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Synthesis, Characterization, and Reactivity of *ansa*-Bis(allyl) Lanthanide Complexes, a New Class of Single-Component Methyl Methacrylate Polymerization Catalysts

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The reaction of the dipotassium salt $K_2\{3\text{-}(C_3H_3SiMe_3\text{-}1)_2SiMe_2\}$ with $LnCl_3$ in THF leads to the formation of the new *ansa*-allyl lanthanate complexes $[Ln\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(THF)\}\cdot n THF]_\infty$ (**1**, Ln = La, $n = 0.5$; **2**, Ln = Y, $n = 1$; **3**, Ln = Sc, $n = 1$). Reaction of $K_2\{3\text{-}(C_3H_3SiMe_3\text{-}1)_2SiMe_2\}$ with $NdI_3(THF)_{3.5}$ affords THF-free $[Nd\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2(\mu\text{-}K)]_\infty$ (**4**). Treatment of $SmI_2(THF)_2$ with $Li\{3\text{-}(C_3H_3SiMe_3\text{-}1)_2SiMe_2\}/KO^tBu$ resulted in the samarium(III) complex $[Li(OEt_2)_4][Sm\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2]$ (**5**), albeit in small yield. Whereas the crystal structure of **1** shows a coordination polymer, with potassium bridging to allyl moieties of two neighboring lanthanide units and close K···CH$_3$Si contacts, complex **5** consists of discrete ions. The complexes **1**−**5** are all found to be efficient catalysts for the polymerization of methyl methacrylate to high-molecular-weight polymers under a variety of conditions, with **2** at 0 °C giving extremely high turnovers of 86 400 mol of MMA (mol of Y)$^{-1}$ h^{-1}.

Introduction

The use of sterically demanding silyl substituents has been a successful way to prepare stable homoleptic allyl complexes of first-row transition metals and lanthanides. Thus, while the compounds $(C_3H_5)_nM$ are either thermally unstable (M = Co, V, Ni)[1] or not known (M = Fe, Mn), the use of the 1,3-bis(trimethylsilyl)allyl[2] ligand allows the isolation of $M\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}_2$ (M = Co,[3] Ni,[3] Fe,[4] Cr[4]) as thermally stable complexes. Eisen reported Zr(III) and Ti(III) complexes bearing the 1,3-bis(*tert*-butyldimethylsilyl)allyl ligand as polymerization catalysts for ethylene and propene.[5] Lappert et al. have described the use of the *ansa*-bis(allyl) ligand $[Me_2Si(C_3H_3SiMe_3)_2]^{2-}$ for the preparation of zirconium(IV) and hafnium(IV) complexes $M\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2$.[6] The zirconium complex was found to polymerize ethylene in the presence of MAO as cocatalyst. The samarium(II) allyl complexes $Sm(C_3H_3R_2)_2(THF)_2$ (R = Ph, SiMe$_3$) have been reported, although they were not fully characterized.[7] We have recently described the synthesis of a series of 1,3-bis(trimethylsilyl)allyl complexes of lanthanides, including $LnCl(THF)_n\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}_2$ (Ln = Y, $n = 0$; Ln = La, $n = 1$), $\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}_2Sc(\mu\text{-}Cl)_2Li(THF)_2$, and $NdI_2\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}(THF)$, and their use as butadiene polymerization catalysts.[8] All attempts to obtain halide-free products and generate homoleptic tris(allyl) complexes $Ln\{C_3H_3(SiMe_3)_2\text{-}1,3\}_3$ from $LaCl_3$ and YCl_3 failed. We now report that, in contrast, the *ansa*-bis(allyl) ligand $[Me_2Si(CHCHCHSiMe_3)_2]^{2-}$ readily gives chloride-free compounds. Thus, the reactions of various lanthanide halide precursors with the dipotassium salt $K_2\{3\text{-}(C_3H_3SiMe_3\text{-}1)_2SiMe_2$ leads to chelating tetrakis(allyl) lanthanate complexes which act as single-component catalysts for the polymerization of methyl methacrylate.

Results and Discussion

Syntheses. The bis(allyl)silane $Me_2Si(CH_2CHCHSiMe_3)_2$ was converted into the dipotassium salt $K_2\{3\text{-}(C_3H_3SiMe_3\text{-}1)_2SiMe_2\}$ via a modification of a literature procedure[6] (Scheme 1). Reaction of equimolar amounts of this potassium salt and $LaCl_3$ in THF afforded a bright orange solid. In contrast to previously isolated complexes of silylated allyls, this product was insoluble in hexanes and only sparingly soluble in toluene but could be extracted with diethyl ether. Qualitative tests showed the absence of halide and the presence of potassium. The ^1H NMR spectrum in THF-d_8 gave the expected pattern for η^3-silylallyl ligands and were similar to the spectra of Lappert's Zr and Hf complexes $[M\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2]$.[6] Crystals suitable for X-

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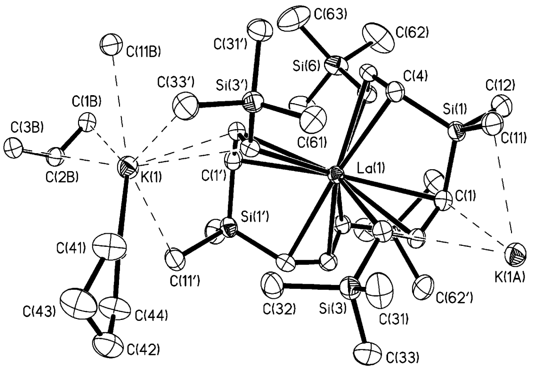
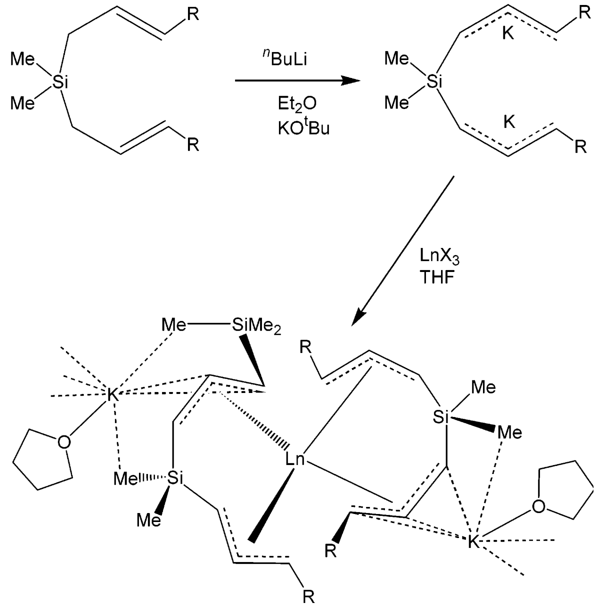


Figure 1. Molecular structure of $[La\{(\eta^3\text{-}C_3H_3SiMe_3)_2\text{-}SiMe_2\}_2\{\mu\text{-}K(THF)\}\cdot 0.5THF]_\infty$ (**1**), showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1



1, Ln = La; **2**, Ln = Y;
3, Ln = Sc; **4**, Ln = Nd

ray analysis were obtained from a toluene solution at −20 °C and identified the product as $[La\{(\eta^3\text{-}C_3H_3\text{-}SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(THF)\}(THF)_{0.5}]_\infty$ (**1**). The molecular structure of **1** is depicted in Figure 1; selected bond lengths and angles are listed in Table 1.

Each lanthanum atom is coordinated to two *ansa*-bis(allyl) ligands, both of which bind to the metal in an η^3 fashion. The coordination environment of the lanthanum consists of 12 carbon atoms, with La−C bond lengths in the range 2.769(3)−2.902(3) Å and an average La−C distance of 2.83 Å. The related unsubstituted lanthanum complex $Li[La(\eta^3\text{-}C_3H_5)_4](1,4\text{-dioxane})_{1.5}$ has rather similar La−C bond distances (2.721−2.842 Å, average 2.811 Å),[9] whereas in the neutral complex $[\{La(\eta^3\text{-}C_3H_5)_3(\eta^1\text{-}C_4H_8O_2)\}_2(\mu\text{-}C_4H_8O_2)]$[10] the range is from 2.751(3) to 2.829(5) Å (average 2.795 Å). The presence of the silyl groups in **1** has evidently very little impact on the bond lengths to the allyl ligand. As in the zirconium complex $[Zr\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2]$,[6] the allyl ligands in **1** adopt an anti,syn arrangement. The C−SiMe$_2$−C bite angles in **1** are significantly greater than in the related Zr complex, 112.86(12) and 113.12(12)°, as compared to 104.2(2)°, a reflection of the larger size of the lanthanum atom.

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

Environment of the La Atom			
La(1)−C(6)	2.768(3)	La(1)−C(4)	2.791(3)
La(1)−C(4′)	2.802(3)	La(1)−C(6′)	2.805(3)
La(1)−C(3′)	2.820(3)	La(1)−C(5)	2.823(3)
La(1)−C(5′)	2.828(3)	La(1)−C(2)	2.850(3)
La(1)−C(3)	2.856(3)	La(1)−C(2′)	2.858(3)
La(1)−C(1)	2.888(3)	La(1)−C(1′)	2.902(3)
Environment of the K Atom			
K(1)−C(1)	3.357(3)	K(1)−C(2)	3.027(3)
K(1)−C(3)	3.327(3)	K(1)−C(2′)	3.146(3)
K(1)−C(3′)	3.126(3)	K(1)−O(4)	2.737(2)
K(1)−C(11′)	3.187(3)	K(1)−C(33′)	3.374(4)
Ligand			
C(1)−C(2)	1.398(4)	C(2)−C(3)	1.409(4)
C(4)−C(5)	1.410(4)	C(5)−C(6)	1.405(4)
C(1′)−C(2′)	1.403(4)	C(2′)−C(3′)	1.412(4)
C(4′)−C(5′)	1.407(4)	C(5′)−C(6′)	1.405(4)
C(1)−C(2)−C(3)	127.9(3)	C(4)−C(5)−C(6)	127.4(3)
C(1′)−C(2′)−C(3′)	128.9(3)	C(4′)−C(5′)−C(6′)	127.0(3)
C(4)−Si(1)−C(1)	112.86(12)	C(4′)−Si(1′)−C(1′)	113.12(12)

The charge of the tetrakis(allyl) lanthanate moiety is balanced by a potassium cation which is coordinated to two allyl moieties of two different lanthanum atoms, thus resulting in the formation of a coordination polymer with infinite chain structure. In addition, the potassium ion binds one THF ligand (K−O = 2.736(2) Å).

The bonding interactions of potassium with the allyl ligands are surprisingly complex. One allyl is η^3-bonded, with K−C bond distances of 3.027(3), 3.326(3), and 3.357(3) Å. In addition, there is a close interaction with one of the methyl groups of the SiMe$_2$ moiety, with K···H agostic interactions of 2.79(3) and 2.96(4) Å. The bonding to the other allyl ligand is consistent with η^2 coordination, with only two carbon atoms within bonding range (K(1)−C(2′) = 3.146(3) Å, K(1)−C(3′) = 3.127(3) Å). In this case there are agostic interactions with the methyl substituents of the Si(1′)Me$_2$ and the Si(3′)Me$_3$ groups. This unexpectedly varied coordination behavior of potassium is shown in Figure 2.

The analogous reactions of $K_2\{3\text{-}(C_3H_3SiMe_3\text{-}1)_2\text{-}SiMe_2\}$ with $YCl_3(THF)_{3.5}$ and $ScCl_3(THF)_3$ in THF gave $[Ln\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(THF)\}(THF)]_\infty$ (**2**, Ln = Y; **3,** Ln = Sc) as orange solids in moderate yield. Although crystals suitable for X-ray diffraction could not be grown, all other methods of analysis suggest a structure closely similar to that of **1**. The compounds are only sparingly soluble in nondonor solvents. The ^{1}H NMR spectra for the scandium complex are broad at room temperature and were recorded at 50 °C.

The reaction of $K_2\{3\text{-}(C_3H_3SiMe_3\text{-}1)_2SiMe_2\}$ (prepared in situ from $Me_2Si(CH_2CHCSiMe_3)_2$, ^{n}BuLi, and KO^{t}Bu in THF) with $NdI_3(THF)_{3.5}$, followed by recrystallization from toluene, yielded $[Nd\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(THF)\}(THF)\cdot(C_7H_8)]_\infty$ (**4**). The solvent molecules are lost when samples of **4** are kept under vacuum at room

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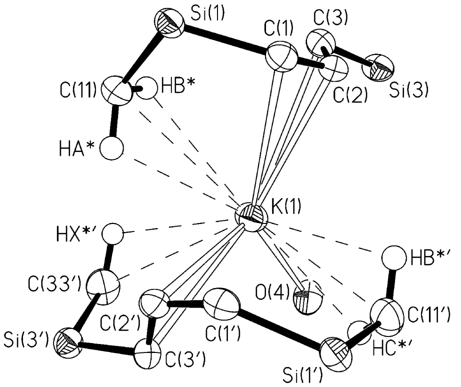

Figure 2. Coordination geometry of the potassium ion, showing η^2, η^3, and agostic bonding to allyl ligands of two neighboring tetrakis(allyl) lanthanate moieties. Selected bond distances (Å): K−C(1) = 3.357(3), K−C(2) = 3.027(3), K−C(3) = 3.327(3), K−C(11) = 3.223(4), K−H(A*) = 2.79(3), K−H(B*) = 2.96(4), K−C(2′) = 3.146(3), K−C(3′) = 3.126(3), K−C(11′) = 3.187(3), K−H(B*′) = 2.90(3), K−H(C*′) = 2.80(4), K−C(33′) = 3.374(4), K−H(X*′) = 2.93(3).

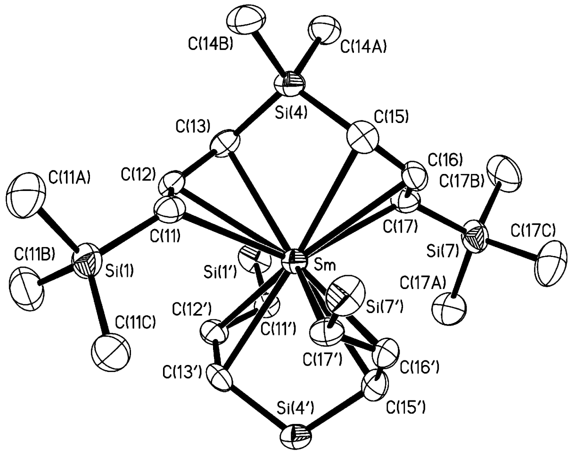

Figure 3. Molecular structure of the complex anion in $[Li(OEt_2)_4][Sm\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2]$ (**5**). Thermal ellipsoids are drawn at the 50% probability level. The methyl groups of one of the two bis(allyl) ligands have been omitted for clarity.

temperature for prolonged periods of time, to give $[Nd\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K\}]_\infty$.

An attempt to prepare a samarium(II) complex by reacting a $Li_2\{(C_3H_3SiMe_3)_2SiMe_2/KO^tBu$ mixture with 1 equiv of $SmI_2(THF)_2$ in THF, followed by recrystallization from light petroleum/diethyl ether, afforded a small quantity of red crystals which were identified by ^1H NMR spectroscopy and X-ray diffraction as the samarium(III) compound $[Li(OEt_2)_4][Sm\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2]$ (**5**). Evidently the lithium salt crystallized preferentially from the K^+- and Li^+-containing mixture. The structure of the anion is depicted in Figure 3; important bond lengths and angles are collected in Table 2. Whereas in **1** and presumably the other potassium-containing complexes the bridging function of the alkali metal leads to the formation of coordination polymers, compound **5** occurs in the crystal as discrete ions, with no close interionic contacts. The arrangement of the allyl ligands around the samarium atom is closely similar to that observed in **1**, with the same anti,syn conformation. The Sm−C bond distances range from 2.695(4) to 2.744(5) Å (average 2.722 Å). These values are slightly greater than in previously reported samarium allyl complexes; for example, $(C_5Me_5)_2Sm(CH_2CHCH_2)$ has bond distances of 2.630(15), 2.668(18), and 2.643(18) Å.[11] This may be a reflection of the larger steric strain imposed by the silyl groups; there is some evidence from the complexes $(C_5Me_5)_2Sm(CH_2CHCHR)$ (R = H, Me, Ph) that an increase in size of the substituent engenders a longer Sm−C distance to the carbon bearing the substituent R.[11] The C−C−C angles within the allyl moieties of **5** (126.6(5) and 126.4(5)°) are essentially the same as those in previously reported complexes; e.g., in $(C_5Me_5)_2Sm(\eta^3\text{-}C_3H_5)$ the angle is 125.6(2)°.[11] The geometric parameters of the Li cation are unremarkable, with Li−O distances in the range 1.957(8)−1.966(9) Å and a geometry close to tetrahedral (O(3)−Li−O(5) = 105.8(2)°).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Environment of the Sm Atom			
Sm−C(13)	2.695(4)	Sm−C(17)	2.702(5)
Sm−C(12)	2.718(4)	Sm−C(11)	2.730(4)
Sm−C(16)	2.743(5)	Sm−C(15)	2.744(5)
C(11)−C(12)	1.398(6)	C(12)−C(13)	1.400(6)
C(15)−C(16)	1.393(6)	C(16)−C(17)	1.405(6)
Environment of the Li Atom			
Li−O(3)	1.957(8)	Li−O(5)	1.966(9)
Ligand			
C(11)−C(12)−C(13)	126.4(5)	C(15)−C(16)−C(17)	126.6(5)
C(13)−Si(14)−C(15)	110.8(2)		

Polymerization Studies. Lanthanide cyclopentadienyl complexes are known to polymerize methyl methacrylate in a living fashion, generating highly syndiotactic PMMA. In particular, the use of $[(C_5Me_5)_2SmH]_2$ as an initiator provides PMMA with M_w/M_n = 1.02−1.04 for M_n > 100 000. This catalyst gives high conversions in a short time period and is active over a wide range of temperatures (−78 to 60 °C). At very low temperatures the syndiotacticity of the resulting polymer exceeds 95%.[12,13]

Complexes **1**−**5** act as highly active single-component catalysts for the polymerization of methyl methacrylate to give high-molecular-weight polymers (Table 3). A variety of polymerization conditions were explored with **1**−**4**. With the exception of **1**, the addition of toluene leads to a significant increase in activity; for example, on toluene addition the turnover number for **2** increases almost 50-fold, from 1750 to 86 400 h^{-1} (cf. entries 4 and 5), while that of **3** rises by almost 2 orders of magnitude (entries 8 and 9). For **1** and **4** the activities are higher at 20 °C than at 0 °C, with a 10-fold increase from 343 to 5080 h^{-1} for **4** (entries 13 and 14). Cooling reduces the activity; thus, for **3** at −78 °C the turnover was 256 h^{-1}, as opposed to 42 700 h^{-1} at 0 °C (entries 9 and 10). The high activity of **1**−**5** contrasts with the behavior of the neutral allyl complexes $Sm(C_3H_3R_2)_2(THF)_2$ (R = Ph, $SiMe_3$), which give only low conversion of MMA over a period of several hours.[7]

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Table 3. Methyl Methacrylate Polymerization Catalyzed by Lanthanide Allyl Complexes[a]

								tacticity[c]					
run no.	cat.	additive	time (min)	temp (°C)	yield (g)	conversn (%)	TON[b]	*rr*	*mr*	*mm*	M_w[d]	M_n[d]	M_w/M_n
1	**1**		3	0	1.463	78.2	15 600	30.5	52.8	16.7	505 000	143 000	3.5
2	**1**	tol	1.5	0	0.728	38.9	15 600	26.2	55.3	18.5	636 000	197 000	3.2
3	**1**	tol	1	20	0.945	50.5	30 300	21.5	50.3	26.2	255 000	107 000	2.4
4	**2**		3	0	0.164	8.8	1 750	33.5	53.6	12.9			
5	**2**	tol	0.5	0	1.348	72.0	86 400	25.0	53.9	21.1	297 000	99 900	3.0
6	**2**	tol	0.5	20	1.060	56.6	67 900	24.8	54.6	20.6	242 000	97 700	2.5
7[e]	**2**	tol	2	0	3.174	33.9	50 900	24.8	54.6	20.6	558 000	257 000	2.2
8	**3**		3	0	0.043	2.3	459	30.3	51.5	18.2			
9	**3**	tol	1	0	1.331	71.1	42 700	24.3	51.1	24.6	207 000	88 600	2.3
10	**3**	tol	15	−78	0.120	6.4	256	35.5	51.4	13.1	346 000	96 900	3.6
11	**3**	tol	1	20	0.719	38.4	23 000	24.0	53.5	22.5	275 000	103 000	2.7
12	**4**		5	20	0.117	6.3	750	34.6	51.6	13.8	327 000	136 000	2.4
13	**4**	tol	10	0	0.107	5.7	343	18.7	54.4	26.9	204 000	85 600	2.4
14	**4**	tol	5	20	0.792	42.3	5 080	23.0	55.6	21.4	258 000	113 000	2.3
15	**5**		1	20	0.207	11.0	6 630	41.9	38.1	20.0	116 000	38 400	3.0
16	**5**		1	0	0.640	34.0	20 500	44.5	32.6	22.9	227 000	72 700	3.1

[a] Polymerization conditions: Ln, 1.87×10^{-5} mol; MMA/Ln = 1000. [b] TON = mol of MMA (mol of Ln)$^{-1}$ h^{-1}. [c] Determined by ^{1}H NMR in $CDCl_3$. [d] Determined by GPC relative to polystyrene standards. [e] MMA/Ln = 5000.

We assume that these lanthanate complexes produce PMMA by an anionic mechanism. The tacticities of the resulting polymers differ, however, from those reported in the literature for other anionic polymerization systems. For instance, the "ate" complex produced by the addition of methyl α-lithioisobutyrate to $Ti(O^iPr)_4$ gave predominately syndiotactic pMMA (*rr* 69%) and became inactive above 0 °C.[14] In contrast, the PMMA produced with complexes **1**−**4** is largely atactic (*rr* ∼25−30%, *mr* ∼50−55%, *mm* ∼15−20%) and, surprisingly, the stereochemistry appears to be almost independent of the polymerization temperature. The polymer molecular weights obtained under these conditions vary between $M_w = 116\,000$ and 636 000, with polydispersities from 2.2 to 3.6.

$Al(C_6F_5)_3$ has been shown to reverse the stereoregulation in the anionic polymerization of MMA with both metallocene and nonmetallocene initiators, presumably via coordination of the monomer to the highly Lewis acidic metal center. The change in stereocontrol is quite striking: whereas *tert*-butyllithium on its own produces isotactic PMMA (75.0% at − 78 °C), on addition of 2 equiv of $Al(C_6F_5)_3$ the polymer becomes up to 95.0% syndiotactic.[15] However, in our system, addition of 2 equiv of $Al(C_6F_5)_3$ generated almost no polymeric product, and it was noted that the solution decolorized rapidly. NMR studies showed that there was facile C_6F_5 exchange with lanthanide complexes to give a mixture of apparently inactive products.

Conclusion

The *ansa*-bis(allyl) ligand $[Me_2Si(CHCHCHSiMe_3)_2]^{2-}$ allows the isolation of a new class of anionic lanthanide tetrakis(allyl) complexes. The potassium countercation prefers bridging interactions with two allyl moieties from two neighboring lanthanide units to THF coordination and thus gives rise to a coordination polymer chain structure, whereas the samarium complex $[Li(OEt_2)_4][Sm\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2]$ (**5**) consists of discrete ions. The preference for the formation of lanthanate complexes, as opposed to neutral complexes of the type $LnX\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}$, may be attributed to the chelate effect, since in our hands reactions of LnX_3 (Ln = Y, La, Nd; X = Cl, I) with an excess of $KC_3H_3(SiMe_3)_2$-1,3 do not generate similar lanthanate complexes. The complexes polymerize methyl methacrylate without the need for an activator or scavenger but are deactivated by Lewis acids such as $Al(C_6F_5)_3$. The addition of toluene increased activities by up to 2 orders of magnitudes, and even at 0 °C turnover numbers of >86 000 h^{-1} were reached.

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, tetrahydrofuran (THF)), or 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 DPX300 spectrometer. ^{1}H NMR spectra (300.1 MHz) were referenced to residual solvent protons of the deuterated solvent. ^{13}C NMR spectra (282.2 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. $LaCl_3$ was prepared by thoroughly drying $LaCl_3(H_2O)_7$ (Aldrich) with Me_3SiCl in refluxing toluene. $YCl_3(THF)_{3.5}$ and $ScCl_3(THF)_3$ were prepared from the corresponding oxides following a literature procedure.[16] $NdI_3(THF)_{3.5}$ was prepared from Nd and CH_2I_2 in THF,[17] while $SmI_2(THF)_2$ was prepared from excess Sm and 1,2-diiodoethane in THF.[18]

Preparation of $Me_2Si(CHCHCHSiMe_3)_2$. This compound was prepared by a modification of a literature procedure.[6] A solution of ^{n}BuLi (59.2 mL, 1.6 M in hexanes, 94.8 mmol) was slowly added to a chilled (0 °C), stirred solution of allyltrimethylsilane (10.8 g, 94.8 mmol) in THF (100 mL). The mixture was allowed to warm to room temperature and was stirred for a further 1 h. The solution was then cooled to 0 °C, dimethyldichlorosilane (6.10 g, 5.73 mL, 47.3 mmol) was added, and the reaction mixture was stirred for 16 h at room temperature. After removal of volatiles in vacuo the residue was extracted with diethyl ether (150 mL), washed with water

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(2 × 50 mL), and dried over magnesium sulfate. Evaporation of the volatiles left a colorless oil, which was distilled at 53−60 °C/0.1 mmHg to give Me$_2$Si(CHCHCHSiMe$_3$)$_2$, yield 12.0 g (42.2 mmol, 89.2%).

Preparation of K$_2${3-(C$_3$H$_3$SiMe$_3$-1)$_2$SiMe$_2$}. *n*-Butyl lithium (20.1 mL, 1.6 M in hexanes, 32.2 mmol) was added dropwise to a solution of Me$_2$Si(CH$_2$CHCHSiMe$_3$)$_2$ (4.59 g, 16.1 mmol) in diethyl ether (100 mL) over 30 min. The reaction mixture was stirred for 16 h at room temperature, at which time a yellow color had developed. Solid KO^{t}Bu (3.44 g, 30.7 mmol) was slowly added to the rapidly stirred solution. After complete addition the reaction mixture was stirred for a further 3 h. The volatiles were removed in vacuo, and the brown sticky residue was washed with light petroleum (3 × 50 mL) to give the title product as a pale cream-colored solid, yield 3.30 g (56.8%). The ^{1}H NMR spectrum of the compound was essentially identical with that reported by Lappert et al.[6]

Preparation of [La{3-(η^3-C$_3$H$_3$SiMe$_{3-}$1)SiMe$_2$}$_2${μ-K(THF)}·0.5THF]$_\infty$ (1). A rapidly stirred solution of K$_2${3-(C$_3$H$_3$SiMe$_3$-1)$_2$SiMe$_2$} (2.76 g, 7.64 mmol) in THF (100 mL) was treated with LaCl$_3$ (0.93 g, 3.80 mmol). The reaction mixture was heated at 50 °C for 2 h and stirred for 16 h at room temperature. The initial red solution became more orange over time. After removal of volatiles the orange residue was extracted with diethyl ether (50 mL). Concentration and cooling to −20 °C afforded **1** as an orange microcrystalline solid, yield 1.61 g (1.89 mmol, 49.7%). Anal. Calcd for C$_{34}$H$_{72}$O$_{1.5}$Si$_6$LaK: C, 47.96; H, 8.52. Found: C, 47.57; H, 7.99. ^{1}H NMR (THF-d_8, 20 °C): δ 6.72 (dd, 4 H, allyl), 3.90 (d, J_{HH} = 11.8 Hz, 4 H, allyl), 3.63 (m, 6 H, *o*-THF), 3.10 (d, J_{HH} = 17.0 Hz, 4 H, allyl), 1.79 (m, 6 H, *m*-THF), 0.04 (s, 36 H, SiMe$_3$), −0.15 (s, 12 H, SiMe$_2$). ^{13}C NMR (THF-d_8, 20 °C): δ 160.72 (allyl), 92.43 (allyl), 77.67 (allyl), 68.21 (*o*-THF), 26.36 (*m*-THF), 1.83 (SiMe$_3$), −3.68 (SiMe$_2$).

Preparation of [Y{3-(η^3-C$_3$H$_3$SiMe$_3$-1)SiMe$_2$}$_2${μ-K(THF)$_2$}]$_\infty$ (2). By the same procedure as that for **1**, **2** was prepared from K$_2${3-(C$_3$H$_3$SiMe$_3$-1)$_2$SiMe$_2$} (2.57 g, 7.12 mmol) and YCl$_3$(THF)$_{3.5}$ (0.70 g, 3.56 mmol) in THF (100 mL) as an orange microcrystalline solid, yield 1.56 g (1.86 mmol, 52.2%). Anal. Calcd for C$_{36}$H$_{76}$O$_2$Si$_6$YK: C, 51.57; H, 9.14. Found: C, 51.44; H, 8.76. ^{1}H NMR (THF-d_8, 20 °C): δ 7.01 (dd, 4 H, allyl), 3.79 (d, J_{HH} = 11.7 Hz, 4 H, allyl), 3.64 (m, 8 H, *o*-THF), 3.41 (d, J_{HH} = 17.2 Hz, 4 H, allyl), 1.79 (m, 8 H, *m*-THF), 0.04 (s, 36 H, SiMe$_3$), −0.17 (s, 12 H, SiMe$_2$). ^{13}C NMR (THF-d_8, 20 °C): δ 163.07 (allyl), 87.64 (allyl), 70.83 (allyl), 68.23 (*o*-THF), 26.36 (*m*-THF), 1.85 (SiMe$_3$), −3.83 (SiMe$_2$).

Preparation of [Sc{(η^3-C$_3$H$_3$SiMe$_3$)$_2$SiMe$_2$}$_2${μ-K(THF)}(THF)]$_\infty$ (3). A rapidly stirred solution of K$_2${3-(C$_3$H$_3$SiMe$_3$-1)$_2$SiMe$_2$} (1.70 g, 4.71 mmol) in THF (100 mL) was treated with ScCl$_3$(THF)$_3$ (0.86 g, 2.34 mmol). The reaction mixture was heated at 50 °C for 2 h and then was stirred for a further 16 h at room temperature. The initial red solution became more orange over time. The volatiles were removed in vacuo, and the orange residue was extracted with light petroleum (50 mL). Concentration and cooling to −20 °C afforded an orange oil, which deposited from the solution. This was separated and pumped in vacuo for 2 h to give the title product as an orange solid, yield 1.04 g (1.32 mmol, 56.4%). Anal. Calcd for C$_{36}$H$_{76}$O$_2$KScSi$_6$: C, 54.55; H, 9.66. Found: C, 54.12; H, 9.34. ^{1}H NMR (benzene-d_6, 50 °C): δ 7.18 (br dd, J_{HH} = 12.4 and 16.7 Hz, 4 H, allyl), 3.50 (br m, 8 H, allyl), 3.43 (m, 4 H, 2-THF), 1.47 (m, 4 H, 3-THF), 0.31 (s, 36 H, SiMe$_3$), 0.21 (s, 12 H, SiMe$_2$). ^{13}C NMR (benzene-d_6, 25 °C): δ 158.92 (allyl), 84.56 (br, allyl), 67.93 (2-THF), 25.62 (3-THF), 1.78 (SiMe$_3$), −0.86 (SiMe$_2$).

Preparation of [Nd{(η^3-C$_3$H$_3$SiMe$_3$)$_2$SiMe$_2$}$_2${μ-K(THF)}(THF)(C$_7$H$_8$)]$_\infty$ (4). A solution of KO^{t}Bu (2.31 g, 20.6 mmol) and Me$_2$Si(CH$_2$CHCHSiMe$_3$)$_2$ (2.93 g, 10.3 mmol) in THF (100 mL) at −78 °C was treated with ^{n}BuLi (12.9 mL, 1.6 M in hexanes, 20.6 mmol). The solution was warmed to room temperature and was then stirred for 3 h. The resulting red solution was treated with solid portions of NdI$_3$(THF)$_{3.5}$ (4.00 g, 5.14 mmol) and then heated at 50 °C for 2 h. After it was stirred at room temperature for a further 16 h, the now orange solution was evaporated to dryness. Extraction with toluene (50 mL), concentration, and cooling to −20 °C gave the title compound as a red crystalline solid, yield 1.57 g (1.77 mmol, 34.4%). Extended exposure to low pressure (ca. 0.01 mm Hg) resulted in solvent loss to give [Nd{(η^3-C$_3$H$_3$SiMe$_3$)SiMe$_2$}$_2${μ-K}]$_\infty$. Anal. Calcd for C$_{28}$H$_{60}$KNdSi$_6$: C, 44.92; H, 8.08. Found: C, 44.98; H, 7.98. ^{1}H NMR (THF-d_8, 20 °C): δ 6.0 (br s, 12 H, SiMe$_2$), −3.1 (br s, 36 H, SiMe$_3$), −7.3 (br s, 4 H, allyl), −9.0 (br s, 8 H, allyl).

Table 4. Crystal Data for Lanthanide Allyl Complexes

	1	**5**
formula	C$_{34}$H$_{72}$KLaO$_{1.5}$Si$_6$	C$_{44}$H$_{100}$LiO$_4$Si$_6$Sm
fw	851.5	1019.06
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	9.873(2)	12.511(3)
b, Å	12.970(3)	12.243(2)
c, Å	19.469(4)	19.609(3)
α, deg	76.66(3)	90
β, deg	77.94(3)	95.79(3)
γ, deg	88.78(3)	90
U, Å^3	2374.6(8)	2988.2(10)
D_c/g cm^{-3}	1.191	1.133
Z	2	2
μ, mm^{-1}	1.162	1.135
F(000)	896	1090
θ range, deg	$2.15 \le \theta \le 25.35$	$1.66 \le \theta \le 25.35$
indices	$-11 \le h \le 11$, $-15 \le k \le 15$, $-21 \le l \le 21$	$-15 \le h \le 15$, $-14 \le k \le 14$, $-23 \le l \le 23$
cryst dimens, mm	0.3 × 0.1 × 0.1	0.15 × 0.15 × 0.05
no. of rflns collected/ indep/"obsd" ($I > 2\sigma(I)$)	13 964/8126/7514	9788/5165/3556
R_{int}[a]	0.0362	0.0549
R1 ($I > 2\sigma(I)$)[b]	0.0272	0.0409
wR2 (all data)[c]	0.0762	0.0857

[a] $\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

Preparation of [Li(OEt$_2$)$_4$][Sm{(η^3-C$_3$H$_3$SiMe$_3$)$_2$SiMe$_2$}$_2$]$_\infty$ (5). A solution of KO^{t}Bu (0.82 g, 7.31 mmol) and Me$_2$Si(CH$_2$CHCHSiMe$_3$)$_2$ (1.04 g, 3.65 mmol) in THF (100 mL) at −78 °C was treated with ^{n}BuLi (4.56 mL, 1.6 M in hexanes, 7.30 mmol). The solution was warmed to room temperature and was then stirred for 3 h. The resulting red solution was treated with solid portions of SmI$_2$(THF)$_2$ (2.00 g, 3.65 mmol) and then heated at 50 °C for 2 h. After it was stirred for a further 16 h at room temperature, the solution was brown with much precipitate. The volatiles were removed in vacuo, and the residue was then extracted with toluene (100 mL). Concentration and cooling to −20 °C gave an orange-red oil which deposited from the solution. This was isolated and dried in vacuo. The solid was recystallized from light petroleum/diethyl ether at −20 °C to give the title compound as red crystals, yield 0.25 g (0.25 mmol, 6.8%). The compound was identified by ^{1}H NMR and single-crystal X-ray diffraction. ^{1}H NMR (toluene-d_8, 20 °C): δ 12.32 (br d, J_{HH} = 15.5 Hz, 4 H, allyl), 7.54 (br d, J_{HH} = 10.3 Hz, 4 H, allyl), 3.20 (br m, 16 H, OCH_2CH$_3$), 2.23 (br s, 12 H, SiMe$_2$), 1.04 (m, 24 H, OCH$_2$CH_3), 0.00 (br s, 36 H, SiMe$_3$), −1.39 (br m, 4 H, allyl).

X-ray Crystallography. A crystal coated in dried perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream (T = 140(1) K). This was mounted on a Rigaku R-Axis II image plate diffractometer equipped with a rotating-anode X-ray source (Mo Kα radiation, λ(Mo Kα) = 0.710 69 Å) and graphite monochromator. For **1**, 48 exposures of 50 min each were made using 4° oscillations. For **5**, 46 exposures of 55 min each were made using 4° oscillations. Data were processed using the DENZO/SCALEPACK[19] programs. The structures were determined by the direct-methods routines in the XS program[20] and refined by full-matrix least-squares methods, on F^2 values, in XL.[20] For **1** the non-hydrogen atoms were refined with anisotropic thermal parameters, except for the noncoordinating THF, which was disordered in two molecules. Hydrogen atoms were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms, except for the hydrogen atoms of the allyl core and the methyl groups C(11), C(11′), and C(33′),. which were refined freely. In the final difference map, the highest peaks (to ca. 0.96 e Å^{-3}) were close to the disordered THF molecule. For **5** the hydrogen atoms were included in idealized positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms, except for the hydrogen atoms of the allyl core, which were refined freely. Scattering factors for neutral atoms were taken from the literature.[21] Computer programs were run on a Silicon Graphics Indy computer at the University of East Anglia.

Crystal data and structure solution and refinement details are given in Table 4.

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

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