5392 *Organometallics* **2000,** *19,* 5392−5399

Alternative η^5- and η^6-Bonding Modes for Bis(fluorenyl)lanthanide Complexes by Reactions with AlR_3 and Succesive Addition of THF

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Received March 20, 2000

Reversible and equilibrium isomerization of η^5-bis(Me_3Si-fluorenyl)−rare earth metal complexes to η^6-bis(Me_3Si-fluorene-AlR_3)−rare earth metal complexes, which is a novel type of metallotropic tautomerism, was realized by the addition of AlR_3 to the former complexes. Resulting η^6-complexes also changed to the initial η^5-complexes reversibly by the addition of excess THF. η^5-Bis(Me_3Si-fluorenyl)Sm$(THF)_2$ (**1**) was prepared by reaction of Me_3Si-fluorenylpotassium with $SmI_2(THF)_2$, and its structure was analyzed by X-ray diffraction. η^6-Bis(Me_3Si-fluorene-$AlMe_3$)Sm (**2**) was synthesized by the reaction of **1** with excess $AlMe_3$. The corresponding reaction of excess $AlEt_3$ with **1** gave η^6-bis(Me_3Si-fluorene-$AlEt_3$)Sm (**3**). The structures of **2** and **3** were determined by X-ray analyses. The reaction of bis(Me_3Si-fluorenyl)Yb$(THF)_2$ (**4**) with an excess amount of $AlMe_3$ gave η^5-(Me_3Si-fluorenyl)-η^6-(Me_3Si-fluorene-$AlMe_3$)Yb (**5**), where one equimolar $AlMe_3$ coordinates to the Yb atom through its two Me groups via an agostic interaction. One of the Me_3Si-fluorenyl groups assumes η^5-coordination, while the other Me_3Si-fluorenyl group shows η^6-coordination. The addition of excess THF to **5** produced (fluorenyl)Yb$(THF)_4$/$AlMe_4$ (**6**) in low yield. To understand the primary factor for the alternative η^5- and η^6-bonding modes, we have synthesized (^{i}Pr-indenyl)$_2$Yb$(THF)_2$ (**7**) without a Me_3Si group and with a rather small indenyl ring and examined the reaction with AlR_3.

The metallotropic $\eta^5-\eta^6$ tautomeric equibrium of late tansition metal tricarbonyl complexes of substituted fluorenes and indenes is reported for Mn, Cr, and Mo complexes. For example, the abstraction of a proton from $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_3]PF_6$ by using weak bases such as triethylamine generates $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ irreversibly.[1] The corresponding reaction using $[Fe(\eta^6\text{-}C_{13}H_{10})(CO)_3]PF_6$ does not produce a η^5-coordinated product but maintains the η^6-coordinated structure, $Fe(\eta^6\text{-}C_{13}H_9)(CO)_3$.[2] Deprotonation of 9-substituted η^6-fluorene chromium tricarbonyl complexes also provides an anionic η^5-(fluorenyl)$Cr(CO)_3$, as evidenced by ^1H NMR.[3] The reaction of alkyl halide with an anionic η^5-(indenyl)$Cr(CO)_3$ complex also gave η^6-(indene)$Cr(CO)_3$ irreversibly.[4] η^5-(Indenyl)$Mo(CO)_3H$ complex is reported to be less stable than η^6-(indene)$Mo(CO)_3$.[5]

In sharp contrast with these behaviors, $\eta^5-\eta^6$ rearrangement has not been reported for early transition metal indenyl and fluorenyl complexes. The reaction of AlR_3 with η^5-$(C_5Me_5)_2Ln(THF)_2$ generally affords η^5-$[(C_5Me_5)_2Ln(\mu\text{-}R)_2AlR_2]_2$ (M = Sm, Y),[6] which exists in equillibrium with monomeric η^5-$(C_5Me_5)_2Ln(\mu\text{-}R)_2AlR_2$ or a 1:1 AlR_3 adduct, η^5-$(C_5Me_5)_2Ln(\mu\text{-}R)AlR_2(THF)$ (Ln = Yb).[7] η^5-$(C_5Me_5)_2Ln(\mu\text{-}R)_2AlR_2$ complexes can be formed also by reaction of η^5-$(C_5Me_5)_2LnX_2$ with $MeLi/AlR_3$.[8] We describe herein the first examples of the $\eta^5-\eta^6$ rearrangement of η^5-bis(Me_3Si-fluorenyl)Sm$(THF)_2$ to η^6-bis(Me_3Si-fluorene-AlR_3)Sm by reaction with AlR_3 and the conversion of η^5-bis(Me_3Si-fluorenyl)Yb$(THF)_2$ to η^6-(Me_3Si-fluorene-$AlMe_3$)-η^5-(Me_3Si-fluorenyl)Yb by reaction with $AlMe_3$. The η^6-complexes can convert to η^5-species by the succesive addition of excess THF.

Experimental Section

General Consideration. All operations were performed under an argon atmosphere by using standard Schlenk

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10.1021/om0002475 CCC: $19.00

techniques. Tetrahydrofuran, toluene, and hexane were dried over Na/K alloy and distilled before use. ^{1}H NMR spectra were recorded on a Bruker AMX 400wb spectrometer (400.13 MHz), and chemical shifts were calibrated using benzene (δ 7.20 ppm). The M_n and M_w/M_n values of poly(ϵ-caprolactone) were determined by gel permeation chromatography (GPC) on a Tosoh SC-8010 using TSKgel G2000, G3000, G4000, and G5000 columns in chloroform at 40 °C. The M_n and M_w/M_n values of polyethylene were determined by GPC on a Waters 150C instrument using Shodex AT806MS column in 1,2,4-trichlorobenzene at 140 °C. The M_n and M_w/M_n values were calibrated using standard polystyrene. Elemental analyses were performed on a PE 2400 series II CHNS/O analyzer. The samples were sealed in tin foil in an argon stream using a drybox. EIMS spectra were recorded on a JEOL JMS-SX-102A spectrometer, and the samples that were sealed in glass capillaries in argon were opened just before operating.

Synthesis of η^5-(Me$_3$Si-fluorenyl)$_2$Sm(THF)$_2$, 1. To a THF solution (90 mL) of fluorene (25.0 g, 151 mmol) held at 0 °C was added dropwise butyllithium in hexane (1.61M, 93.6 mL, 151 mmol) with a dropping funnel. The reaction mixture was stirred at room temperature for 5 h. The resulting orange solution was added to a THF solution of trimethylchlorosilane (28.6 mL, 226 mmol) at 0 °C, and the mixture was stirred for 3 h at room temperature. Then the mixture was poured into an aqueous solution saturated with NaHCO$_3$ (500 mL), and the orange layer was extracted with 3 portions of THF/hexane (1:3) mixed solvent (30 mL × 3) to give Me$_3$Si-fluorene in 90% yield (32.1 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ −0.07 (s, 9H, SiMe$_3$), 3.87 (s, 1H, Cp-H), 7.30 (t, 2H × 2, fluorenyl-H2, 3, 6, 7), 7.49, 7.85 (d, 2H × 2, fluorenyl-H1, 4, 5, 8). To a 300 mL rouud-bottomed flask equipped with a reflux condenser and a three-way stopcock were placed potassium hydride (washed with hexane) (1.94 g, 48.3 mmol) and Me$_3$Si-fluorene (12.7 g, 48.3 mmol). After the addition of 75 mL of THF, the mixture was refluxed for 12 h to give Me$_3$Si-fluorenylpotassium. To a 500 mL round-bottomed flask was placed Sm turnings (3.55 g, 23.6 mmol) and 1,2-diiodoethane (6.64 g, 23.6 mmol). After the addition of THF (160 mL), the resulting deep blue solution was stirred for 3 h and Me$_3$Si-fluorenylpotassium in THF was added to the solution at ambient temperature. The stirring was continued overnight, and the mixture was evaporated to dryness to give a black oily product. After separation of the soluble part from the black oily product by extracting with hexane, the insoluble part was recrystallized from THF/hexane to yield 8.07 g (45%) of (Me$_3$Si-fluorenyl)$_2$Sm(THF)$_2$ as black crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.67 (bs, 8H, THF), 1.06 (bs, 18H, SiMe$_3$), 7.80 (bs, 8H, THF), 8.06, 8.39 (m, 4H × 2, fluorenyl-H2, 3, 6, 7), 11.46, 11.72 (m, 4H × 2, fluorenyl-H1, 4, 5, 8). Anal. Calcd for C$_{40}$H$_{50}$O$_2$SmSi$_2$: C, 62.47; H, 6.55; Sm, 19.55. Found: C, 62.33; H, 6.78; Sm, 20.10 (oxidation method as Sm$_2$O$_3$). EIMS for ^{152}Sm: m/z (relative ratio), 627 (M-2THF, 39), 390 (M-2THF-C$_{16}$H$_{17}$Si, 100).

Synthesis of η^6-(Me$_3$Si-fluorene-AlMe$_3$)$_2$Sm, 2. To a stirred solution of (Me$_3$Si-fluorenyl)$_2$Sm(THF)$_2$ (0.55 g, 0.71 mmol) in toluene (75 mL) was slowly added excess AlMe$_3$(0.35 mL, 3.5 mmol). The color of the solution turned to dark red immediately after the mixing. After stirring for 12 h, the solution was evaporated to dryness and the residue was washed with excess hexane (30 mL × 3) to remove AlMe$_3$. After separation of the hexane solution by centrifugation, the resulting solid was recrystallized from toluene/hexane (1:3 vol ratio) to give (Me$_3$Si-fluorene-AlMe$_3$)$_2$Sm (**2**) as dark red crystals in 57% yield (0.32 g). Anal. Calcd for C$_{38}$H$_{52}$Al$_2$Si$_2$Sm: C, 59.32; H, 6.81. Found: C, 59.05; H, 6.64. EIMS for ^{152}Sm: m/z (relative ratio), 626(M − 2AlMe$_3$, 14), 389 (M − 2AlMe$_3$ − C$_{13}$H$_8$SiMe$_3$, 41), 238 (C$_{13}$H$_8$SiMe$_3$, 100).

Synthesis of η^6-(Me$_3$Si-fluorene-AlEt$_3$)$_2$Sm, 3. To a stirred solution of (Me$_3$Si-fluorenyl)$_2$Sm(THF)$_2$ (1.66 g, 2.2 mmol) in toluene (75 mL) was slowly added excess AlEt$_3$ (1.48 mL, 10.8 mmol). Immediately after mixing, the color of the solution turned to dark red. The stirring was continued for 12 h, and the solution was evaporated to dryness. The residue was washed with excess hexane to remove AlEt$_3$. After separation of the solid by centrifugation, the resulting solid was recrystallized from toluene/hexane (1:3) to afford (Me$_3$Si-fluorene-AlEt$_3$)$_2$Sm (**3**) as dark red crystals in 25.3% yield (0.47 g). Anal. Calcd for C$_{44}$H$_{62}$Al$_2$Si$_2$Sm: C, 62.06; H, 7.34. Found: C, 62.00; H, 7.41. EIMS for ^{152}Sm: m/z (relative ratio), 626(M − 2AlEt$_3$, 21), 389 (M − 2AlEt$_3$ − C$_{13}$H$_8$SiMe$_3$, 41), 238 (C$_{13}$H$_{89}$SiMe$_3$, 100).

Synthesis of η^5-(Me$_3$Si-fluorenyl)$_2$Yb(THF)$_2$, 4. To a 300 mL round-bottomed flask equipped with a reflux condenser and a three-way stopcock were placed potassium hydride (0.95 g, 23.6 mmol) and Me$_3$Si-fluorene (5.6 g, 23.6 mmol). After the addition of THF (75 mL), the mixture was refluxed for 12 h to give Me$_3$Si-fluorenylpotassium. To a 500 mL round-bottomed flask were added Yb turnings (2.05 g, 11.8 mmol) and 1,2-diiodoethane (3.3 g, 11.8 mmol). After the addition of THF (180 mL), the resulting light green solution was stirred for 12 h and Me$_3$Si-fluorenylpotassium in THF was added in one stroke to this solution at ambient temperature. Stirring was continued overnight at ambient temperature, and then the mixture was evaporated to dryness. The residual red oil was dissolved in toluene (90 mL), and the KI salt was removed by centrifugation. The toluene solution was evaporated to dryness, and the resulting red oil was washed with hexane to give η^5-(Me$_3$-Si-fluorenyl)$_2$Yb(THF)$_2$ (**4**) as red oil in 91% yield (8.4 g). ^{1}H NMR (400 MHz): δ 0.65 (bs, 18H, SiMe$_3$), 1.17 (bs, 8H, THF), 2.87 (bs, 8H, THF), 6.87, 7.16 (m, 4H × 2, fluorenyl-H2, 3, 6, 7), 7.78, 7.83 (m, 4H × 2, fluorenyl-H1, 4, 5, 8). EIMS for ^{174}Yb: m/z (relative ratio), 648 [M − 2THF, 25], 411 [M − 2THF − C$_{13}$H$_8$SiMe$_3$, 41].

Synthesis of η^6-(Me$_3$Si-fluorene-AlMe$_3$)-η^5-(Me$_3$Si-fluorenyl)Yb, 5. To a stirred solution of (Me$_3$Si-fluorenyl)$_2$Yb-(THF)$_2$ (**4**) (4.5 g, 5.6 mmol) in toluene (75 mL) was added excess AlMe$_3$ (2.75 mL, 28.0 mmol). After stirring the mixture for 12 h, the solution was evaporated to dryness, and hexane (100 mL) was added. The red, hexane-soluble part was allowed to stand at −25 °C for 5 days without concentration of solution, and orange crystals were precipitated to provide η^6-(Me$_3$Si-fluorene-AlMe$_3$)-η^5-(Me$_3$Si-fluorenyl)Yb (**5**) as red crystals in 32% yield (0.30 g). ^{1}H NMR(400 MHz): δ −1.24 (bs, 9H, AlMe$_3$), 0.15, 0.53 (bs, 9H × 2, SiMe3), 6.84, 7.10, 7.24 (m, 4H, 2H × 2, fluorenyl-H2, 3, 6, 7), 7.45, 7.82, 7.95 (d, 2H × 4, fluorenyl-H1, 4, 5, 8). Anal. Calcd for C$_{35}$H$_{43}$Si$_2$AlYb: C, 58.39; H, 6.02. Found: C, 58.35; H, 6.04. EIMS for ^{174}Yb: m/z (relative ratio), 648 (M − 2AlMe$_3$, 18), 411 (M − 2AlMe$_3$−C$_{13}$H$_8$SiMe$_3$, 49), 238 (C$_{13}$H$_8$SiMe$_3$, 100).

Synthesis of (fluorenyl)Yb(THF)$_4$/AlMe$_4$, 6. To a stirred solution of η^6-(Me$_3$Si-fluorene-AlMe$_3$)-η^5-(Me$_3$Si-fluorenyl)Yb (0.10 g, 1.0 mmol) was added excess THF (30 mL). After evaporation of the solution, the residue was washed with hexane (20 mL), and the resulting solid was recrystallized from hexane/THF to give (fluorenyl)Yb(THF)$_4$/AlMe$_4$ (**6**) in 15% yield. ^{1}H NMR(400 MHz): δ −0.33 (bs, 12H, AlMe$_4$), 1.29 (bs, 16H, THF), 3.28(bs, 16H, THF), 6.23 (bs, 1H, Cp−H), 7.04−7.07 (t, 2H × 2, fluorenyl-H2, 3, 6, 7), 7.72, 8.08 (d, 2H × 2, fluorenyl-H1, 4, 5, 8). Anal. Calcd for C$_{33}$H$_{53}$O$_4$AlYb: C, 53.51; H, 7.21. Found: C, 53.46; H, 7.22.

Synthesis of (^{i}Pr-indenyl)$_2$Yb(THF)$_2$ 7. To a solution of indene (30.0 mL, 258 mmol) in THF (75 mL) held at 0 °C was dropwise added butyllithium in hexane (2.52 M, 102 mL, 258 mmol) via a dropping funnel. The reaction mixture was stirred for 5 h at ambient temperature to give indenyllithium. The color of the solution turned to orange during the stirring. To a 500 mL round-bottomed flask equipped with a three-way stopcock was added a THF solution of isopropyl bromide (28.8 mL, 309 mmol). The solution was cooled to 0 °C with vigorous stirring, and the THF solution of indenyllithium was added to this solution. The mixture was stirred for 3 h and then poured into an aqueous solution saturated with Na$_2$CO$_3$ (500

Table 1. Crystal Data for 1, 2, 3, 5, 6, and 7

	1	**2**	**3**	**5**	**6**	**7**
formula	$C_{40}H_{50}O_2SmSi_2$	$C_{38}H_{52}SmSi_2Al_2$	$C_{44}H_{64}SmSi_2Al_2$	$C_{35}H_{43}YbSi_2Al$	$C_{33}H_{53}O_4YbAl$	$C_{32}H_{42}O_2Yb$
fw	769.40	769.33	853.52	719.92	713.80	631.72
cryst syst	orthorhombic	tetragonal	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$(#19)	$P\bar{4}2_1c$(#114)	$P2_1/a$(#14)	$P2_1/a$(#14)	$P2_1/a$(#14)	$P2_1/a$(#14)
a/Å	16.951(3)	14.424(7)	15.427(3)	9.681(4)	16.94(7)	12.98(2)
b/Å	20.536(4)		18.213(3)	14.322(4)	10.71(6)	11.63(1)
c/Å	10.718(3)q	18.74(1)	17.148(3)	24.713(5)	21.20(8)	19.06(1)
β/deg			114.68(1)	94.32(3)	111.2(3)	92.45(7)
V/Å^3	3731(1)	3898(3)	4377(1)	3416(1)	3584(26)	2874(4)
Z	4	4	4	4	4	4
D_{calcd}/g cm^{-3}	1.370	1.307	1.295	1.119	1.323	1.460
F(000)	1584	1576	1776	1456	1464	1280
μ(Mo Kα)/cm^{-1}	16.73	16.39	14.67	28.54	26.64	32.78
no. of measd rflns	4793	2624	4467	6963	8245	6980
no. of obsd rflns ($I > 3.0\sigma(I)$)	3312	1802	2083[c]	1365[d]	5553	3465
$R^a(R_w)^b$	0.060(0.087)	0.033(0.046)	0.09(0.099)	0.080(0.077)	0.050(0.093)	0.071(0.102)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2))^{1/2}$; $w = 1/\sigma^2(F_o)$. [c] $I > 1.0\sigma(I)$. [d] $I > 1.5\sigma(I)$.

mL). After the separation of the organic layer, the aqueous layer was extracted with three portions of hexane (each 30 mL) and the combined organic layer was washed with water (30 mL × 3). Distillation of the solution (2 Torr/55−58 °C) afforded isopropylindene (33.9 g) in good yield (83%). ^{1}H NMR (400 MHz): δ 0.62, 1.13 (d, 3H × 2, CH-*Me*$_2$), 2.30 (m, 1H, C*H*Me$_2$), 3.42 (d, indenyl-H1), 6.50, 6.83 (d, 1H × 2, indenyl-H2, 3), 7.16, 7.23 (t, 1H × 2, indenyl-H5, 6), 7.34, 7.41(d, 1H × 2, indenyl-H4, 7).

To a 300 mL round-bottomed flask equipped with a reflux condenser and a three-way stopcock were added potassium hydride (0.95 g, 23.4 mmol) in THF (75 mL). After the addition of ^{i}Pr-indene (3.27 mL, 23.4 mmol), the mixture was refluxed for 10 h to give ^{i}Pr-indenylpotassium. To a 500 mL round-bottomed flask were added Yb turnings (2.03 g, 11.7 mmol), THF (180 mL), and then 1,2-dibromoethane (1.01 mL, 11.7 mmol). The mixture was stirred for 12 h, during which time the color of the solution turned to green. The above-mentioned ^{i}Pr-indenylpotassium was added to the resulting $YbBr_2$ at ambient temperature, and the stirring was continued overnight. The solution was evaporated to dryness, and the resulting red oily product was dissolved in 90 mL of toluene. KI salt was separated by centrifugation, and toluene was removed by flash distillation. The oily product changed to powder by the addition of hexane (40 mL). Crystallization of the solid from THF/hexane (1:5) afforded (^{i}Pr-indenyl)$_2$Yb(THF)$_2$ (1.58 g) in 21% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 1.26(bs, 8H, THF), 1.40, 1.44, 1.51, 1.67 (d, 3H x 4, CH*Me*$_2$), 3.11 (bs, 8H, THF), 3.37 (m, 2H, C*H*Me$_2$), 5.93, 6.42, 6.84 (m, 1H x 12, indenyl-H). Anal. Calcd for $C_{32}H_{42}O_2Yb$: C, 60.86; H, 6.70; Yb, 27.40. Found: C, 60.78; H, 6.67; Yb, 27.33 (oxidation method as Yb_2O_3). EIMS for ^{174}Yb: *m*/*z* (relative ratio), 488 (M − 2THF, 18), 331 (M − 2THF − $C_{12}H_{13}$, 36), 157 ($C_{12}H_{13}$, 100).

X-ray Analyses of 1, 2, 3, 5, 6, and 7. All the diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite-monochromatized Mo Kα radiation (Table 1). As the complexes are all air-sensitive, crystals were sealed in thin-walled glass capillary tubes under an argon atmosphere. The X-ray data were collected at room temperature using $\omega-2\theta$ scan techniques to a maximum 2θ value of 55.0°. The data were corrected for conventional absorption, Lorentz, and polarization effects. The crystal structures were solved by the heavy-atom method and were expanded by succesive Fourier syntheses. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods except for **3** and **5** (only metal atoms were refined anisotropically), while the hydrogen atoms were fixed at their standard geometries and were not refined. All the calculations were performed by the use of the teXsan crystallographic software package (teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992).

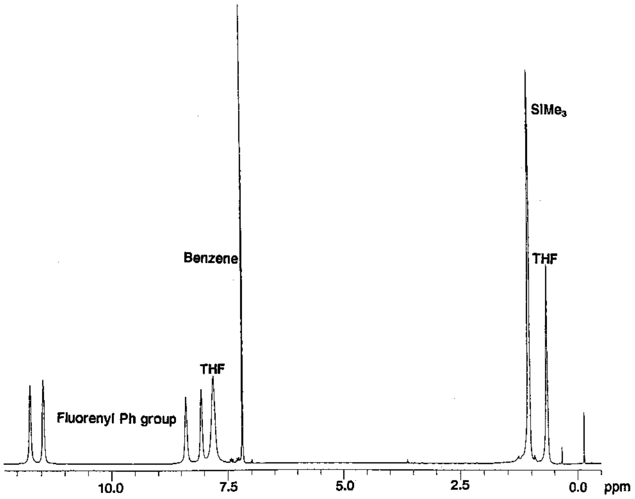
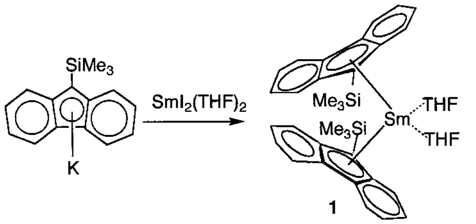


Figure 1. ^{1}H NMR spectrum of η^5-bis(Me$_3$Si-fluorenyl)-Sm(THF)$_2$, **1**, in C_6D_6.

Scheme 1



Results and Discussion

Reaction of $AlMe_3$ with Bis(Me$_3$Si-fluorenyl)Sm-(THF)$_2$. Reaction of bis(fluorenyl)Sm(THF)$_2$ with AlR_3 should give rise to the formation of bis(fluorenyl)Sm(μ-R)$_2$AlR$_2$ or bis(fluorenyl)Sm·AlR$_3$ according to the literature.[6−8] However, $AlMe_3$ did not react with bis(fluorenyl)Sm(THF)$_2$ because of its low solubility in toluene. Therefore we improved its solubility by introducing a trimethylsilyl group into the fluorenyl group. Addition of the potassium salt of Me$_3$Si-fluorene prepared from potassium hydride and Me$_3$Si-fluorene to SmI_2(THF)$_2$ generated bis(Me$_3$Si-fuluorenyl)Sm(THF)$_2$, **1** (Scheme 1). The ^{1}H NMR spectrum reveals the formation of the desired bis(η^5-Me$_3$Si-fluorenyl)Sm-(THF)$_2$ (Figure 1), and the molecular structure was determined by X-ray analysis. Figure 2 shows the

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 1, 2, 3, 5, and 7 with Estimated Standard Deviations (parentheses)

	1	2	3	5	7
C(1)–C(2)	1.37(2)	1.46(1)	1.50(5)	1.52(5)	1.40(3)
C(2)–C(7)	1.43(3)	1.42(1)	1.45(4)	1.38(5)	1.46(3)
C(7)–C(8)	1.46(3)	1.43(1)	1.50(4)	1.41(5)	1.40(3)
C(8)–C(13)	1.38(3)	1.41(1)	1.36(6)	1.41(5)	1.38(4)
C(1)–C(13)	1.45(2)	1.48(1)	1.48(4)	1.48(4)	1.42(3)
C(21)–C(22) or C(1*)–C(2*)	1.43(3)	1.46(1)	1.45(4)	1.43(5)	1.41(3)
C(22)–C(27) or C(2*)–C(7*)	1.41(2)	1.42(1)	1.37(4)	1.46(5)	1.47(3)
C(27)–C(28) or C(7*)–C(8*)	1.49(2)	1.43(1)	1.47(4)	1.43(5)	1.43(3)
C(28)–C(33) or C(8*)–C(13*)	1.45(3)	1.41(1)	1.42(4)	1.44(5)	1.34(3)
C(21)–C(33) or C(1*)–C(13*)	1.46(3)	1.48(1)	1.50(4)	1.48(5)	1.47(3)
M–O(1)	2.58(1)				2.47(1)
M–O(2)	2.51(1)				2.77(2)
M–Cp(1)(centroid)	2.70	3.59	3.56	3.35	2.50
M–Cp(2)(centroid)	2.67	3.59	3.65	2.41	2.48
M-Ph(1)(centroid)	3.43	2.74	2.75	4.94	
M–Ph(2)(centroid)	3.41	5.08	5.10	2.53	
M–Ph(3)(centroid)	3.66	2.74	2.77	3.34	
M–Ph(4)(centroid)	3.58	5.08	5.15	3.30	
Cp(centroid)–M–Cp(centroid)	142.4	118.6	113.5	168.1	123.5
O(1)–M–O(2)	86.6				120.5
Cp(1)–Cp(2)	45.3	55.4	65.7	40.2	120.7

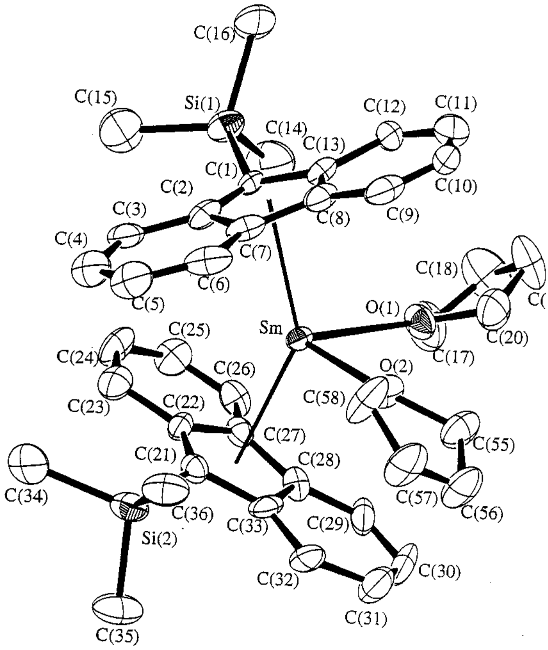


Figure 2. ORTEP drawing of η^5-bis(Me$_3$Si-fluorenyl)Sm(THF)$_2$, **1**.

ORTEP drawing of **1**. The five-membered ring in the fluorenyl group coordinates to the Sm metal, and the Sm–Cp(centroid) distances (2.66–2.77 Å) are nearly equal to 2.633 Å for $(C_5Me_5)_2Sm(THF)_2$[9] and 2.629 Å for (fluorenyl)$_2$Sm(THF)$_2$.[10] As a whole, this complex assumes the coordination geometry of C_2-symmetry, while C_{2v}-symmetry was repoted for bis(fluorenyl)$_2$Sm(THF)$_2$. The dihedral angle between the two Cp planes is ca. 45.3° (Table 2).

The reaction of an excess amount of AlMe$_3$ (5 equiv) with complex **1** gave bis(Me$_3$Si-fluorene-AlMe$_3$)Sm, **2**, as revealed by the ^{1}H NMR spectrum (Scheme 2, Figure 3). The complex **2** promptly decomposes in a moist air. Its exact structure was determined by X-ray analysis using the sample sealed in a thin glass capillary (Figure 4). The most important finding of this complex lies in the η^6-coordination of the Sm atom toward the phenyl

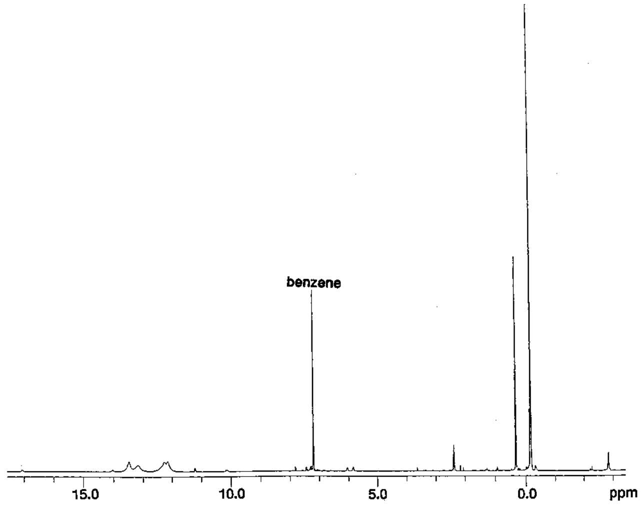
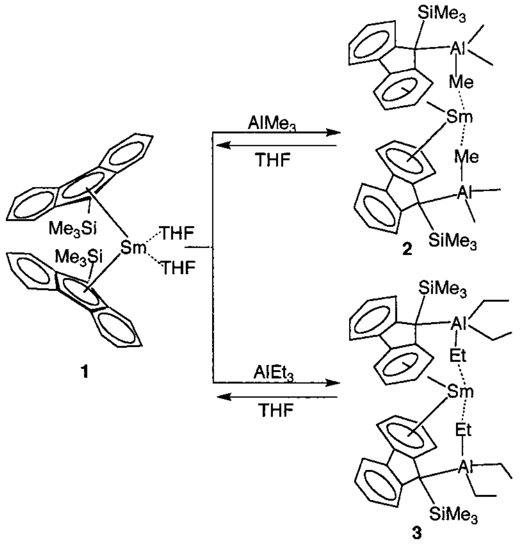


Figure 3. ^{1}H NMR spectrum of η^6-bis(Me$_3$Si-fluorene-AlMe$_3$)Sm, **2**, in C_6D_6.

Scheme 2



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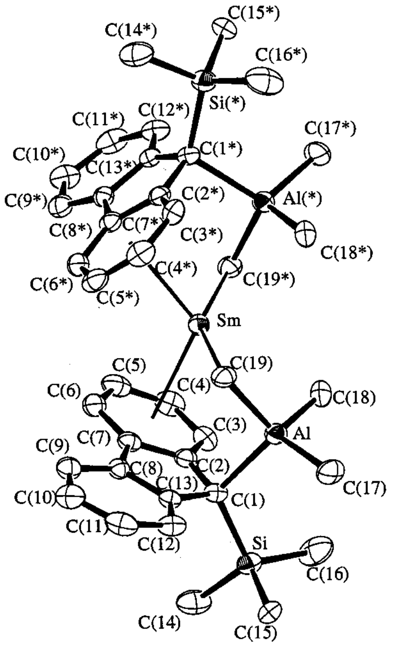


Figure 4. ORTEP drawing of η^6-bis(Me_3Si-fluorene-$AlMe_3$)-Sm, **2**.

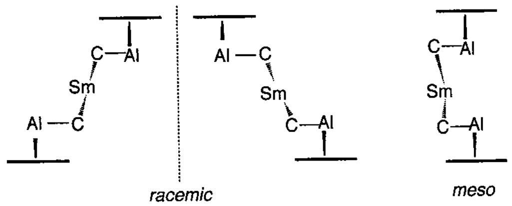


Figure 5. Geometry of η^6-bis(Me_3Si-fluorene-AlR_3)Ln.

group, while in the initial complex η^5-coordination of the Sm atom to the Cp group was observed. The distances of Sm−Cp(centroid) and Sm−Ph(centroid) are 3.59 and 2.74 Å, respectively. The complex assumes a chiral, *racemic* structure, rather than *meso* structure as a result of steric repulsion (Figure 5). The $AlMe_3$ molecule assumes σ-bonding with the C(1) atom of the five-membered ring, and an agostic interaction was observed between the Sm metal and one of the Me groups of $AlMe_3$. The Sm−Me bond length is 2.86 Å. The $AlMe_3$ molecule is located near the Sm atom, while the Me_3Si group exists far from the Sm atom. The C(1)−C(2) and C(1)−C(13) distances are 0.09 and 0.03 Å longer than those of complex **1**. The dihedral angle of the two Cp planes is ca. 55.4°, 10.1° larger than that of the complex **1**.

Reaction of $AlEt_3$ with Bis(Me_3Si-fluorenyl)samarium. The reaction of excess $AlEt_3$ (5 equiv) with complex **1** affords compex **3** in good yield, as revealed by the ^1H NMR spectrum (Scheme 2). Its ORTEP drawing is shown in Figure 6. The coordination geometry of **3** resembled that of **2**. It assumed the *racemic* structure. One of the Et groups exhibited an agostic interaction with the Sm metal at its CH_2 group. The Sm−CH_2 distance (2.92 Å) is a little longer than that (2.87 Å) of **2**, reflecting the bulkier AlR_3 group substituent (Table 2). The dihedral angle of the two Cp rings is 65.7°, much larger than that of the complex **2**. The Sm−Cp(centroid) and Sm−Ph(centroid) distances, 3.56 and 2.76 Å, respectively, are also consistent with those of **2**.

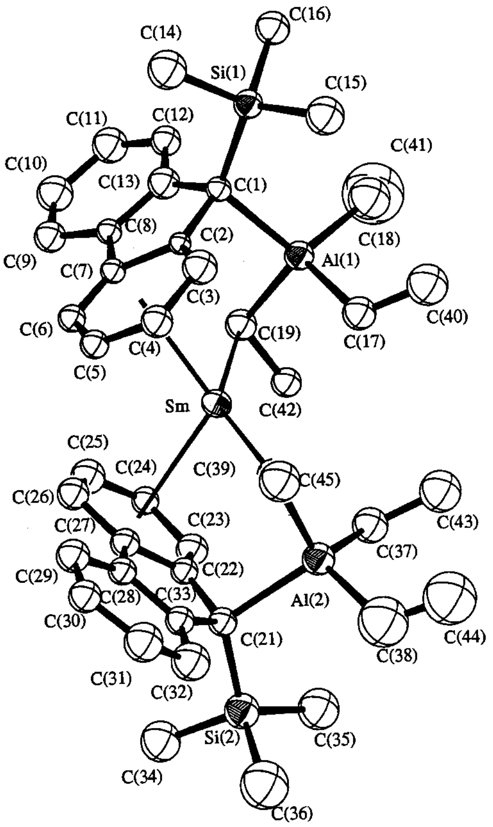
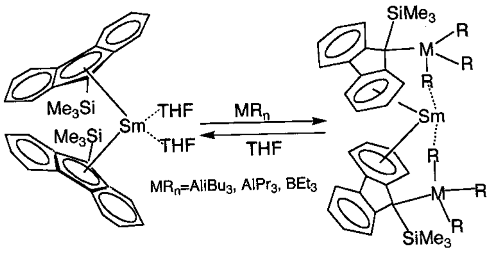


Figure 6. Molecular structure of η^6-bis(Me_3Si-fluorene-$AlEt_3$)Sm, **3**.

Scheme 3



When complexes **2** and **3** were dissolved in THF, the initial complex **1** was formed in quantitaive yield immediately after mixing with THF. Thus, an alternative η^5- and η^6-bonding mode was observed by the reaction of AlR_3 and the succesive addition of a donor molecule.

Reaction of $AlPr_3$, $AliBu_3$, or BEt_3 with Bis(Me_3Si-fluorenyl)samarium. The reaction of $AlPr_3$ or $AliBu_3$ with complex **1** was carried out to find a new type of complexation due to its large steric bulk. The reaction proceeds smoothly to produce complexes that are very soluble even in hexane at low tempertures. Therefore we could not identify the mode of complexation in detail. However, (1) the initial complex **1** is insoluble in hexane, but the resulting complex is freely soluble in hexane, and (2) the ^1H NMR spectra of the adducts are nearly identical with those of complexes **2** and **3**, regarding the absorptions for Me_3Si-fluorene group (10.0−15.0 ppm). Therefore we can readily estimate the structure as shown in Scheme 3. In the same manner, BEt_3 reacted with complex **1** to produce the identical complex as determined by the ^1H NMR spec-

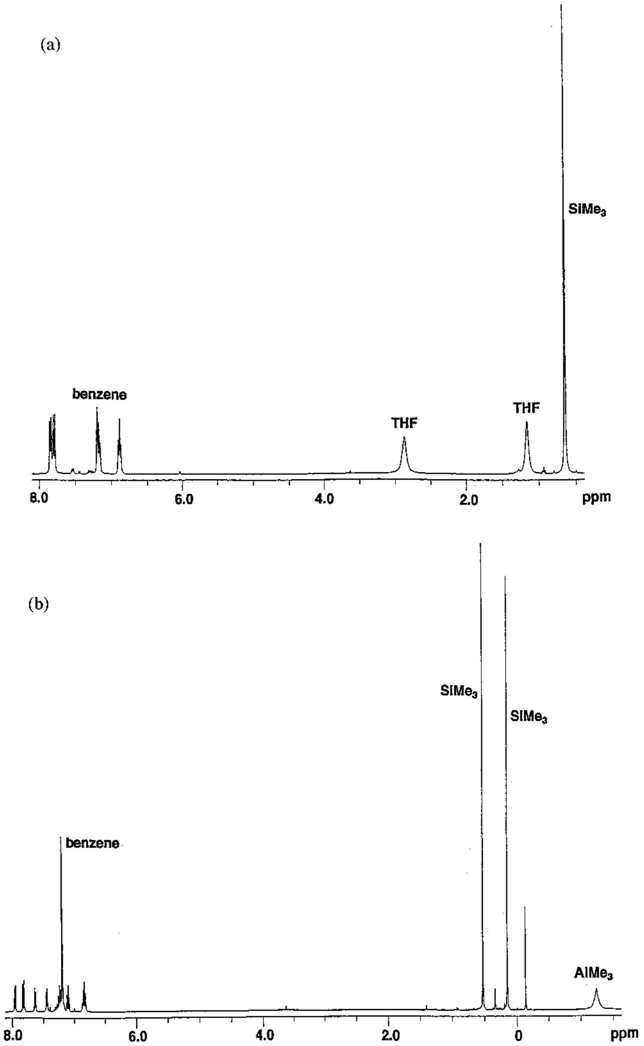


Figure 7. ^{1}H NMR spectrum of (a) η^5-bis(Me$_3$Si-fluorenyl)-Yb(THF)$_2$, **4**, and (b) η^6-(Me$_3$Si-fluorene-AlMe$_3$)-η^5-(Me$_3$Si-fluorenyl)Yb, **5**.

trum, although we could not isolate the respective complexes.

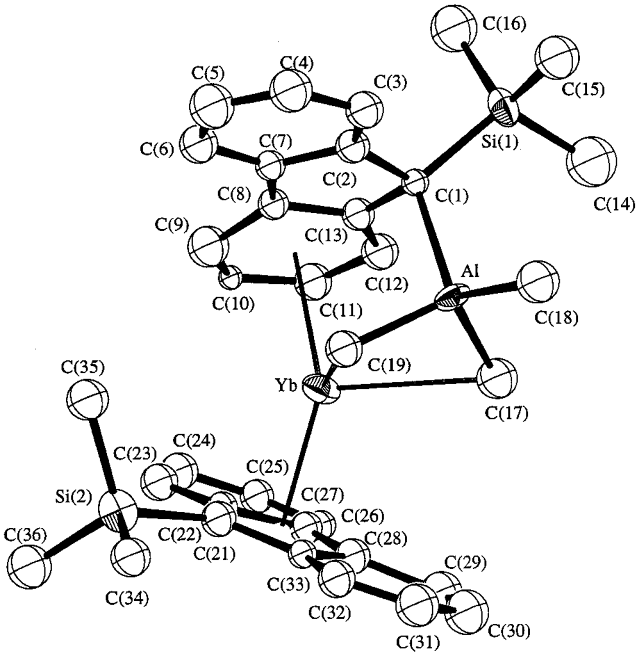
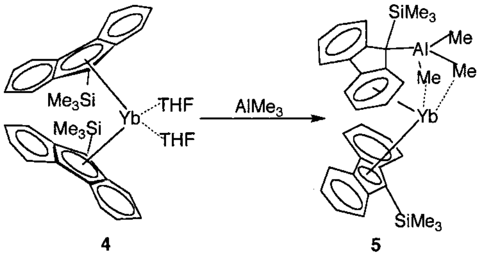
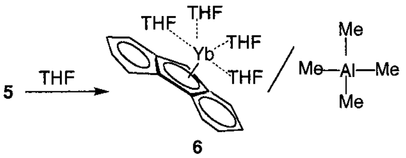


Figure 8. Molecular structure of η^6-(Me$_3$Si-fluorene-AlMe$_3$)-η^5-(Me$_3$Si-fluorenyl)Yb, **5**.

Scheme 4



Scheme 5



Reaction of AlMe$_3$ with Bis(Me$_3$Si-fluorenyl)-ytterbium. To understand the unique reactivity of the corresponding bis(Me$_3$Si-fluorenyl)Yb(THF)$_2$, bearing a small ionic radius of the metal as compared with Sm, toward AlR$_3$, we have prepared bis(Me$_3$Si-fluorenyl)Yb-(THF)$_2$ (**4**) starting from (Me$_3$Si-fluorenyl)K and YbI$_2$. Complex **4** was obtained as red crystals, and its ^{1}H NMR spectrum (Figure 7a) reveals the η^5-coordination of the fluorenyl group. The reaction of excess AlMe$_3$ with **4** gave a mixture of hexane-soluble complex **5** and hexane-insoluble complex **6** in a 9:1 ratio. The ^{1}H NMR spectrum of the hexane-soluble complex indicates the formation of complex **5**, which consists of bis(Me$_3$Si-fluorenyl)Yb/AlMe$_3$ in a 1:1 ratio (Figure 7b, Sheme 4). The molecular structure of **5** was finally determined by X-ray crystallography, and the resulting ORTEP drawing is shown in Figure 8. Complex **5** exhibits an unsymmetrical structure, where AlMe$_3$ binds to the Me$_3$-Si-fluorenyl group at its C(1) position, while the other Me$_3$Si-fluorenyl group is free from the coordination by AlMe$_3$ (it keeps η^5-coordination). The Yb atom is tetracoordinated, and we cannot observe any coordination of the THF molecule in this molecule. An agostic interaction exists between Yb−C(17) and Yb−C(19), whose bond distances are 2.80 and 2.70 Å, respectively, a little shorter than those of **2** and **3**, reflecting the small diameter of the Yb atom as compared with Sm. The geometry of the present coordination should originate from the preferential formation of the agostic interaction between Yb−C(17) and Yb−C(19), which prevents the further coordination of AlMe$_3$ to another Me$_3$Si-fluorenyl group. The dihedral angle of two Cp planes is 40.9°, the smallest angle among **1**, **2**, **3**, and **5**.

We can readily estimate the structure of the complex **6** based on the ^{1}H NMR spectra (see Supporting Information). The Me$_3$Si group is absent in this complex, and the signal of AlMe$_3$ or AlMe$_4$ is observed. The X-ray analysis reveals the presence of only one fluorenyl group, four-coordinated THF molecules, and one AlMe$_4^-$ group (Scheme 5, Figure 9). This complex is also obtained by the addition of excess THF to **5** in a low yield. The reaction pathway for the formation of **6** is unclear at present. However, we could obtain (indenyl-*d*)Yb(THF)$_4$/AlMe$_4$ with a *d*-labeled indenyl group at the

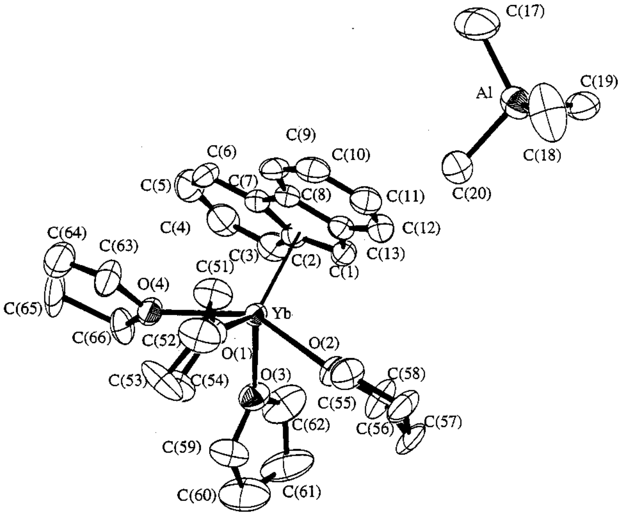


Figure 9. ORTEP drawing of η^5-(fluorenyl)Yb(THF)$_4$/AlMe$_4$, **6**.

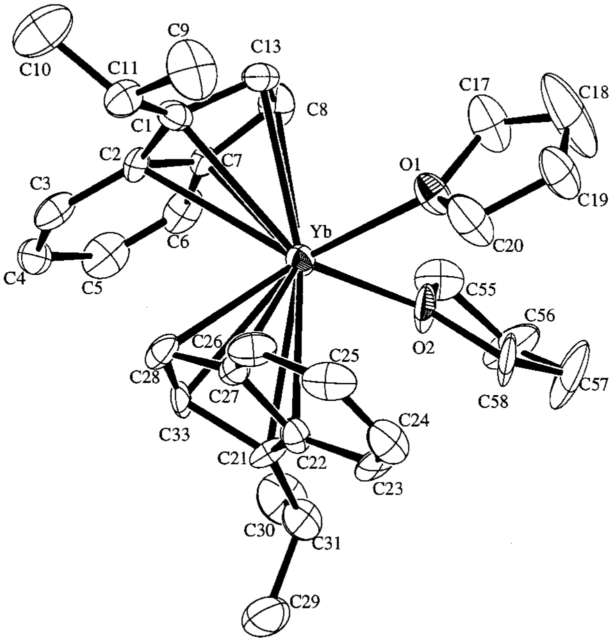


Figure 10. ORTEP drawing of η^5-bis(^{i}Pr-indenyl)Yb(THF)$_2$, **7**.

C(1) position, when we used THF-d_8 in place of THF. Therefore, the Me$_3$Si group should be liberated from the indenyl group by the attack of THF-d_8 molecule.

Scheme 6

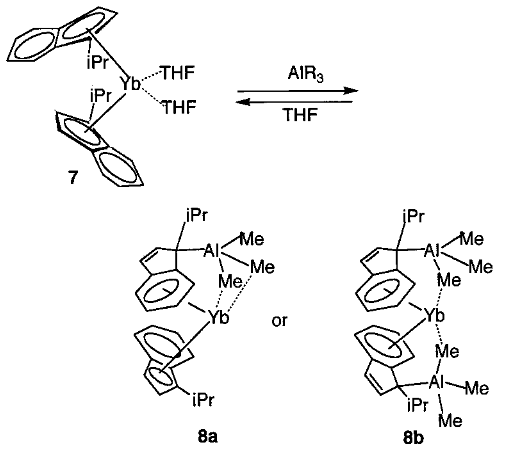


Table 3. Catalytic Activities of 1, 2, and 3 for Polymerization of Ethylene[a]

complex	polym time/min	polym temp/°C	activity (g/(mol h atm))	$M_n/10^4$	M_w/M_n
1	60	25	32	25 800	2.03
2	20	25	125	43 600	2.56
3	60	25	7556	53 200	1.98
	20	65	1719	45 700	2.23

[a] Polymerization conditions: solvent toluene. Ethylene was added at 1 atm.

The Reaction of Bis(^{i}Pr-indenyl)$_2$Yb(THF)$_2$ with AlR$_3$. To understand the role of the Me$_3$Si group bonded with the fluorenyl group and the role of the fluorenyl ring, we have explored the use of bis(^{i}Pr-indenyl)Yb(THF)$_2$ (**7**) and examined the reaction with excess AlMe$_3$. The ^{1}H NMR spectrum of **7** indicates that all the indenyl protons appeared at different positions, and the signasls of ^{i}Pr groups are split into four peaks to indicate that this complex exhibits an unsymmetrical structure due to the distriction of free rotation around the Yb−Cp(centroid) axis (see Supporting Information). The final molecular structure was determined by X-ray analysis, and Figure 10 shows its ORTEP drawing. The molecular structure of the present complex resembles that of **1**. The addition of excess AlMe$_3$ to **7** produced toluene-insoluble compound **8** in quantitative yield, which readily affords initial **7** by the addition of excess THF. Although the molecular structure is unknown due to its low solubility in toluene, we can readily estimate the structure **8a** or **8b** based on the reactions similar to **1** (Scheme 6). This result suggests that $\eta^5-\eta^6$ rearrangement can occur even when we used the indenyl ring bearing a ^{i}Pr group. Thus, the addition of AlR$_3$ to bis(η^5-fluorenyl)Ln(THF)$_2$ or bis(η^5-indenyl)Ln(THF)$_2$ brings about the formation of bis(η^6-fluorene-AlR$_3$)Ln or bis[η^6-indene-(AlR$_3$)$_n$]Ln (n = 1 or 2).

Catalytic Activities of Complexes 1, 2, and 3 for Polymerizations of Ethylene and ϵ-Caprolactone. Kaminsky[11] and Brookhart[12] catalysts, which are known as effective homogeneous catalysts for the polymerization of ethylene and 1-olefins, generally require the presence of cocatalysts such as methylaluminoxane (MAO) or modified methylaluminoxane (MMAO). In sharp contrast to these catalyst systems, rare earth metal complexes exhibit high catalytic activity toward the polymerization of ethylene[13] and polar monomers[14] without the presence of any cocatalyst. We have examined here the catalytic activity of **1**, **2**, and **3** for the polymerization of ethylene and some polar monomers.

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Table 4. Catalytic Acitivities of 1, 2, and 3 for Polymerization of ϵ-Caprolactone[a]

complex	polym time/h	polym temp/°C	$[M]_0/[I]_0$	yield/%	$M_n/10^4$	M_w/M_n
1	5	25	176	97	6.43	1.20
2	5	25	150	99	5.45	1.18
3	5	25	176	100	7.28	1.17

[a] Polymerization conditions: solvent toluene, [solvent]/[monomer] = 2.0 (v/v), $[M]_0/[I]_0$ initial ratio of monomer to the initiator (mol/mol).

The result of the polymerization of ethylene is summarized in Table 3. Complex **1** shows very low activity, while complex **3** has relatively high catalytic activity toward the polymerization of ethylene. Every catalyst provides polyethylene, whose molecular weight exceeds 50 000 with a rather narrow polydispersity. However, their catalytic activities are lower than those of *racemic* $Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}tBu\text{-}C_5H_2)_2Sm(THF)$ and *meso* $Me_2Si(SiMe_2OSiMe_2)(C_5H_2\text{-}3\text{-}tBu)_2Sm(THF)_2$.[13]

The complexes **1**−**3** also showed good catalytic activity toward the polymerization of ϵ-caprolactone (Table 4). The conversion is quantitative, and the molecular weight exceeds 50 000 with narrow polydispersity. However, these complexes show rather low activity for polymerization of methyl methacrylate and styrene. Polymer yield is only 3.0−8.0% after 12 h of reaction.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 283, “Innovative Synthetic Reactions”) from Monbusho.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond distances, bond angles, and hydrogen atom coordinates for complexes **1**, **2**, **3**, **5**, **6**, and **7**, and ^{1}H NMR spectra for complexes **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0002475