# The First Fluorenyl *ansa*-Yttrocene Complexes: Synthesis, Structures, and Polymerization of Methyl Methacrylate

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A novel $C_s$-symmetric yttrocene complex, *ansa*-$Me_2Si(\eta^3\text{-Flu})(\eta^5\text{-Cp}')YCl_2Li(OEt_2)_2$ (**3**; Flu = $C_{13}H_8$, fluorenyl; Cp′ = $C_5Me_4$), has been prepared via a salt metathesis reaction from anhydrous $YCl_3$ and the dilithium salt of the ligand *ansa*-$Me_2Si(FluH)(Cp'H)$. Treatment of **3** with $NaN(SiMe_3)_2$ gave the corresponding bis(trimethylsilyl)amide derivative *ansa*-$Me_2Si(Flu)(\eta^5\text{-Cp}')YN(SiMe_3)_2$ (**4**). The X-ray structure of **3** reveals unusual $\eta^3$-fluorenyl coordination to the $Y^{3+}$ ion. In **4**, the Y−Flu bonding being partially slipped toward $\eta^3$ from $\eta^5$, $\pi$-dative bonding nature in the Y−N bond and a direct interaction of the Y atom with one methyl group of the $N(SiMe_3)_2$ fragment are present. Both compounds constitute the first examples of structurally characterized fluorenyl *ansa*-yttrocenes. The neutral compound **4** is active for the polymerization of methyl methacrylate (MMA) in toluene, affording iso-rich poly(MMA)s.

## Introduction

Homogeneous metallocene catalytic systems utilizing early-metal complexes have been rapidly developed during the last few decades.[1] Along with group 4 metallocene catalysts for the olefin polymerization reactions, rare-earth-metal complexes have received extensive interest owing to their activity for the polymerization of ethylene, α-olefins,[2] polar monomers,[3,4] and various organic transformation reactions.[5] In contrast to the group 4 systems which include a broad range of cyclopentadienyl derivatives (Cp, Cp*, indenyl, and fluorenyl),[1a−c] however, synthetic routes to rare-earth metallocenes are much more limited, mainly due to the high Lewis acidity, large ionic radius, and lower covalency of rare-earth-metal ions, which often result in ligand disproportionation[6] or solvent coordination to the metal center.[7] To partially overcome this problem and to investigate the role of a $\pi$-ligand in governing the overall molecular geometry and electronic properties of organo-rare-earth-metal complexes, many efforts have been made toward substituted ring systems such as permethylated cyclopentadienyl[8,9] or indenyl[5b,10] and their *ansa* analogues.[11] Nevertheless, the synthesis,

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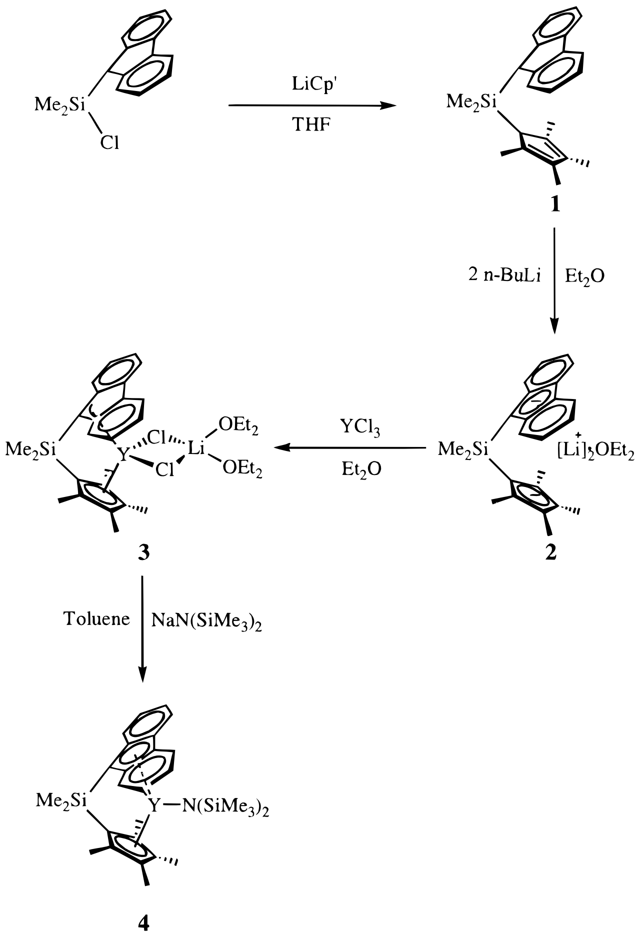
**Scheme 1**[a]



[a] Legend: Cp' = $C_5Me_4$

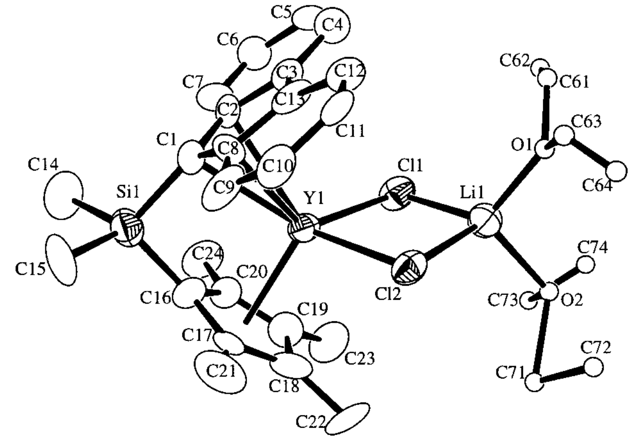


**Figure 1.** Molecular structure of **3** (molecule 1) showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

structure, and investigation of the catalytic effect of the fluorenyl congener, which in turn has played a unique role in group 4 metallocene catalyst systems in olefin polymerization reactions,[12] have not been properly elucidated yet. The only reports have been the synthesis and the structural characterization of bis(fluorenyl) divalent samarium complexes[13] and the synthesis of poly(fluorenyl) complexes of trivalent yttrium[14a] and lanthanides,[14b,c] none of which have been structurally clarified.

Here we report the synthesis and characterization of novel *ansa*-yttrocene complexes $Me_2Si(\eta^3\text{-Flu})(\eta^5\text{-Cp}')YCl_2\text{-}Li(OEt_2)_2$ (**3**) and $Me_2Si(Flu)(\eta^5\text{-Cp}')YN(SiMe_3)_2$ (**4**) which constitute the first examples of structurally characterized fluorenyl group 3 *ansa*-metallocenes. In addition, the catalytic behavior of **4** for the polymerization of methyl methacrylate (MMA) is also described.

## Results and Discussion

An *ansa*-ligand system containing a fluorenyl ring fragment and its yttrium complexes were prepared according to the synthetic routes outlined in Scheme 1. The chelating *ansa* ligand $Me_2Si(FluH)(Cp'H)$ (**1**)[15] was obtained in 96% yield as a viscous yellow orange liquid from the reaction of $Me_2Si(FluH)Cl$[16] with LiCp′ in THF. The reaction of a solution of **1** in $Et_2O$ with 2 equiv of *n*-butyllithium afforded the yellow powder *ansa*-$Me_2Si(Flu)(Cp')Li_2Et_2O$ (**2**) in a yield of 72%. The synthesis of the fluorenyl *ansa*-yttrocene **3** as bright yellow columnar shaped crystals in 33% yield was effected by direct transmetalation of **2** with anhydrous $YCl_3$ in ether at −78 °C followed by the recrystallization at −20 °C. Treatment of **3** with $NaN(SiMe_3)_2$ in toluene gave the corresponding orange-yellow amide complex **4** quantitatively. Compound **4** is highly soluble in toluene, methylene chloride, and ethereal solvents but sparingly soluble in hydrocarbon solvents. These extremely air- and moisture-sensitive complexes, **3** and **4**, were further characterized by NMR, elemental analysis, and X-ray diffraction methods.

The molecular structure of **3** depicted in Figure 1 represents one (molecule 1) of two independent molecules in the asymmetric unit and reveals a pseudotetrahedral bent-metallocene nature. The plane perpendicular to the Cl−Y−Cl plane and bisecting the Cl−Y−Cl angle is a $\sigma$-symmetric plane, giving idealized $C_s$ symmetry in **3**. The ring centroid−metal−ring centroid

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**Table 1. Selected Bond Distances (Å) and Angles (deg) for 3 and 4**

| | **3**[c] | **4** |
|---|---|---|
| | Distances | |
| Y−C1 | 2.56(2) | 2.602(3) |
| Y−C2 | 2.66(2) | 2.707(3) |
| Y−C3 | 2.95(2) | 2.787(4) |
| Y−C8 | 2.74(2) | 2.715(3) |
| Y−C13 | 2.96(2) | 2.788(4) |
| Y−C16 | 2.56(2) | 2.619(3) |
| Y−C17 | 2.59(2) | 2.649(3) |
| Y−C18 | 2.68(2) | 2.790(4) |
| Y−C19 | 2.72(2) | 2.758(4) |
| Y−C20 | 2.60(2) | 2.612(3) |
| Y−C25 | | 2.827(2) |
| Y−$C_f$[a] | 2.487(9) | 2.436(4) |
| Y−$C_p$[b] | 2.339(10) | 2.386(4) |
| Y−Cl1 | 2.595(5) | |
| Y−Cl2 | 2.614(5) | |
| Y−N | | 2.243(11) |
| N−Si2 | | 1.709(14) |
| N−Si3 | | 1.713(13) |
| | Angles | |
| Cl1−Y−Cl2 | 88.04(16) | |
| Cl1−Li−Cl2 | 98.52(16) | |
| O1−Li−O2 | 105.82 | |
| C1−Si1−C16 | 100.4(9) | 100.9(2) |
| $C_f$−Y−$C_p$ | 125.3 | 123.7 |
| Y−N−Si2 | | 103.6(6) |
| Y−N−Si3 | | 132.0(7) |
| Si2−N−Si3 | | 124.4(7) |

[a] $C_f$ = centroid of C1,2,3,8,13. [b] $C_p$ = centroid of C16,17,18,19,20. [c] Refers to molecule 1 only.

($C_f$−Y−$C_p$) angle (125.3°) and the inner angle (100.4(9)°) at the bridging Si atom (C1−Si1−C16) are in a range similar to that seen in other ring-bridged rare-earth-metal complexes.[17]

An interesting structural feature in **3** arises from the bonding modes of the Y atom to the $\pi$-ring planes. As can be seen from the bond distance data listed in Table 1, the Cp′ ring forms rather uniform Y−C distances to give the average Y−$C_{Cp'}$ bond distance of 2.63 Å with a small standard deviation of 0.05 Å, indicating that the Cp′ ring is bonded to the Y atom in the usual $\eta^5$ fashion. On the other hand, the fluorenyl ring in **3** can be best regarded as being $\eta^3$-bonded to the Y atom, as judged by the extent of scattering in Y−$C_{Flu}$ bond distances: the average Y−$C_{Flu}$ bond distance of 2.65 Å between the Y atom and bridgehead (C1) and α-carbon atoms (C2, C8), which is similar to the average Y−$C_{Cp'}$ distance (2.63 Å), is much shorter than that (2.95 Å) between the Y atom and the $\beta$-carbon atoms (C3, C13). The difference (0.30 Å) in the foregoing two average Y−$C_{Flu}$ distances is similar to those observed for the $\eta^3$-fluorenyl ligand in ($\eta^5$-fluorenyl)($\eta^3$-fluorenyl)$ZrCl_2$ (0.28 Å)[18] and the $\eta^3$-indenyl ligand in $Me_2Si$($\eta^5$-1-indenyl)($\eta^3$-2-indenyl)$Hf(NMe_2)_2$ (0.32 Å)[19] but is somewhat larger than that (0.16 Å) in $(fluorenyl)_2Sm(thf)_2$,[13] in which the fluorenyl ring is known to be in the stage of approaching an $\eta^3$-fluorenyl orientation. Extreme distortions toward $\eta^3$ coordination have also been observed in lithium and barium complexes.[20] The smaller angle between the $C_{bridgehead}$−Si bond and the $\pi$-ring plane for the fluorenyl ring (11.8(10)°) than for the Cp′ ring (18.7(11)°) indicates that the strain at the bridgehead carbon atoms of the $\pi$-ring planes is reduced for the fluorenyl ring compared with the Cp′ ring. The acute dihedral angle of 69.9° between two $\pi$-ring planes is somewhat larger than those observed in other Si-bridged bent metallocenes.[12c,21] The $YCl_2Li$ rhombus is nearly planar. The Cl−Y−Cl angle of 88.04(16)° and bond parameters around $Li^+$ fall within ranges similar to those observed in other $Cp^*_2MCl_2LiL_2$ types of complexes,[5e,9,11c,17] indicating that the change in the chelating ligands around the rare-earth center has little influence on the bonding sphere of the ether-coordinated $Li^+$ ion.

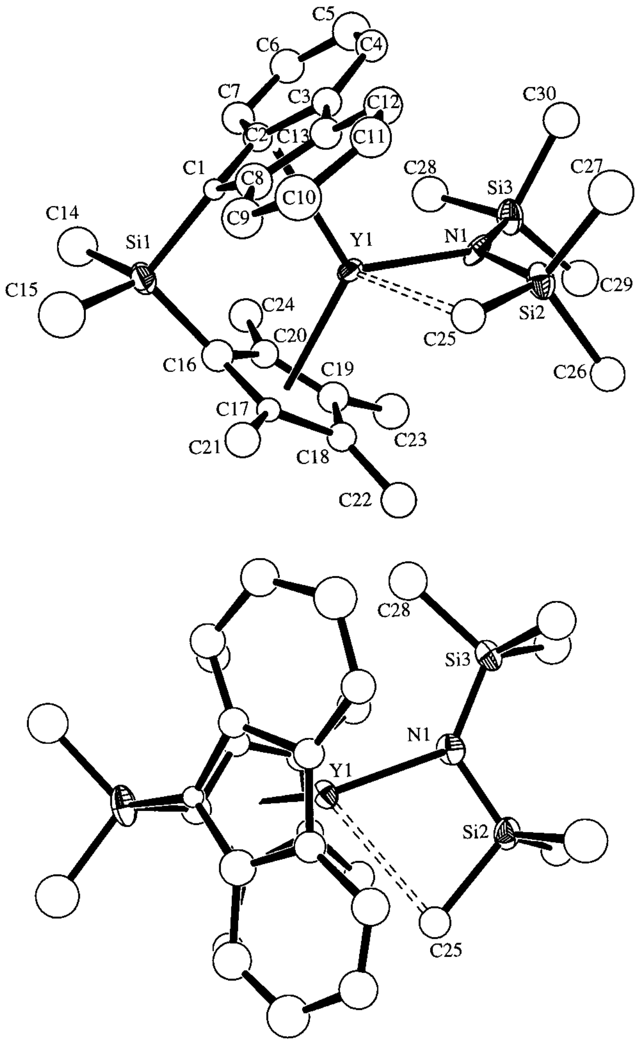

**Figure 2.** Molecular structure of **4** (side and top views) showing 35% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The molecular structure of **4**, given in Figure 2, shows a similar *ansa* ligand environment around the Y atom, except that the direct bonding of the nitrogen atom in

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[17] For typical ranges of ring centroid−metal−ring centroid angles (119−130°) and inner angles at the bridging Si atom (93−104°), see refs 5e, 8b,i, 11c, and: Yoder, J. C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1998**, *17*, 4946.

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the $N(SiMe_3)_2$ fragment with the metal center forms a neutral complex. Detailed structural analysis (Table 1) reveals three major structural aspects.

The first aspect is involved with the bonding mode of the five-membered ring of the fluorenyl fragment to Y. The differences of five Y−C bond distances range from 2.602(3) Å for Y−C1 to 2.788(4) Å for Y−C13, indicating that the central five-membered ring might be described as being partially slipped toward $\eta^3$ from the $\eta^5$ mode. This feature is further supported by the increased strain at the bridgehead carbon atom of the fluorenyl ring and thus an increased angle (17.7(3)°) between the Si1−C1 bond and the $\pi$-ring plane compared with that (11.8(10)°) in **3**. Consistent with this argument are the decreased ring centroid−metal−ring centroid ($C_f$−Y−$C_p$) angle (123.7 vs 125.3° in **3**) and the dihedral angle between two $\pi$-ring planes (66.5 vs 69.9° in **3**). This change of the bonding mode in **4** could be the consequence of pulling out of the metal center from the *ansa* ligand pocket to release the steric hindrance between both ring fragments and the methyl groups of the bulky $N(SiMe_3)_2$ fragment. The bond distances (Y−C = 2.612(3)−2.790(4) Å) between the metal center and the five carbon atoms of the Cp′ ring fragment are somewhat longer than those in **3** but show the typical pattern of normal $\eta^5$ bonding fashion.

The second interesting structural characteristic in **4** is related to the bonding between the Y atom and the amide group. The short Y−N bond distance of 2.243(11) Å is similar to the range observed in $Cp^*_2YN(SiMe_3)_2$ (2.274(5) Å and 2.253(5) Å)[22] and other yttrium amide complexes,[23] suggesting that $\pi$-dative bonding[24] between the Lewis acidic Y atom and the lone electron pair on the N atom is involved to produce the coplanarity of Y, N, and two Si atoms. The fact that the sum of the bond angles at the N atom is 360°, which is typical for an $sp^2$-hybridized nitrogen atom, further supports this coplanarity.

The third aspect is the possible presence of an agostic Y−H(Me) interaction. Although the solution $^1H$ and $^{13}C$ NMR spectral data show only one methyl peak for both $SiMe_3$ groups, thus indicating the magnetic equivalence of Me groups as expected for free rotation in the solution state, both $SiMe_3$ groups are not in a symmetrical position with respect to the Y−N axes, actually showing distorted $C_s$ symmetry in the solid state. The large angle (16.5(3)°) between the plane made by Y−C1−Si1−C16 and the Y−N bond vector and the close contact (2.827(2) Å) of C25 to the Y atom indicate the presence of a secondary interaction of the electron-deficient Y atom with the methyl group.[8h,11b,25] The Y−H(Me) interaction in **4** is stronger than that found in $Cp^*_2YN(SiMe_3)_2$ (2.970(6) Å),[22] indicating that the metal−carbon interaction is more sterically accessible, presumably due to the increased open nature in **4** by adoption of *ansa* ligand geometry. In particular, the increased bond distance of Si2−C25 (1.931(5) Å) compared to those of Si2−C26 (1.886(12) Å) and Si2−C27 (1.865(12) Å) and the much smaller bond angle for Y−N−Si2 (103.6(6)°) than that for the free $SiMe_3$ group (132.0(7)° for Y−N−Si3) further demonstrate the metal−carbon interaction. Moreover, such a contracted angle for Y−N−Si2 is the most apparent among other rare-earth metallocene amide complexes[11c,22,26] and is even similar to that observed in the sterically less demanding $YN(SiMe_2H)_2$ fragment.[11a] The slightly decreased angle for N−Si2−C25 (107.2(4)°) and the eclipsed conformation of two $SiMe_3$ groups are in good agreement with the other observations.[26]

**Table 2. Data for the Polymerization of Methyl Methacrylate by 4**[a]

| run | $T_p$ (°C)[b] | $t_p$ (h) | yield (g) | conversn (%) | $M_w$ | $M_w/M_n$ | mm (%)[c] |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 10 | 0.21 | 4.2 | 109 700 | 1.28 | 56 |
| 2 | 25 | 20 | 0.52 | 10.4 | 113 000 | 1.39 | 58 |

[a] Conditions: catalyst, 0.2 mmol; MMA, 50 mmol; solvent, 50 mL of toluene. [b] At 50 °C, the conversion is very low. [c] Triad values from methyl region of $^1H$ NMR spectra in $CDCl_3$ at 25 °C.

To examine the catalytic ability of compound **4** toward polar monomers, polymerization of methyl methacrylate (MMA) has been tested under the conditions given in Table 2. The polymerization data show that conversion of MMA is low over the various reaction temperatures. The sterically encumbered environment around the metal center coupled with the relatively low reactivity of amide complex compared to the situation for the corresponding alkyl or hydride derivatives[4] seems to act as a major reason for such a low conversion. High molecular weight ($>10^5$) and narrow molecular weight distributions (MWD) of poly(MMA)s are typical of MMA polymerization initiated by organo-rare-earth-metal complexes.[3d−f,4] The characteristic feature of the polymerization involving **4** is the microstructure of poly(MMA)s. Despite the achiral $C_s$ symmetric nature of **4** in solution, all the resulting poly(MMA)s are iso-rich and the mm triad values increase slightly with increasing reaction temperature. This is rather unusual, since isotactic poly(MMA)s have been generally accessed by using chiral $C_1$-symmetric rare-earth metallocenes[4] as catalysts which provide inequivalent coordinating sites via unsymmetrical steric crowding. In compound **4**, however, there is no evident difference in steric crowding for both coordinating sites due to the achiral $C_s$ symmetry. Thus, it is likely that the isotactic propaga-

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(23) (a) $Y[N(SiMe_3)_2]_3$ Y−N = 2.224(6) Å, see: Westernhausen, M.; Hartmann, M.; Pfitzner, A.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 837. (b) $[Y\{N(SiMe_3)_2\}_3(NCPh)_2]$ Y−N = 2.248(4)−2.265(4) Å, see ref 22a. (c) $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)YN(SiMe_3)_2$ Y−NSiMe$_2$ = 2.184(7) Å, Y−N(SiMe$_3$)$_2$ = 2.255(8) Å, see: Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233. (d) (*R*)-$Me_2Si(C_5Me_4)[(-)\text{-menthylCp}]YN(SiMe_3)_2$ Y−N = 2.281(8) and 2.211(8) Å, see ref 11c. (e) $Y[DAC][N(SiMe_3)_2]$ (DAC = 4,13-diaza-18-crown-6) Y−N(SiMe$_3$)$_2$ = 2.338(11) Å, Y−N(DAC) = 2.283(12), 2.29(2) Å, see: Lee, L.; Berg, D. J.; Bushnell, G. W. *Inorg. Chem.* **1994**, *33*, 5302. (f) *rac*-$Me_2Si(2\text{-MeInd})_2YN(SiHMe_2)_2$ Y−N = 2.237(4) Å, see ref 11a.

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tion comes out of the different steric effects of two $\pi$-ring fragments which might influence the monomer coordination and the 1,4-addition process.

In summary, we were able to successfully synthesize the fluorenyl *ansa*-yttrocene complexes $Me_2Si(\eta^3\text{-Flu})(\eta^5\text{-Cp}')YCl_2Li(OEt_2)_2$ and $Me_2Si(Flu)(\eta^5\text{-Cp}')YN(SiMe_3)_2$, characterize their structural features by X-ray diffraction studies, and observe the possible attributes for an isospecific PMMA catalyst in the case of the amide compound.

## Experimental Section

**General Considerations**. All operations were performed under an inert argon atmosphere using standard Schlenk and glovebox techniques. THF, toluene, *n*-pentane, and *n*-hexane were distilled from Na−K alloy; $Et_2O$ was distilled from Na−benzophenone ketyl and $CH_2Cl_2$ from $CaH_2$. Chemicals were used without any further purification after purchasing from Aldrich (anhydrous $YCl_3$, fluorene, $Me_2SiCl_2$, *n*-butyllithium, and $NaN(SiMe_3)_2$) and Strem (LiCp′). Methyl methacrylate (Aldrich) was purified by distillation from $CaH_2$ followed by storage over activated molecular sieves (4A) and then vacuum-transferred using a high-vacuum line ($<10^{-5}$ Torr) prior to use. $CDCl_3$, $C_6D_6$, and THF-$d_8$ were obtained from Aldrich, dried over activated molecular sieves (4A), and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve. The $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker AC 200, Bruker AM 300, and Bruker Avance 400 spectrometers at ambient temperature. HRMS experiments were performed with a VG Auto Spec. Elemental analyses were carried out by Oneida Research Service, Inc., Whitesboro, NY, or on an EA 1110-FISONS instrument (CE Instruments) at KAIST. Molecular weights and molecular weight distributions of the polymers were determined by GPC (Waters 150C, 130 °C) in 1,2,4-trichlorobenzene using polystyrene columns as a standard.

**Synthesis of $Me_2Si(FluH)(Cp'H)$ (1).** A solid mixture of $Me_2Si(FluH)Cl$ (2.58 g, 10.0 mmol) and LiCp′ (1.28 g, 10.0 mmol) was suspended in 50 mL of THF at −78 °C and stirred briefly at this temperature. Then, the reaction mixture was warmed to room temperature and stirred continuously for 1 day. The resulting light brown solution was evaporated to dryness, and 50 mL of hexane was added to dissolve the sticky residue. Filtration and evaporation of the solvent under vacuum gave 3.33 g (96%) of **1** as sticky yellow-orange oil. $^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$ 7.90 (d, 2H, Flu), 7.60 (d, 2H, Flu), 7.37 (m, 4H, Flu), 4.16 (s, 1H, 9-Flu*H*), 3.28 (s, 1H, $C_5Me_4H$), 2.02 (s, 6H, $C_5Me_4$), 1.84 (s, 6H, $C_5Me_4$), −0.27 (s, 6H, $SiMe_2$). HR EIMS: *m*/*z* calcd for $C_{24}H_{28}Si$, 344.20; found, 344.19.

**Synthesis of $Me_2Si(Flu)(Cp')Li_2Et_2O$ (2).** A solution of 1.72 g (5.0 mmol) of **1** in 30 mL of $Et_2O$ was treated with 2 equiv of *n*-butyllithium (10.0 mmol, 2.5 M solution in hexane) at 0 °C. The reaction mixture was then warmed to room temperature and stirred overnight. The dark brown solution over a yellow precipitate was decanted off, and the solid was washed twice with $Et_2O$. Drying in vacuo afforded 1.55 g (72%) of the yellow powder **2**. Due to its high air and moisture sensitivity even in the solid state, the nature of **2** was only established by $^1H$ NMR spectroscopy. In synthetic use, **2** was immediately used as isolated. $^1H$ NMR (200.13 MHz, 5/1 $C_6D_6$/THF-$d_8$): $\delta$ 8.27 (d, 2H, Flu), 8.10 (d, 2H, Flu), 7.29 (t, 2H, Flu), 6.94 (t, 2H, Flu), 3.24 (q, 4H, $OCH_2CH_3$), 2.58 (s, 6H, $C_5Me_4$), 1.99 (s, 6H, $C_5Me_4$), 1.30 (s, 6H, $SiMe_2$), 1.10 (t, 6H, $OCH_2CH_3$).

**Synthesis of $Me_2Si(\eta^3\text{-Flu})(\eta^5\text{-Cp}')YCl_2Li(OEt_2)_2$ (3).** A mixture of 2.42 g (5.60 mmol) of **2** and 1.09 g (5.60 mmol) of anhydrous $YCl_3$ was suspended in 50 mL of $Et_2O$ at −78 °C and stirred for 2 h at this temperature. The reaction mixture was then slowly warmed to room temperature and stirred continuously for 4 h to form a slightly orange solution over a white precipitate. The solution part was carefully transferred to another flask. Concentration and cooling to −20 °C gave 1.20 g (33%) of bright yellow columnar shaped crystalline **3**. $^1H$ NMR (300.13 MHz, $C_6D_6$): $\delta$ 8.09 (m, 4H, Flu), 7.31 (m, 4H, Flu), 3.21 (q, 8H, $OCH_2CH_3$), 2.32 (s, 6H, $C_5Me_4$), 1.97 (s, 6H, $C_5Me_4$), 1.27 (s, 6H, $SiMe_2$), 1.01 (t, 12H, $OCH_2CH_3$). $^{13}C$ NMR (75.1 MHz, $C_6D_6$): $\delta$ 134.76, 128.10, 127.78, 126.91, 125.98, 125.49, 123.07, 123.00, 119.55, 101.72, 65.63, 15.12, 14.98, 12.07, 4.02. Anal. Calcd for $C_{32}H_{46}Cl_2LiO_2SiY$: C, 58.45; H, 7.05. Found: C, 58.32; H, 6.82.

**Table 3. Crystallographic Data and Parameters for 3 and 4**

| | 3 | 4 |
|---|---|---|
| formula | $C_{32}H_{46}Cl_2LiO_2SiY$ | $C_{30}H_{44}NSi_3Y$ |
| fw | 657.53 | 591.84 |
| cryst syst | orthorhombic | monoclinic |
| space group | $P2_12_12_1$ (No. 19) | $P2_1$ (No. 4) |
| *a* (Å) | 22.553(2) | 9.305(1) |
| *b* (Å) | 26.776(2) | 14.520(1) |
| *c* (Å) | 11.680(2) | 11.781(2) |
| α (deg) | 90 | 90 |
| $\beta$ (deg) | 90 | 108.667(11) |
| $\gamma$ (deg) | 90 | 90 |
| *V* (Å$^3$) | 7053.3(15) | 1508.0(3) |
| *Z* | 8 | 2 |
| $d_{calcd}$ (g/cm$^3$) | 1.238 | 1.303 |
| *F*(000) | 2752 | 624 |
| *T* (K) | 293 | 293 |
| $\mu$ (Mo Kα) (mm$^{-1}$) | 1.864 | 2.072 |
| scan mode | $\omega-\theta$ | $\omega-\theta$ |
| $\theta$ range (deg) | 2.11; 20.00 | 2.30; 25.06 |
| no. of unique rflns | 5564 | 2670 |
| no. of obsd rflns ($I > 2\sigma(I)$) | 3608 | 1682 |
| no. of params refined | 605 | 177 |
| R1[a] | 0.0755 | 0.0862 |
| *w*R2[b] | 0.1487 | 0.1943 |
| GOF | 1.126 | 1.290 |
| Flack param | −0.01(2) | 0.08(4) |
| min and max dens (e Å$^{-3}$) | −0.304, 0.461 | −1.352, 1.477 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

**Synthesis of $Me_2Si(Flu)(\eta^5\text{-Cp}')YN(SiMe_3)_2$ (4).** A mixture of 0.33 g (0.50 mmol) of **3** and 0.10 g (0.50 mmol) of $NaN(SiMe_3)_2$ was suspended in 10 mL of toluene at −78 °C and warmed to room temperature. After overnight stirring, the resulting light yellow-orange suspension was filtered and the filtrate was dried in vacuo, affording the spectroscopically pure yellow powder **4** quantitatively. Crystallization from the concentrated toluene solution at −20 °C gave the orange-yellow crystalline product. $^1H$ NMR (300.13 MHz, $C_6D_6$): $\delta$ 7.97 (m, 4H, Flu), 7.16 (m, 4H, Flu), 2.13 (s, 6H, $C_5Me_4$), 1.72 (s, 6H, $C_5Me_4$), 1.14 (s, 6H, $SiMe_2$), −0.35 (s, 18H, $NSiMe_3$). $^1H$ NMR (400.13 MHz, $CDCl_3$): $\delta$ 8.08 (d, 2H, Flu), 7.95 (d, 2H, Flu), 7.28 (m, 2H, Flu), 7.10 (m, 2H, Flu), 2.18 (s, 6H, $C_5Me_4$), 1.80 (s, 6H, $C_5Me_4$), 1.24 (s, 6H, $SiMe_2$), −0.52 (s, 18H, $NSiMe_3$). $^{13}C$ NMR (100.62 MHz, $CDCl_3$): $\delta$ 134.79, 127.95, 126.32, 125.05, 124.27, 123.68, 122.54, 119.41, 110.37, 82.31, 14.85, 12.02, 3.50, 2.93. Anal. Calcd for $C_{30}H_{44}NSi_3Y$: C, 60.88; H, 7.49; N, 2.36. Found: C, 61.26; H, 7.09; N, 1.96.

**Polymerization of MMA.** A solution of preweighed catalyst (0.2 mmol) in 50 mL of toluene was adjusted to a constant temperature using an external bath. Into the well-stirred solution was syringed 50 mmol of methyl methacrylate, and the reaction mixture was continuously stirred for an appropriate period at that temperature. The polymerization was stopped by the addition of methanol. The resulting precipitated poly(MMA) was collected, washed with methanol several times, and dried in vacuo at 50 °C for 12 h.

**X-ray Structure Determination of 3 and 4.** Single crystals suitable for X-ray structure determinations were sealed in thin-walled glass capillary tubes under an argon atmosphere. The measurements of diffraction intensity were carried out on an Enraf-Nonius CAD4TSB diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 293 K. Accurate unit cell parameters and orientation matrixes were determined from the least-squares fit of 25 accurately centered reflections in the range of $18.36° < 2\theta < 26.69°$ for **3** and $13.74° < 2\theta < 31.64°$ for **4**. Intensity data were collected by using the $\omega-\theta$ scan mode with a range of $2.11° < \theta < 20.00°$ for **3** and $2.30° < \theta < 25.06°$ for **4**. All the intensity data were corrected for Lorentz and polarization effects. The structures were solved by semi-invariant direct methods (SIR 92 in MoleN)[27] and refined by full-matrix least-squares refinement (SHELXL 93)[28] with anisotropic thermal parameters for all non-hydrogen atoms except the lithium atom and the disordered diethyl ether molecules for **3** and the Y, N, and Si atoms for **4**. Hydrogen atoms, except those on C25 in **4**, were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Final refinement based on the reflections ($I > 2.0\sigma(I)$) converged at R1 = 0.0755, wR2 = 0.1487, and GOF = 1.126 for **3** and at R1 = 0.0862, wR2 = 0.1943, and GOF = 1.290 for **4**. All calculations were performed on a Silicon Graphics Indigo2XZ workstation. The detailed data are given in Table 3.

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**Supporting Information Available:** Tables of atomic coordinates, thermal parameters, and interatomic distances and angles for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] Sheldrick, G. M. SHELXL 93: Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1993.