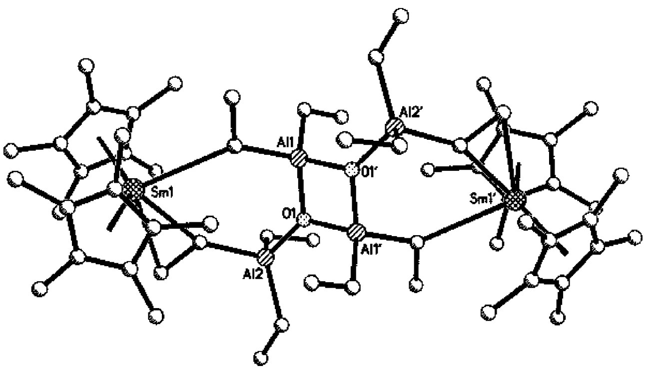

Figure 1. Ball and stick diagram of $[(C_5Me_5)_2Sm]_2[(Al_2Et_5O)_2]$ (**2**).

Although repeated crystallographic data collections on crystals of **2** have not provided data sufficient to discuss the metrical parameters of this unusual bonding in detail, a crystallographically well-defined example of μ-η^1:η^2-Et ligation has been obtained by examining the reactivity of $AlEt_3$ with the metallocene chloride, $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$.[28] This reaction generates the dimeric mixed-bridge complex $[(C_5Me_5)_2Sm(\mu\text{-}\eta^1{:}\eta^2\text{-}Et)(\mu\text{-}Cl)AlEt_2]_2$ (**3**; Figure 2 and eq 3), a reaction that, in contrast with eqs 1 and 2, does not involve ligand redistribution.[29,30] In comparison, the reactions of $AlMe_3$ and Al^iBu_3 with $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ provided $[(C_5Me_5)_2Sm(\mu\text{-}Cl)(\mu\text{-}Me)AlMe_2]_2$ (**4**)[31a] and $(C_5Me_5)_2Sm(\mu\text{-}Cl)(\mu\text{-}^iBu)Al^iBu_2$ (**5**),[31b] respectively. Complex **4** crystallizes as a dimer,[32] but the structure was disordered. However, as

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(20) $AlEt_3$ (123 μL, 0.9 mmol) was added dropwise to a solution of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$ (162 mg, 0.15 mmol) in toluene (12 mL). After the mixture was stirred overnight, a red solution formed. Solvent was removed from the red solution under vacuum to yield an oily red solid. A concentrated hexane solution yielded crystals of **1** (39 mg, 47%) identified by ^1H and ^{13}C NMR spectroscopy.[19] Layering the mother liquor with $(Me_3Si)_2O$ yielded crystals of **2** (57 mg, 30%). Data for **2**: ^1H NMR (C_7D_8) δ 1.51 (s, C_5Me_5); ^{13}C NMR (C_7D_8) δ 18.6 (C_5Me_5), 115.7 (C_5Me_5). Additional resonances were observed but could not be definitively assigned to individual ethyl protons in this paramagnetic system. IR (thin film) 3095 w, 3071 m, 3016 m, 2940 m, 2905 m, 2870 m, 1760 s, 1572 w, 1518 w, 1445 m, 1410 w, 1392 w, 1382 w, 1309 w, 1265 w, 1230 w, 1185 w, 1110 w, 1090 m, 1020 m, 990 w, 945 w, 924 w, 895 w, 841 w, 755 w, 722 s, 700 w cm^{-1}. Anal. Calcd for $C_{60}H_{110}O_2Al_2Sm_2$: Sm, 24.68; C, 59.14; Al, 4.43; H, 9.12. Found: Sm, 25.05; C, 58.91, Al, 4.49; H, 8.89.

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(22) Crystal data for **2**: $C_{60}H_{110}Al_4O_2Sm_2$, M_r = 1272.10, triclinic, $P\bar{1}$, a = 11.275(4) Å, b = 13.083(4) Å, c = 21.353(7) Å, α = 87.104(6)°, β = 89.239(5)°, γ = 87.396(6)°, V = 3142.5(17) Å^3, Z = 2, ρ_{calcd} = 1.344 Mg m^{-3}.

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(29) $AlEt_3$ (20 μL, 0.15 mmol) was added dropwise to a suspension of $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ (68 mg, 0.05 mmol) in toluene (10 mL). A red solution immediately formed, and the mixture was stirred overnight. Removal of solvent under vacuum yielded a red solid (52 mg, 92%). The complex displays a monomer−dimer equilibrium in solution. ^1H NMR (monomer; toluene-d_8, 25 °C) δ 0.38 (br, 30H, C_5Me_5), 1.11 (t, 6H, $AlCH_2CH_3$). ^1H NMR (dimer; toluene-d_8, −35 °C): δ 1.22 (s, 30H, C_5Me_5), 0.59 (s, 30H, C_5Me_5), 1.06 (s), 0.85 (d), −0.41 (s), −1.08 (d), −19.14 (s), −20.64 (s). ^{13}C NMR (toluene-d_8): δ 115.8, 21.8, 17.9, 16.8, 9.5, 0.6. ^{27}Al NMR (toluene-d_8) δ 49.8. IR (thin film) 3088 w, 3061 m, 3030 m, 2922 m, 2864 m, 1606 m, 1575 w, 1521 w, 1494 s, 1459 m, 1378 w, 1316 w, 1212 w, 1177 w, 1158 w, 1104 w, 1081 m, 1031 m, 984 w, 953 w, 926 w, 895 w, 841 w, 722 s, 690 s cm^{-1}. Anal. Calcd for $C_{26}H_{45}ClAlSm$: C, 54.73; H, 7.97; Cl, 6.21; Al, 4.73; Sm, 26.35. Found: C, 54.49; H, 8.04; Cl, 6.48; Al, 3.88; Sm, 26.90. X-ray-quality crystals of **3** were grown from hexane.

(30) Crystal data for **3**: $C_{52}H_{90}Al_2Cl_2Sm_2$, M_r = 1140.80, monoclinic, $P2_1/c$, a = 13.0879(12) Å, b = 11.8639(11) Å, c = 18.2465(17) Å, α = 90°, β = 104.622°, γ = 90°, V = 2741.4(4) Å^3, Z = 2, ρ_{calcd} = 1.382 Mg m^{-3}, R1 = 0.0253 ($I > 2\sigma(I)$), wR2 = 0.0665, GOF = 1.097.

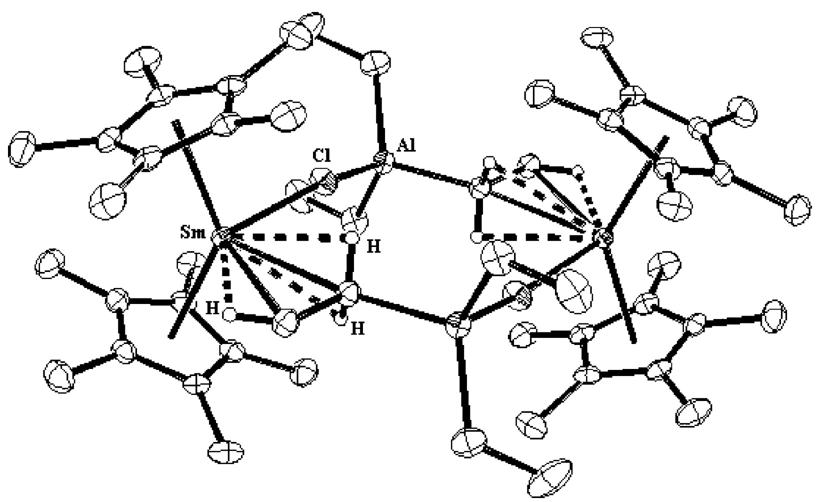
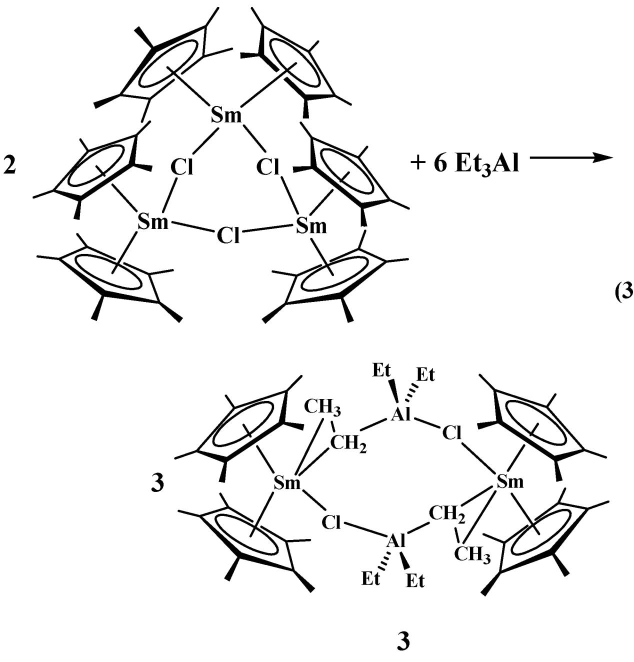


Figure 2. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm(\mu\text{-}\eta^1\text{:}\eta^2\text{-Et})(\mu\text{-Cl})AlEt_2]_2$ (**3**).

shown in Figure 3, **5** is a $(C_5Me_5)_2Sm(\mu\text{-Cl})(\mu\text{-R})AlR_2$ analogue of **3** that has conventional Sm(μ-Cl)(μ-R) bonding suitable for comparison with **3**.[33]



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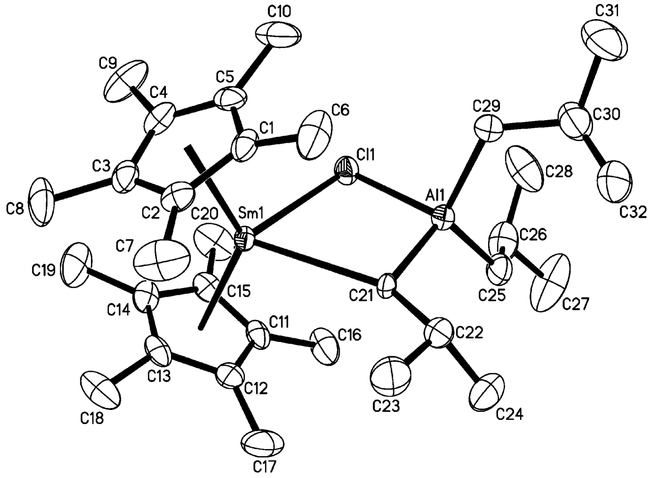

Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(\mu\text{-Cl})(\mu\text{-}^iBu)Al^iBu_2$ (**5**).

The μ-η^1:η^2-Et group in **3** has 2.749(3) and 2.976(3) Å Sm(1)−C(21) methylene and Sm(1)−C(22) methyl distances, respectively. These values bracket the 2.836(3) Å Sm−C(21) distance in **5**. In contrast, $(C_5Me_5)_2Sm[(\mu\text{-Et})_2AlEt_2]$ (**1**) has 2.662(4) Å average Sm−C(methylene) lengths with the attached methyl groups oriented away from samarium with an unusual 170(4)° Sm−C−C angle (cf. Sm(1)−C(21)−C(22) is 82.9(2)° in **3**). The Al−C(methylene) distances in **1**, **3**, and **5** are 2.106(5), 2.015(3), and 2.040 (4) Å, respectively; i.e., the shortest Sm−C is paired with the longest Al−C in the series.

As shown in Figure 2, both methylene hydrogens and one methyl hydrogen of each of the μ-η^1: η^2-Et bridges in **3** refined into positions oriented toward samarium. Hence, the μ-η^1: η^2-Et ligand functions as a polyagostic bridge between the lanthanide and aluminum.

In summary, $AlEt_3$ reacts differently from $AlMe_3$ and Al^iBu_3 with lanthanide carboxylates and chlorides. The carboxylate reaction has provided the first metallocene ethyl aluminum oxide complex, and the chloride reaction shows how the ethyl group can provide extra coordination to the lanthanide center in a simple Ln-(μ-R)(μ-Cl) linkage. The connection between these special features and the common choice of specifically

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(31) (a) In a similar procedure, reaction of $AlMe_3$ (15 μL, 0.16 mmol) with $[(C_5Me_5)_2Sm(\mu\text{-Cl})]_3$ (67 mg, 0.05 mmol) gave **3** (49 mg, 92%). ^{1}H NMR (monomer; toluene-d_8, 25 °C): δ 0.28 (br, 30H, C_5Me_5). ^{1}H NMR (dimer; toluene-d_8, −35 °C): δ 0.50 (br, 60H, C_5Me_5), −0.99 (s, 12H, $AlMe_2$). ^{13}C NMR (toluene-d_8) δ 120.2, 119.5, 21.8, 21.7. ^{27}Al NMR (toluene-d_8): δ 52.2. IR (thin film): 3030 m, 2962 m, 2905 m, 2863 m, 1611 m, 1498 s, 1447 m, 1376 w, 1263 s, 1210 m, 1075 m, 1019 s, 799 w, 715 w, 498 s, 467 s cm^{-1}. Anal. Calcd for $C_{23}H_{39}ClAlSm$: C, 52.27; H, 7.45; Cl, 6.71; Al, 5.11; Sm, 28.45. Found: C, 52.04; H, 7.30; Cl, 6.86; Al, 5.22; Sm, 28.60. (b) Al^iBu_3 (44 μL, 0.17 mmol) and $[(C_5Me_5)_2Sm(\mu\text{-Cl})]_3$ (69 mg, 0.05 mmol) gave **5** (31 mg, 94%). ^{1}H NMR (C_6D_6, 25 °C) δ 0.29 (s, 30H, C_5Me_5), 0.42 (br, 4H, CH_2CHMe_2). ^{13}C NMR (C_6D_6) δ 119.9 (C_5Me_5), 21.1 (C_5Me_5), 27.8 (CH_2CHMe_2), 25.4 (CH_2CHMe_2), 23.5 (CH_2CHMe_2). ^{27}Al NMR (C_6D_6): δ 54.3. IR (thin film) 2961 s, 2926 s, 2876 s, 2358 w, 1463 m, 1378 m, 1343 w, 1135 w, 1065 w, 888 w, 795 w, 726 m cm^{-1}. Anal. Calcd for $C_{32}H_{57}ClAlSm$: C, 58.70; H, 8.79; Al, 4.12; Sm, 22.96. Found: C, 58.26; H, 8.44; Al, 4.74; Sm, 23.50.

(32) Crystal data for **4**: $C_{46}H_{78}Al_2Cl_2Sm_2\cdot 4C_7H_8$, M_r = 1425.18, triclinic, $P\bar{1}$; a = 11.2045(19) Å, b = 12.681(2) Å, c = 15.032(3) Å, α = 105.105(3)°, β = 100.660(3)°, γ = 112.517(3)°, V = 1805.1(5) Å^3, Z = 1, ρ_{calcd} = 1.311 Mgm^{-3}, R1 = 0.0469 ($I > 2\sigma(I)$), wR2 = 0.1283, GOF = 1.091.

(33) Crystal data for **5**: $C_{32}H_{57}AlClSm$, M_r = 654.56, monoclinic, $P2_1/c$, a = 17.621(3) Å, b = 8.7670(17) Å, c = 23.030(5) Å, α = 90°, β = 108.022°, γ = 90°, V = 3383.2(11) Å^3, Z = 4, ρ_{calcd} = 1.285 Mg m^{-3}, R1 = 0.0301 ($I > 2\sigma(I)$), wR2 = 0.0735, GOF = 1.080.

ethylaluminum rather than methylaluminum reagents as activators for lanthanide-based polymerization catalysts is not yet known. However, the ethyl group clearly can provide special chemistry that is not available with methyl and isobutyl analogues. These results also raise the possibility that the lanthanide carboxylate/ethylaluminum activation step in the preparation of diene polymerization catalysts may involve formation of ethyl aluminum oxide ligands that could be involved in the high 1,4-cis composition of the resulting polymer.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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