Sterically Hindered Lanthanide Allyl Complexes and Their Use as Single-Component Catalysts for the Polymerization of Methyl Methacrylate and ε-Caprolactone

Timothy J. Woodman, Mark Schormann, David L. Hughes, and
Manfred Bochmann*

*Wolfson Materials and Catalysis Center, School of Chemical Sciences,
University of East Anglia, Norwich, NR4 7TJ, U.K.*

Received February 3, 2004

The reaction of KL^3 (L^3 = 1,3-$C_3H_3(SiMe_3)_2$) with $NdI_3(THF)_{3.5}$ affords two products, $L^3NdI_2(THF)_{1.25}$ and $(L^3)_2NdI(THF)_2$ (**1**). The latter has been crystallographically characterized; it has a distorted trigonal-bipyramidal structure with the THF ligands in trans position. The reaction of YCl_3 with 2 equiv of the *ansa*-bis(allyl) ligand $K_2[3-(C_3H_3SiMe_3-1)_2SiPh_2]$ in tetrahydrofuran followed by recrystallization from diethyl ether gives $[Y\{3-(\eta^3-C_3H_3SiMe_3-1)_2SiPh_2\}_2\{\mu-K\}(THF)_{0.5}(Et_2O)_{1.5}]_\infty$ (**2**) as a bright orange solid. Reaction of $Cp''_2LnCl_2Li(THF)_2$ (Cp'' = 1,3-$C_5H_3(SiMe_3)_2$); Ln = Y or Sm) with $[K_2\{3-(\eta^3-C_3H_3SiMe_3-1)_2SiMe_2]$ in THF leads to ligand redistribution to give $[Li(OEt_2)(THF)_3][Ln\{3-(\eta^3-C_3H_3SiMe_3-1)_2SiMe_2\}_2]$ (**3**, Ln = Y; **4**, Ln = Sm). The identity of **3** was confirmed by single-crystal X-ray diffraction. Reaction of $Cp''_2YCl_2Li(THF)_2$ with $[K_2\{3-(\eta^3-C_3H_3SiMe_3-1)_2SiPh_2]$ affords **2**, while $Cp''_2SmCl_2Li(THF)_2$ and $[K_2\{3-(\eta^3-C_3H_3SiMe_3-1)_2SiPh_2]$ give a red crystalline solid, identified by single-crystal X-ray analysis as the mono-Cp complex $[Cp''Sm\{3-(\eta^3-C_3H_3SiMe_3-1)_2SiPh_2\}(\mu-Cl)Li(THF)_3]$ (**5**). Above 50 °C complexes **1** as well as $(L^3)_2LnCl(THF)$ (**7**) and $(L^3)_2YCl$ (**8**) initiate the rapid polymerization of ε-caprolactone. The anionic complexes **2**, **3**, **4**, and $[Y\{3-(\eta^3-C_3H_3-SiMe_3-1)SiMe_2\}_2\{\mu-K(THF)\}\cdot(THF)_n]_\infty$ (**6**) are very active for both ε-caprolactone and methyl methacrylate polymerization at room temperature. The stereoselectivity is dependent on the solvent and the countercation, with lithium salts of **3** and **4** in THF producing syndio-rich poly(methyl methacrylate).

Introduction

Organometallic complexes of the lanthanide metals have been shown to be extremely versatile as catalysts for a wide range of polymerizations, of both polar[1] and nonpolar monomers.[2] The most commonly studied systems have traditionally been those derived from the cyclopentadienyl ligand; for instance, Cp_2LnR (R = H, alkyl) complexes are excellent single-component catalysts for the polymerization of ethylene (Cp = C_5Me_5, Ln = La, Nd, R = H),[3] 1-alkenes (Cp_2 = *rac*-$Me_2Si(2-SiMe_3-4-CMe_3C_5H_2)_2$, Ln = Y, R = H),[2b] alkyl methacrylates (Cp = C_5Me_5, Ln = Sm, R = H),[4] alkyl acrylates (Cp = C_5Me_5, Ln = Y, Sm, R = Me),[5] alkyl isocyanates (Cp = C_5Me_5, Ln = La, R = CH(SiMe_3)_2),[6] ε-caprolactone (Cp = C_5Me_5, Ln = Sm, R = Me)[7] and styrene (Cp = ^tBuCp, Ln = Pr, Nd, Gd, R = Me).[6,8] Catalysts derived from allyl lanthanide complexes are less well-known; notable exceptions are the use of neodymium and lanthanum complexes as stereospecific butadiene polymerization catalysts[9] and the recent use of samarium and ytterbium complexes for the polymerization of methyl methacrylate.[10] Sterically demanding silyl substituents allow the isolation of stable homoleptic allyl complexes of first-row transition metals, whereas the compounds $M(C_3H_5)_n$ are either thermally

* Corresponding author. E-mail: m.bochmann@uea.ac.uk.
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Chart 1

Figure 1. Molecular structure of one of the two independent molecules of **1**, showing the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

unstable (M = Co, V, Ni)[11] or not known (M = Fe, Mn). Thus the 1,3-bis(trimethylsilyl)allyl ligand (Chart 1, ligand **L³**)[12] has been used to prepare the complexes M(**L³**)₂ (M = Co,[13] Ni,[13] Fe,[14] and Cr[14]), with the iron and chromium complexes being stable to sublimation at relatively high temperatures (ca. 60−80 °C). Recently some Zr(III) and Ti(III) ethene and propene polymerization catalysts containing the 1,3-bis(*tert*-butyldimethylsilyl)allyl ligand have been reported.[15] Lappert et al. have used the *ansa*-bis(allyl) ligand [Me₂Si(CHCH-CHSiMe₃)₂]²⁻ (**L⁴**) to prepare the complexes M(**L⁴**)₂ (M = Zr, Hf); the zirconium complex polymerizes ethene in the presence of methylalumoxane (MAO).[16] The samarium(II) complexes (1,3-C₃H₃R₂)₂Sm(THF)₂ (R = Ph, SiMe₃) have been reported, although they were not fully characterized.[10] We have recently described complexes such as Y(**L¹**)₃ and Y(**L²**)₃, (**L³**)₂LnCl(THF)ₙ (Ln = Y, *n* = 0; Ln = La, *n* = 1), the mono-allyl compound (**L³**)NdI₂(THF)₁.₂₅, and the structurally characterized "ate" complex (**L³**)₂ScCl₂Li(THF)₂.[17] With the *ansa*-bis(allyl) ligand **L⁴** we unexpectedly obtained the lanthanate complexes [Ln(**L⁴**)₂{μ-K(THF)}·(THF)ₙ]∞ (Ln = La, *n* = 0.5; Ln = Y, *n* = 1; Ln = Sc, *n* = 1), [Nd(**L⁴**)₂{μ-K}]∞, and [Li(OEt₂)₄][Sm(**L⁴**)₂].[18] The lanthanum complex features potassium ions playing an important structural role as bridging atoms by means of π and agostic interactions. This bridging role of K⁺ was also seen in the first structurally characterized samarium(II) allyl complex [Sm(**L³**)₃{μ-K(THF)₂}]₂, where the potassium atoms allow the formation of a K₂Sm₂ tetrametallic ring structure.[19] These "ate" complexes initiate the polymerization of methyl methacrylate with very high activities. We report here further synthetic and structural studies on this class of allyl complexes.

Results and Discussion

The reaction of NdI₃(THF)₃.₅ with K**L³** leads to two products, the less soluble mono-allyl complex (**L³**)NdI₂-(THF)₁.₂₅[17] and the bis-allyl (**L³**)₂NdI(THF)ₙ (**1**) (eq 1); the latter was mentioned in a preliminary communica-

tion.[19] During the course of this work we have now been able to obtain crystals of **1** suitable for X-ray crystallography, by recrystallization from light petroleum at − 20 °C. There are two discrete essentially identical molecules of **1** in the crystal structure, one of which is depicted in Figure 1, with selected bond lengths and interatomic distances collected in Table 1.

The coordination environment of the neodymium atom is comprised of the two η³-allyl ligands, the iodide, and the two molecules of THF. The neodymium−carbon bond distances lie in the range 2.671(6)−2.781(6) Å, with an average of 2.73 Å (molecule 1) and 2.72 Å (molecule 2). These values compare closely with those in previously reported complexes; for instance in [{η³-C₃H₅}₂-NdCl(THF)₂]₂·2THF the Nd−C distances are in the range 2.674(5)−2.748(5) Å, with an average of 2.717 Å.[9e] This implies that the bulky silyl substituents of the allyl ligands in the current example have little effect on the bond distances. The Nd−O(THF) distances are in the range 2.512(4)−2.519(4) Å and, as such, are shorter than in previously described complexes, e.g., [{η³-C₃H₅}₂-

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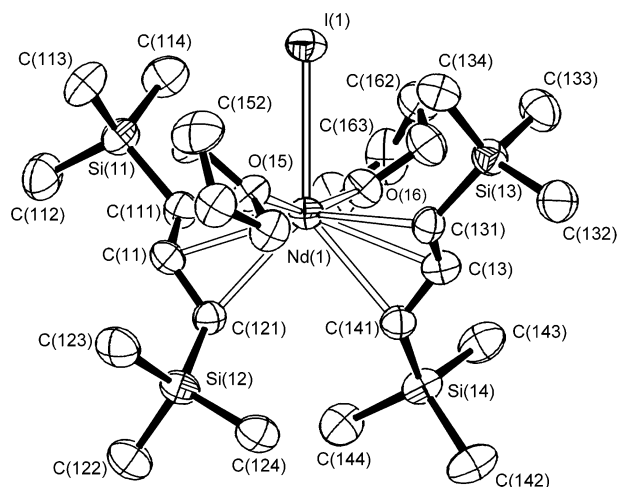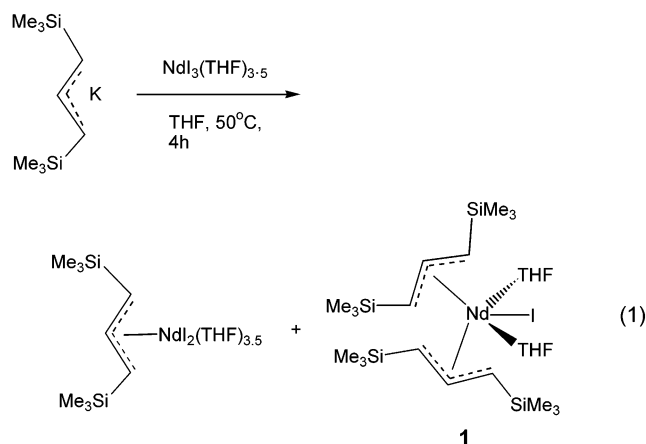
Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) for 1

molecule 1		molecule 2	
Nd(1)−I(1)	3.1547(7)	Nd(2)−I(2)	3.1419(7)
Nd(1)−C(111)	2.781(6)	Nd(2)−C(211)	2.757(5)
Nd(1)−C(11)	2.758(5)	Nd(2)−C(21)	2.752(5)
Nd(1)−C(121)	2.671(6)	Nd(2)−C(221)	2.678(5)
Nd(1)−C(131)	2.760(6)	Nd(2)−C(231)	2.719(6)
Nd(1)−C(13)	2.754(6)	Nd(2)−C(23)	2.748(6)
Nd(1)−C(141)	2.683(6)	Nd(2)−C(241)	2.679(6)
Nd(1)− O(15)	2.519(4)	Nd(2)− O(25)	2.513(4)
Nd(1)−O(16)	2.512(4)	Nd(2)−O(26)	2.514(4)
C(11)−C(111)	1.385(7)	C(21)−C(211)	1.404(7)
C(11)−C(121)	1.413(8)	C(21)−C(221)	1.399(8)
C(13)−C(131)	1.391(8)	C(23)−C(231)	1.390(8)
C(11)−C(141)	1.390(8)	C(23)−C(241)	1.397(7)
C(111)−C(11)−C(121)	126.1(6)	C(211)−C(21)−C(221)	128.2(5)
C(131)−C(13)−C(141)	126.2(6)	C(231)−C(23)−C(241)	127.3(5)

NdCl(THF)$_2$]$_2$·2THF, where the corresponding distance is 2.555(3) Å, and the dioxane adduct {η^3-C$_3$H$_5$}$_3$Nd-(C$_4$H$_8$O$_2$) (Nd−O 2.612(3) and 2.605(3) Å).[9a] The Nd−I bond distances, 3.1547(7) and 3.1419(7) Å, resemble those in the hydrotris(pyrazolyl)borate complex (Tp^H)-NdI$_2$(THF)$_2$ (Nd−I 3.062(3) and 3.136(3) Å).[20]

As stated above, lanthanide complexes of the *ansa*-bis(allyl) ligand **L^4** are highly active in the polymerization of methyl methacrylate but give limited stereoselectivity. It was hoped that a sterically more hindered ligand, [Ph$_2$Si(CHCHCHSiMe$_3$)$_2$]$^{2-}$ (**L^5**), might produce higher syndiotacticity. Ph$_2$Si(CH$_2$CHCHSiMe$_3$)$_2$ was prepared from allyltrimethylsilane and diphenyldichlorosilane in high yield. Reaction with ^{n}BuLi followed by addition of KO^{t}Bu in diethyl ether allows the facile isolation of the dipotassium salt K$_2$L^5. The reaction of 2 equiv of this salt with YCl$_3$ in THF, removal of the volatiles, and recrystallization from diethyl ether provides [Y(**L^5**)$_2${μ-K}(THF)$_{0.5}$(Et$_2$O)$_{1.5}$]$_\infty$ (**2**) in moderate yield as a bright orange microcrystalline solid (Scheme 1). As with the similar complexes derived from **L^4**, **2** is only sparingly soluble in hydrocarbons such as light petroleum and toluene, and NMR spectra had to be recorded in THF-d_8. The spectra and solubility were similar to the previously isolated tetra(allyl) ate complexes, which suggests that **2** is likely to possess a similar structure, although it was not possible to confirm this crystallographically.

In view of the successful use of the bis-cyclopentadienyl ligand environment in lanthanide polymerization catalysts, attempts were made to extend the family of allyl complexes to mixed-ligand compounds of the type [Cp$_2$Ln(allyl)$_2$]$^-$, with the aim of generating catalysts that could combine high polymerization activity with improved control of polymer microstructure. Thus a range of reactions was undertaken with Cp″$_2$LnCl$_2$Li-(THF)$_2$ (Cp″ = 1,3-C$_5$H$_3$(SiMe$_3$)$_2$; Ln = Sm or Y) and the potassium salts K$_2$L^4 and K$_2$L^5. Treatment of Cp″$_2$-LnCl$_2$Li(THF)$_2$ with K$_2$L^4 in THF gave brightly colored solutions (orange for yttrium, deep red for samarium). Removal of volatiles, washing with light petroleum, and recrystallization of the solids from diethyl ether at −20 °C afforded [Li(OEt$_2$)(THF)$_2$][Ln(**L^4**)$_2$] (**3**, Ln = Y; **4**, Ln = Sm) as orange and deep red crystalline solids, respectively (Scheme 2). The NMR spectra of **3** and **4** closely correspond to those of [Y(**L^4**)$_2${μ-K(THF)}·

(THF)$_n$]$_\infty$ and [Li(OEt$_2$)$_4$][Sm(**L^4**)$_2$]. In both cases cooling of the light petroleum washings from the preparation of **3** and **4** to −20 °C yielded crystals of Cp″$_2$LnCl$_2$Li-(THF)$_2$ and, in the case of **4**, also Cp″$_3$Sm, as shown by comparison of the NMR spectra with literature reports.[21,22] Clearly **3** and **4** have formed as the result of ligand redistribution, a well-known phenomenon when attempting to prepare mixed-ligand lanthanide complexes.

The identity of **3** was confirmed by a single-crystal X-ray diffraction (Figure 2). Selected bond lengths and angles collected in Table 2. The structure of **3** resembles that of the previously reported samarium complex [Li(OEt$_2$)$_4$][Sm(**L^4**)$_2$],[18] with the same *anti*, *syn* arrangement of the *ansa*-bis(allyl) ligands around the metal. The yttrium−carbon bond lengths are in the range 2.625(3)−2.727(3) Å, with an average of 2.682 Å. These are longer than those in the complex Y(η^3-C$_3$H$_5$){N(SiMe$_2$-CH$_2$PMe$_2$)$_2$}(μ-Cl)$_2$ (Y−C = 2.587(5), 2.609(5), and 2.621-(5) Å),[23] indicating greater steric congestion in **3**. The C−C−C bond angles in **3** are 127.7(3)°, 128.9(3)°, 127.2(3)°, and 127.5(3)° compared with 126.1(6)° in Y(η^3-C$_3$H$_5$){N(SiMe$_2$CH$_2$PMe$_2$)$_2$}(μ-Cl)$_2$.

In a similar manner, the reaction of Cp″$_2$YCl$_2$Li-(THF)$_2$ with K$_2$L^5 in THF gave **2**. In this case a potassium atom was retained as the counterion, even in the presence of lithium cations. The reaction of Cp″$_2$SmCl$_2$Li(THF)$_2$ with K$_2$L^5 in THF produced a deep red solution. Removal of the solvent and extraction of the resulting solids with light petroleum afforded a crop of maroon crystals of **5**. The ^{1}H NMR spectrum of this compound was complicated; however, in contrast to the formation of **2**−**4** it was clear that cyclopentadienyl as well as allyl ligands were present. The solubility properties also suggested a different structure from the tetra-(allyl) lanthanate complexes. This was confirmed by single-crystal X-ray diffraction, which identified compound **5** as a zwitterionic mixed-ligand complex, [Cp″Sm-(**L^5**){μ-ClLi(THF)$_3$}] (Scheme 3).

The formation of **5** is an unusual example of the displacement of a cyclopentadienyl ligand while a chloride ligand has been retained. It seems likely that the steric congestion at the lanthanide center is the principal reason for the preferential loss of the Cp″ ligand. The reaction exemplifies the sensitivity of ligand exchange equilibria in lanthanide mixed-ligand complexes to steric factors.

The crystal structure of **5** is depicted in Figure 3, with selected bond lengths and angles collected in Table 3. The ligand environment of the samarium atom is comprised of the η^5-bonded cyclopentadienyl group, the *ansa*-bis(allyl) ligand, and a chloride ion bridging to a lithium cation. The bond distances to the cyclopentadienyl group are similar to those reported previously; for example, in Cp″$_3$Sm the average Sm−C bond distance is 2.76(4) Å,[22] whereas in **5** the distances lie in the range 2.705(4)−2.741(4) Å (average 2.73 Å). In contrast to the situation found in Cp″$_3$Sm, the shortest Sm−C bond distance is to the carbon between the two Me$_3$Si-

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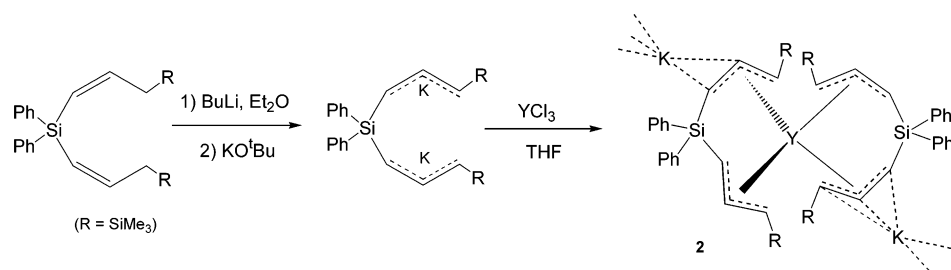
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Scheme 1

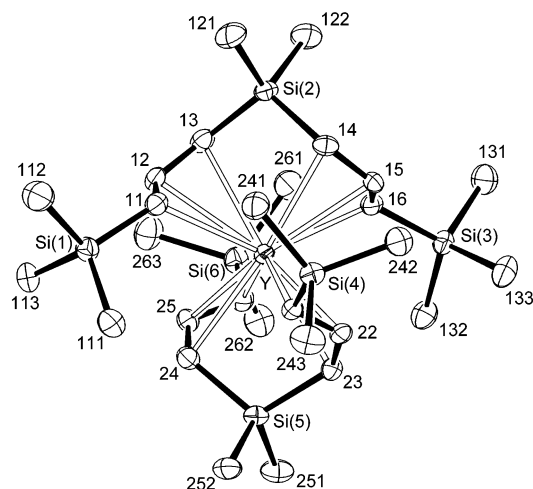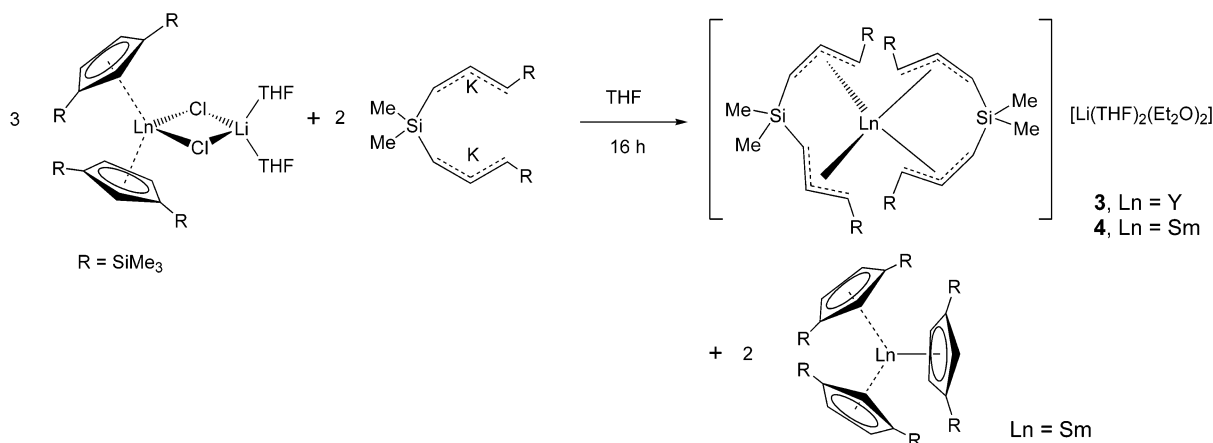(R = SiMe$_3$)

Scheme 2

R = SiMe$_3$

Ln = Sm

Figure 2. Molecular structure of one of the complex anions in **3**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for 3

Y−C(16)	2.625(3)	Y−C(21)	2.631(3)
Y−C(15)	2.671(3)	Y−C(24)	2.675(3)
Y−C(26)	2.680(3)	Y−C(22)	2.679(3)
Y−C(25)	2.682(3)	Y−C(12)	2.688(3)
Y−C(11)	2.701(3)	Y−C(14)	2.705(3)
Y−C(13)	2.720(3)	Y−C(23)	2.727(3)
C(11)−C(12)	1.407(4)	C(12)−C(13)	1.390(4)
C(14)−C(15)	1.401(4)	C(15)−C(16)	1.401(4)
C(21)−C(22)	1.401(4)	C(22)−C(23)	1.450(4)
C(24)−C(25)	1.396(4)	C(25)−C(26)	1.405(4)
Li−O(5)	1.927(6)	Li−O(6)	1.958(6)
Li−O(3)#1	1.958(6)	Li−O(4)	1.961(6)
C(13)−C(12)−C(11)	128.9(3)	C(14)−C(15)−C(16)	127.7(3)
C(21)−C(22)−C(23)	127.2(3)	C(24)−C(25)−C(26)	127.5(3)

substituted carbons (C(12)); in Cp″$_3$Sm this is regarded as the most sterically crowded position. As in other *ansa*-allyl complexes, the ligand adopts an *anti, syn* configuration. The Sm−C(allyl) bond distances lie in the range 2.681(4)−2.759(4) Å (average 2.712 Å), very similar to those in [Li(OEt$_2$)$_4$][Sm(**L^4**)$_2$] (2.695(4)−2.744-(5) Å, average 2.722 Å), whereas in (C$_5$Me$_5$)$_2$Sm(CH$_2$-CHCH$_2$) the allyl ligand is slightly more tightly bonded (Sm−C 2.630(15), 2.668(18), and 2.643(18) Å).[24] A single halide ligand bridging to lithium has precedence in lanthanide chemistry and is found, for example, in a series of structurally characterized compounds L$_3$Ln-(μ-Cl)Li(solv)$_3$ (L = 2,2,5,5-tetramethyl-2,5-disila-1-aza-

cyclopentanide, solv = THF or Et$_2$O; Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb)[25] and in the amides [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ (Ln = Nd, Sm, Eu).[26] In these complexes the Ln−Cl−Li bridge deviates from linearity by 10° or less. By contrast, in complex **5** the Sc−Cl−Li angle is more acute, 143.30(19)°. This may well be due to increased steric hindrance at the metal center.

Polymerization Studies. The activities of **2**, **3**, **4**, and, for comparison, [Y(**L^4**)$_2$\{μ-K(THF)\}·(THF)$_n$]$_\infty$·(**6**)[18] for the polymerization of methyl methacrylate were investigated under a range of conditions. The results are collected in Table 5. All the complexes were found to be efficient catalysts, with the highest activity being found for **3** with a TON of 45 100 mol MMA (mol Y)$^{-1}$ h^{-1} in toluene at 0 °C. It was hoped that the use of a more sterically hindered ligand would have some effect

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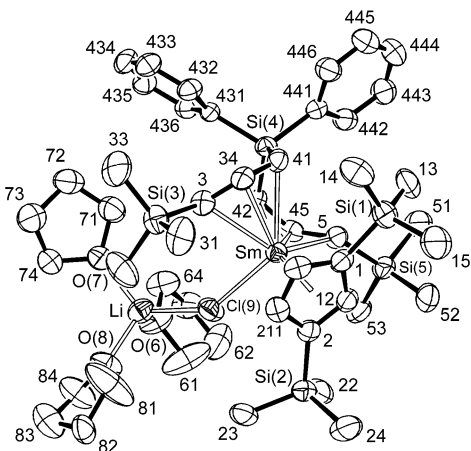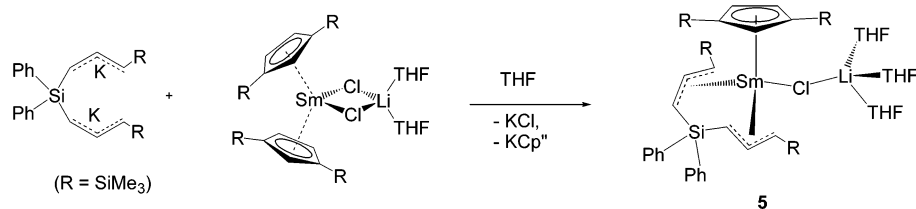
Scheme 3

(R = SiMe₃)

Figure 3. Molecular structure of **5**, showing the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for 5[a]

Sm−C(1)	2.733(4)	Sm−C(34)	2.704(4)
Sm−C(12)	2.705(4)	Sm−C(41)	2.681(4)
Sm−C(2)	2.741(4)	Sm−C(34)	2.759(4)
Sm−C(211)	2.729(4)	Sm−C(45)	2.706(4)
Sm−C(121)	2.734(4)	Sm−C(5)	2.699(4)
Sm−C(3)	2.724(4)	Sm−Cl(9)	2.6930(13)
Sm−C(1x)	2.449	Sm−C(5x)	2.506
Sm−C(3x)	2.486		
C(1x)−Sm−C(3x)	106.4	C(3x)−Sm−C(5x)	99.9
C(1x)−Sm−C(5x)	139.1	C(3x)−Sm−Cl(9)	112.0
C(1x)−Sm−C(19)	107.5	C(5x)−Sm−Cl(9)	90.4
Li(1)−O(6)	1.910(8)	Li(1)−O(8)	1.923(8)
Li(1)−O(7)	1.925(8)	Li(1)−Cl(9)	2.320(8)
Li(1)−Cl(9)−Sm(1)	143.30(19)		
C(3)−C(34)	1.383(6)	C(34)−C(41)	1.403(6)
C(45)−C(5)	1.396(6)	C(42)−C(45)	1.378(5)

[a] C(1x) is the centroid of the cyclopentadienyl ring; C(3x) and C(5x) are the centroids of the allyl-C₃ groups about C(34) and C(45).

in the polymerization. The comparison of the activities of **2** and **6** is instructive. The most obvious contrast is the relatively poor activity of **2** in toluene (TON 564 mol MMA (mol Y)$^{-1}$ h^{-1}) when compared with **6** (86 400 mol MMA (mol Y)$^{-1}$ h^{-1}, both at 0 °C). The activities are solvent-dependent; for example in the case of complex **4**, the TON in toluene is >30 times higher than in THF. The situation is even more striking for **6**, where the presence of THF reduces the TON to 970 mol MMA (mol Y)$^{-1}$ h^{-1} (entries 11 and 13).

Recent studies have emphasized the effect of solvent polarity on both activity and the resulting PMMA microstructure, with more polar solvents (THF and dimethoxyethane) for the system [(Me₃Si)₂N]₃Ln(μ-Cl)-Li(THF)₃ (Ln = Nd, Sm, and Eu) giving increased

syndiotacticity.[26] The lithium salts **3** and **4** show a similar behavior, with an *rr* triad content in THF of up to 65.7%. By contrast, the stereoselectivity of PMMA samples obtained with potassium compounds **2** and **6** is little affected by either temperature or solvent.

The reasons for this tacticity difference may well lie in some degree of monomer activation by coordination to the alkali metal cation, with the smaller and thus more Lewis acidic lithium cation showing a more effective coordination than potassium. Changes in PMMA tacticity upon addition of a Lewis acid, for example Al-(C₆F₅)₃, have been seen for both metallocene and non-metallocene initiators. For example, *tert*-butyllithium on its own produces isotactic PMMA (*mm* = 75.0% at −78 °C), whereas the addition of 2 equiv of Al(C₆F₅)₃ gives PMMA with up to 95.0% *rr*.[27]

In general these tetraallyl lanthanate systems produce high molecular weight poly(methyl methacrylate) (M_w typically ≈ 80 000−300 000). There is a significant difference between polymers produced in toluene and in THF. THF reactions tend to give PMMA with lower molecular weights (e.g., entry 8, M_w 83 300) and polydispersities closer to 2, whereas polymers obtained in toluene show higher M_w but broader polydispersity (entry 9, M_w 183 000 and M_w/M_n 5.4).

The neutral allyl complexes **1**, the previously reported compounds (L³)₂LaCl(THF) (**7**) and (L³)₂YCl (**8**),[17] and the ionic compounds **2**, **3**, **4**, and **6** are highly effective catalysts for the polymerization of ε-caprolactone (CL) (Table 6). With the neutral catalysts at 20 °C only traces of polymer were detected, whereas at 50 °C polymerization was extremely rapid, with 85−95% conversion in 60 s. The anionic complexes are already highly active at 20 °C. Surprisingly, **2** gave significantly higher conversions than the closely related yttrium compounds **3** and **6**. In these cases there was little discernible influence of the nature of the alkali cation. The resulting polymers have narrow polydispersities (typically 1.2−1.5). In all cases high molecular weight polymers were obtained, with the neodymium complex **1** giving the highest values, $M_w = 165\,000$.

Conclusion

Silyl-substituted allyl ligands give facile access to a range of stable lanthanide complexes with good solubility and crystallization characteristics. While allyl ligands such as [Me₃SiCHCHCHSiMe₃]$^-$ give neutral lanthanide complexes of the type (allyl)₂LnX, *ansa*-bis(allyl) ligands favor ate complexes, [Ln(allyl)₄]$^-$, even if bulky cyclopentadienyl complexes are used as starting materials. Clean routes to the isolation of three new members of the *ansa*-bis(allyl) class of complexes were found, including two fully characterized complexes with lithium

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Table 4. Crystal Data and Summary of Data Collection and Refinement Details for 1, 3, and 5

	1	**3**	**5**
formula	$C_{26}H_{58}INdO_2Si_4$	$C_{28}H_{60}Si_6Y$, $C_{16}H_{34}O_4Li$	$C_{47}H_{79}ClLiO_3Si_5Sm$, $0.5(C_6H_{14})$
cryst size (mm)	$0.45 \times 0.30 \times 0.15$	$0.60 \times 0.50 \times 0.40$	$0.13 \times 0.13 \times 0.12$
cryst color, shape	green blocks	orange blocks	red cubes
fw	786.2	951.6	1068.5
cryst class	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$ (no. 2)	*Pbca* (no. 61)	$P2_1/n$ (no. 14)
a, Å	10.770(1)	17.065(3)	13.669(3)
b, Å	19.056(3)	20.137(4)	30.451(6)
c, Å	19.453(1)	32.896(7)	14.158(3)
α, deg	72.94(2)		
β, deg	89.61(1)		96.24(3)
γ, deg	80.44(1)		
V, Å³	3760.0(7)	11304(4)	5858(2)
Z	4	8	4
D_{calcd}, Mg/m³	1.389	1.118	1.211
μ, mm⁻¹	2.348	1.193	1.185
F(000)	1596	4218	2246
no. of indep reflns	12 001 (R_{int} = 0.053)	9784 (R_{int} = 0.038)	10 732 (R_{int} = 0.091)
no. of obsd reflns ($I > 2\sigma_i$)	9476	7431	6555
no. of params refined	609	537	544
goodness of fit	1.032	1.046	0.900
final *R* indices (all data)	R_1 = 0.064, wR_2 = 0.146	R_1 = 0.0612, wR_2 = 0.1047	R_1 = 0.086, wR_2 = 0.096
final *R* indices (obsd data)	R_1 = 0.051, wR_2 = 0.137	R_1 = 0.0401, wR_2 = 0.0947	R_1 = 0.043, wR_2 = 0.089
largest diff peak and hole, e Å⁻³	1.00 and −1.91	0.361 and −0.830	0.60 and −0.89
location of largest diff peak(s)	close to Nd or I atoms	close to Si(3)	remote from all molecules not resolved

Table 5. Polymerization of MMA with Anionic Lanthanide Allyl Complexes[a]

run	cat.	solvent (5 mL)	time (min)	temp (°C)	yield (g)	conversion (%)	TON[b]	tacticity[c] rr	tacticity[c] mr	tacticity[c] mm	M_w[d]	M_n[d]	M_w/M_n
1	**2**	toluene	60	20	0.686	36.5	366	27.1	53.8	19.1	192 000	103 000	1.85
2	**2**	toluene	60	0	1.056	56.2	564	27.9	51.9	20.2	358 000	174 000	2.06
3	**2**	THF	20	20	0.728	38.8	1170	32.9	54.2	12.9	112 000	62 600	1.79
4	**2**	THF	85	0	0.662	35.3	250	33.5	57.4	9.1	104 000	50 700	2.05
5	**3**	THF	15	20	0.298	15.9	637	61.8	34.2	4.0	83 100	44 900	1.85
6	**3**	toluene	3	0	0.422	22.5	45 100	31.4	26.9	41.7	288 000	52 900	5.40
7	**4**	THF	30	20	0.367	19.5	392	62.6	33.2	4.2	73 500	43 300	1.70
8	**4**	THF	30	0	0.112	6.0	120	65.7	30.7	3.6	83 300	45 900	1.82
9	**4**	toluene	3	20	0.149	7.9	1590	28.8	28.2	43.0	183 000	33 900	5.39
10	**4**	toluene	2	0	0.257	13.7	4120	31.2	25.6	43.2	221 000	44 800	4.92
11	**6**[e]	toluene	0.5	0	1.348	72.0	86 400	25.0	53.9	21.1	297 000	99 900	2.97
12	**6**[e]	toluene	0.5	20	1.060	56.6	67 900	24.8	54.6	20.6	242 000	97 700	2.48
13	**6**	THF	15	0	0.454	24.2	970	33.7	55.4	10.9	195 000	101 000	1.94

[a] Conditions: Ln 1.87 × 10⁻⁵ mol, MMA/Ln = 1000. [b] TON = mol MMA (mol Ln)⁻¹ h⁻¹. [c] Determined by triad analysis of the ¹H NMR spectra in CDCl₃.[29] [d] Determined by GPC relative to polystyrene standards. [e] See ref 18.

Table 6. Polymerization of ε-Caprolactone with Neutral and Anionic Lanthanide Catalysts[a]

run	catalyst	time (min)	temp (°C)	yield (g)	conversion (%)	TON[b]	M_w[c]	M_n[c]	M_w/M_n
1	**1**	20	20	traces					
2	**1**	1	50	1.768	85.8	25 700	165 000	127 000	1.30
3	L^3_2LaCl(THF) (**7**)	1	50	1.828	88.7	26 600	63 700	51 300	1.24
4[e]	L^3_2YCl (**8**)	1	50	1.934	93.9	28 200	129 000	87 500	1.48
5	**2**	1	20	1.729	83.9	25 200	46 700	24 400	1.91
6	**3**	2	20	0.397	19.3	2790	25 000	16 800	1.49
7	**4**	1	20	1.246	60.3	17 500	27 900	16 800	1.66
8	**6**	3	20	0.641	31.1	3110	53 000	37 600	1.42

[a] Conditions: Ln 3.61 × 10⁻⁵ mol, CL/Ln = 500. [b] TON = mol CL (mol Ln)⁻¹ h⁻¹. [c] Determined by GPC relative to polystyrene standards.

as the countercation. The synthesis of a mixed-ligand Cp-allyl complex was, however, successful in the case of samarium, which gave the zwitterionic product [Cp″Sm(**L⁵**){μ-ClLi(THF)₃}].

The anionic lanthanate complexes are highly active for the polymerization of methyl methacrylate. While the allyl ligands have limited influence on polymer stereochemistry, the simple expedient of conducting polymerization reactions in the more polar THF as solvent, rather than toluene, did result in polymer with a much higher syndiotactic content. The most pro-

nounced effect was seen for catalysts with a lithium cation rather than potassium.

Both the neutral (L³)₂LnX complexes and the *ansa*-bis(allyl) complexes are active for the ring-opening polymerization of ε-caprolactone. While the neutral complexes are active at only elevated temperatures, the anionic complexes rapidly activate polymerization at ambient temperature. Since such ROP reactions are initiated by nucleophilic attack on the monomer, the observed reactivity differences may well reflect differences in the nucleophilicity of the allyl ligands in the

neutral compounds and anionic complexes, respectively. In all cases high molecular weight polymers with good conversions and narrow polydispersities were obtained.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk line techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium benzophenone (diethyl ether, THF), and sodium−potassium alloy (light petroleum, bp 40−60 °C). Deuterated solvents were degassed by several freeze−thaw cycles and stored over 4 Å molecular sieves. NMR spectra were recorded on a Bruker DPX-300 spectrometer. ^{1}H NMR spectra (300.1 MHz) were referenced to residual solvent protons; ^{13}C NMR spectra were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. Polymer molecular weights were determined by gel permeation chromatography in THF using a Polymer Laboratories GPC-220 instrument equipped with a refractive index and a PD2040 dual-angle light scattering detector and PL gel 2 × mixed bed-B, 30 cm, 10 μm columns. YCl$_3$(thf)$_{3.5}$ was prepared from the corresponding oxide following a literature procedure;[28] NdI$_3$(thf)$_{3.5}$ was prepared from Nd and CH$_2$I$_2$ in THF.[9b] 1,3-Bistrimethylsilylpropene[12] and Me$_2$Si(CH$_2$CHCHSiMe$_3$)$_2$[16] were prepared via modifications of literature procedures. Complexes **6**,[18] **7**, **8**,[17] and Cp″$_2$LnCl$_2$Li(THF)$_2$ (Ln = Sm and Y)[21] were prepared according to the published methods.

(L^3)$_2$NdI(THF)$_2$ (1). Solid NdI$_3$(THF)$_{3.5}$ (3.80 g, 4.89 mmol) was added slowly in small portions to a solution of K{1,3-C$_3$H$_3$-(SiMe$_3$)$_2$} (KL^3, 2.20 g, 9.79 mmol) in 150 mL of THF over 30 min. Copious amounts of precipitate formed. After stirring the light green mixture for 16 h at 20 °C the volatiles were removed. The residue was extracted with light petroleum (2 × 100 mL), concentrated, and cooled to −20 °C to give dark green crystals of **1** (2.71 g, 70.5%). Anal. Calcd for C$_{26}$H$_{58}$INdO$_2$-Si$_4$: C, 39.72; H, 7.44. Found: C, 39.34; H, 7.01. ^{1}H NMR (benzene-d_6, 20 °C): δ −8.67 (br s, 8 H, THF), −4.00 (br s, 8 H, THF), 3.41 (br s, 36 H, SiMe$_3$), 4.76 (br s, 4 H, allyl), 11.89 (br s, 2 H, allyl).

[Y(L^5)$_2${μ-K}(THF)$_{0.5}$(Et$_2$O)$_{1.5}$]$_\infty$ (2). A solution of K$_2${3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiPh$_2$} (4.55 g, 9.38 mmol) in THF (100 mL) was treated with solid portions of YCl$_3$ (0.92 g, 4.71 mmol). After complete addition the reaction was heated at ca. 50 °C for 4 h, during which time an intense orange color developed. The solvent was removed in vacuo, and the resulting orange solid extracted with diethyl ether (150 mL). Concentration of this solution to ca. 30 mL and cooling to −20 °C overnight afforded a crop of orange crystals, yield 2.34 g (22.9%). Anal. Calcd for C$_{56}$H$_{87}$KO$_2$Si$_6$Y: C, 61.72; H, 8.05. Found: C, 61.35; H, 8.06. ^{1}H NMR (THF-d_8, 20 °C): δ −0.14 (s, 36 H, SiMe$_3$), 1.13 (t, 9 H, J_{HH} = 7 Hz, OCH$_2$CH_3), 1.78 (m, 2 H, m-THF), 3.39 (q, 6 H, J_{HH} = 7 Hz, OCH$_2$CH_3) 3.48 (d, 4 H, J_{HH} = 17.5 Hz, allyl), 3.63 (m, 2 H, o-THF), 4.24 (d, 4 H, J_{HH} = 11.6 Hz, allyl), 7.03 (m, 12 H, phenyl), 7.38 (dd, 4 H, J_{HH} = 17.5 Hz, 11.6 Hz), 7.55 (m, 8 H, phenyl). ^{13}C NMR (THF-d_8, 20 °C): δ 1.45 (SiMe$_3$), 15.68 (OCH$_2$CH_3), 26.36 (m-THF), 66.30 (OCH$_2$CH$_3$), 68.21 (o-THF), 76.04 (allyl), 81.60 (allyl), 127.12 (Ph), 127.60 (Ph), 136.37 (Ph), 140.27 (i-Ph), 164.24 (allyl).

Reaction of Cp″$_2$YCl$_2$Li(THF)$_2$ with K$_2$L^5. A solution of Cp″$_2$YCl$_2$Li(THF)$_2$ (1.83 g, 2.50 mmol) in THF (100 mL) was treated with solid portions of K$_2${3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiPh$_2$} (1.21 g, 2.50 mmol). The reaction rapidly became orange and was stirred for 16 h at room temperature. The volatiles were removed in vacuo and the resulting solids extracted with light petroleum (100 mL). The remaining solid was extracted with diethyl ether (100 mL). Concentration of the bright orange

filtrate to ca. 30 mL and cooling of the solution to −20 °C afforded orange crystals of **2**, yield 1.10 g (1.01 mmol, 40.4%).

Reaction of Cp″$_2$YCl$_2$Li(THF)$_2$ with K$_2$L^4. A solution of Cp″$_2$YCl$_2$Li(THF)$_2$ (2.01 g, 2.75 mmol) in THF (100 mL) was treated with solid portions of K$_2${3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiMe$_2$} (1.00 g, 2.75 mmol). The reaction rapidly became orange and was stirred for 16 h at room temperature. The volatiles were removed in vacuo, and the resulting solids were extracted with light petroleum (150 mL). The remaining solids were extracted with diethyl ether (100 mL), concentrated, and cooled to −20 °C to give orange crystals of [Li(THF)$_2$(OEt$_2$)][Y(L^4)$_2$] (3), yield 0.87 g (0.99 mmol, 35.9%). Anal. Calcd for C$_{40}$H$_{86}$LiO$_3$Si$_6$Y: C, 54.57; H, 9.85. Found: C, 54.12; H, 9.21. ^{1}H NMR (THF-d_8, 20 °C): δ −0.16 (s, 12 H, SiMe$_2$), 0.04 (s, 36 H, SiMe$_3$), 1.11 (t, 6 H, J_{HH} = 7 Hz, OCH$_2$CH_3), 1.78 (m, 8 H, m-THF), 3.37 (q, 4 H, J_{HH} = 7 Hz, OCH$_2$CH_3), 3.39 (d, 4 H, J_{HH} = 17.2 Hz, allyl), 3.60 (m, 8 H, o-THF), 3.79 (d, 4 H, J_{HH} = 11.8 Hz, allyl), 7.02 (dd, 4 H, J_{HH} = 11.8, 17.2 Hz, allyl). ^{13}C NMR (THF-d_8, 20 °C): δ −3.82 (SiMe$_2$), 1.85 (SiMe$_3$), 15.69 (OCH$_2$CH_3), 26.36 (m-THF), 66.30 (OCH$_2$CH$_3$), 68.22 (o-THF), 70.86 (allyl), 87.64 (allyl), 163.07 (allyl).

Reaction of Cp″$_2$SmCl$_2$Li(THF)$_2$ with K$_2$L^4. A solution of Cp″$_2$SmCl$_2$Li(THF)$_2$ (2.48 g, 3.13 mmol) in THF (100 mL) was treated with solid portions of K$_2${3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$-SiMe$_2$} (1.13 g, 3.13 mmol). The reaction rapidly became red-orange and was stirred for 16 h at room temperature. The volatiles were removed in vacuo, the resulting solids were extracted with light petroleum (150 mL), and the filtrate was concentrated to ca. 40 mL and cooled to −20 °C to give a mixture of Cp″$_3$Sm and Cp″$_2$SmCl$_2$Li(THF)$_2$ as orange and yellow crystals, total yield 0.77 g (0.99 mmol, 31.6% based on Cp″$_2$SmCl$_2$Li(THF)$_2$). The remaining solids were extracted with diethyl ether (100 mL); concentrating and cooling the filtrate afforded red crystals of [Li(THF)$_2$(OEt$_2$)][Sm(L^4)$_2$] (4), yield 0.64 g (0.68 mmol, 21.7%). Anal. Calcd for C$_{40}$H$_{86}$LiO$_3$-Si$_6$Sm: C, 51.06; H, 9.21. Found: C, 50.06; H, 9.27 (some loss of the donor solvent occurred under reduced pressure). ^{1}H NMR (THF-d_8, 20 °C): δ −2.46 (dd, 4 H, J_{HH} = 11.3 Hz, 16.4 Hz, allyl), 0.24 (s, 36 H, SiMe$_3$), 1.12 (t, 6 H, J_{HH} = 7.2 Hz, OCH$_2$CH_3), 1.78 (s, 12 H, SiMe$_2$), 1.78 (m, 8 H, m-THF), 3.39 (q, 4 H, J_{HH} = 7.2 Hz, OCH$_2$CH$_3$), 3.61 (m, 8 H, o-THF), 6.82 (d, 4 H, J_{HH} = 11.3 Hz, allyl), 12.85 (d, J_{HH} = 16.4 Hz, 4 H, allyl).

Reaction of Cp″$_2$SmCl$_2$Li(THF)$_2$ with K$_2$L^5. A solution of Cp″$_2$SmCl$_2$Li(THF)$_2$ (1.05 g, 1.32 mmol) in THF (40 mL) was treated with solid portions of K$_2${3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiPh$_2$} (0.54 g, 1.32 mmol). After stirring for 16 h the solution was deep red. Removal of volatiles in vacuo gave a red solid. Extraction with light petroleum (100 mL), concentration to ca. 40 mL, and cooling to −20 °C afforded red crystals, yield 0.35 g. The ^{1}H NMR spectrum of these crystals could not be fully assigned; however there were resonances associated with both cyclopentadienyl and *ansa*-allyl groups. A suitable crystal was selected and subjected to X-ray diffraction analysis, and was identified as [Cp″Sm{3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiPh$_2$}{μ-Cl}Li(THF)$_3$] (5).

Polymerizations. A solution of the catalyst in either toluene or THF (5 mL) was maintained at the chosen temperature. Neat monomer was then added (2 mL), with a catalyst/monomer ratio of 1000:1 for MMA and 500:1 for CL. The polymerizations were terminated by methanol addition (10 mL). The resulting polymer was precipitated from methanol (150 mL), filtered, and dried in vacuo. Polymer microstructure was determined by ^{1}H NMR in chloroform-d_1.[29]

X-ray Crystallographic Analyses. Crystal data and refinement results are collated in Table 4. Suitable single crystals were selected under dried perfluoropolyether, mounted

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on a glass fiber, and fixed in a cold nitrogen stream (140 K) on a Rigaku R-Axis II image plate diffractometer equipped with a rotating anode X-ray source (Mo Kα radiation) and graphite monochromator. For each 48 exposures were made using 4° oscillations; max θ for each was 25.4°. Data were processed using the DENZO/SCALEPACK programs.[30] The structures were determined by direct methods using the XS program[31] and were refined by full-matrix-least-squares methods, on F^2, in SHELXL.[32] For **1** there are two independent molecules in the crystal, one of which has a disordered (and not fully resolved) THF ligand. The non-hydrogen atoms (except for the carbon atoms of the disordered ligand) were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions (except in the disordered ligand), and their U_{iso} values were set to ride on the U_{eq} values

of the parent carbon atoms. For **3** the non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were treated as for **1**, with the exception of the hydrogen atoms on the C_3 allyl core labeled with a "*", which were refined freely. In **5** the solvent molecule is disordered about a center of symmetry and not fully resolved; four distinct carbon atoms with site occupancies of 0.7−0.8 were refined isotropically. For each analysis, scattering factors for neutral atoms were taken from ref 33. Computer programs were run on a Silicon Graphics Indy at the University of East Anglia or on a DEC Alpha Station in the Biological Chemistry Department, John Innes Centre.

Supporting Information Available: Tables of crystallographic information for compounds **1**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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