(Pentamethylcyclopentadienyl)lanthanide(II) Alkyl and Silyl Complexes: Synthesis, Structures, and Catalysis in Polymerization of Ethylene and Styrene

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The reactions of $(C_5Me_5)_2Ln(THF)_2$ with 1 equiv of $KCH(SiMe_3)_2$ in THF afforded the corresponding Ln(II) alkyl complexes $[(C_5Me_5)Ln(CH(SiMe_3)_2)(C_5Me_5)K(THF)_2]_n$ (Ln = Sm (**1a**), Eu (**1b**), Yb (**1c**)) in 90−92% isolated yields. In the presence of $PhSiH_3$ the reactions of $(C_5Me_5)_2Ln(THF)_2$ with an unidentified "$KH + H_3SiPh$" reaction product (presumably containing $KSiH_2Ph$ and $KSiH_3$) gave the $Ln^{II}-SiH_3$ complexes $[(C_5Me_5)Ln(SiH_3)(THF)(C_5Me_5)K(THF)]_n$ (Ln = Sm (**2a**), Eu (**2b**), Yb (**2c**)) in 81−85% yields. Complexes **1a**−**c** and **2b**,**c** were structurally characterized by X-ray analyses. The "$(C_5Me_5)K$" unit in these complexes acted as a neutral stabilization ligand. An "intermolecular" interaction between the K atom and the Ln(II)-bound C_5Me_5 group resulted in formation of a polymeric structure. In the case of **2b**,**c**, an "interchain" interaction between the K atom and the SiH_3 group was also observed, which thus led to formation of a two-dimensional layer structure. Complexes **1a**−**c** represent the first examples of structurally characterized (cyclopentadienyl)lanthanide(II) alkyl complexes and **2b**,**c** the first examples of lanthanide(II)−SiH_3 complexes. The $Sm^{II}-CH(SiMe_3)_2$ complex **1a** showed high activity for the polymerization of ethylene and styrene through initiative one-electron transfer from the Sm(II) center to a monomer. The less reducing Eu(II) and Yb(II) analogues **1b**,**c** showed no activity under the same conditions. In contrast, the SiH_3 complexes of Eu(II) (**2b**) and Yb(II) (**2c**) were active for the polymerization of ethylene and styrene, which was probably initiated by migratory addition of the SiH_3 group to a monomer. Complex **1a** was also active for the block-copolymerization of ethylene with styrene.

Introduction

Organolanthanide alkyl and silyl complexes, which can effect a variety of useful transformations such as hydrogenation,[1] hydrosilylation,[2] and polymerization[3] of olefins and dehydrogenative coupling of hydrosilanes,[4] are among the most important organolanthanide compounds.[5] These complexes, especially the silyl complexes,[6] have so far been dominated by lanthanide(III) metallocenes bearing two cyclopentadienyl ancillary ligands, while mono(cyclopentadienyl)lanthanide(II) alkyl or silyl complexes remained almost unexplored, owing to their susceptibility to ligand redistribution to yield the corresponding homoleptic analogues.[7−9] We recently found that the potassium or sodium pentamethylcyclopentadienide unit "C_5Me_5M" (M = K, Na) could act as

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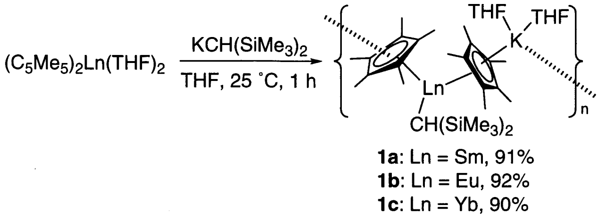
an excellent neutral stabilization moiety for lanthanide(II) complexes bearing both pentamethylcyclopentadienyl (C_5Me_5) and a heteroatom-containing monodentate anionic ligand such as an aryloxide, thiolate, amido, or phosphido group.[10] Such mixed-ligand-supported lanthanide(II) complexes offer a sterically and electronically unique ligand environment for the metal center and thus show novel reactivities.[10,11] In continuation of this study, we examined the "C_5Me_5K" ligation for the isolation of analogous lanthanide(II) alkyl and silyl complexes. In this paper, we report the synthesis, structures, and olefin polymerization activity of the mixed $C_5Me_5/CH(SiMe_3)_2$- and C_5Me_5/SiH_3-supported Sm(II), Eu(II), and Yb(II) complexes. The $CH(SiMe_3)_2$ complexes represent the first examples of structurally characterized cyclopentadienyl-supported lanthanide(II) alkyl complexes,[12] and the SiH_3 complexes represent the first examples of lanthanide(II)–SiH_3 complexes.

Results and Discussion

Synthesis and Structures of Lanthanide(II) Alkyl Complexes. Similar to the synthesis of Sm(II) complexes bearing a heteroatom-containing monodentate anionic ligand,[10a,c] the reactions of $(C_5Me_5)_2Ln(THF)_2$ (Ln = Sm, Eu, Yb) with 1 equiv of $KCH(SiMe_3)_2$ in THF afforded straightforwardly the corresponding Ln(II) alkyl complexes **1a**–**c** in 90–92% isolated yields (eq 1).



(1)

Complexes **1a**–**c** are isostructural and isomorphous with each other. Their overall structural features are almost the same as those of the previously reported aryloxide, thiolate, and amido analogues.[10a] Thus, **1a**–**c** could all formally be viewed as a $C_5Me_5/CH(SiMe_3)_2$-ligated Ln(II) species stabilized by the neutral "$(C_5Me_5)K(THF)_2$" ligand. The "intermolecular" interactions between the K atom and the Ln(II)-bound C_5Me_5 group resulted in formation of a polymeric structure. An ORTEP view of the "monomeric form" of **1a** is shown in Figure 1.[13] Selected bond lengths and angles are summarized in Table 1.

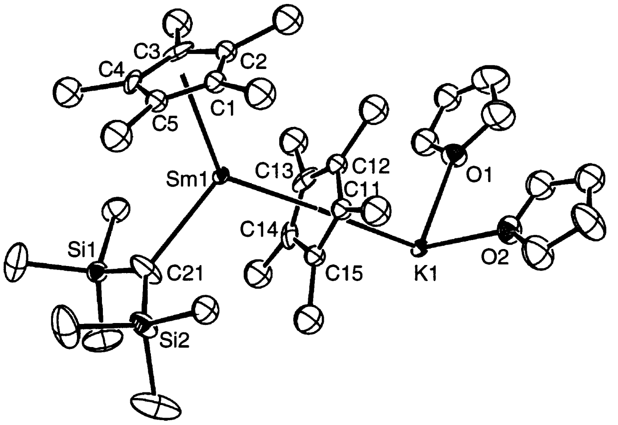


Figure 1. ORTEP drawing of a monomeric form of **1a** with 30% thermal ellipsoids. Complexes **1b**,**c** are isostructural with **1a**.

Table 1. Summary of Selected Bond Lengths (Å) and Angles (deg) for Lanthanide(II) Complexes of the Type "$(Cp^{*1})Ln(R)(Cp^{*2}K)$"

	1a	**1b**	**1c**	**2b**	**2c**
			Lanthanides and Ligands		
Ln	Sm	Eu	Yb	Eu	Yb
R	$CH(SiMe_3)_2$	$CH(SiMe_3)_2$	$CH(SiMe_3)_2$	SiH_3	SiH_3
			Bond Distances		
Ln-Cp^{*1} (av)	2.85(2)	2.83(2)	2.74(3)	2.85(1)	2.76(1)
Ln-Cp^{*2} (av)	2.86(2)	2.91(2)	2.79(3)	2.86(1)	2.76(1)
Ln-R	2.64(1)	2.65(1)	2.56(1)	3.239(3)	3.091(3)
K–Cp^{*2} (av)	3.10(2)	3.12(2)	3.09(3)	3.12(1)	3.15(1)
K–$Cp^{*1'}$ (av)	3.12(2)	3.18(2)	3.18(3)	3.19(1)	3.20(1)
K–R				3.614(3)	3.684(3)
			Bond Angles		
∠Cp^{*1}–Ln–Cp^{*2}	136(1)	137(1)	134(1)	135.9(6)	136.8(5)
∠Cp^{*1}–Ln–R	114(1)	111(1)	110(1)	104.8(3)	104.3(2)
∠Cp^{*2}–Ln–R	109(1)	111(1)	116(1)	107.8(3)	107.2(2)
∠Ln–R–K				172.0(1)	171.6(1)

The Sm–C_5Me_5 bond distances in **1a** (average 2.85(2) and 2.86(2) Å) are in the 2.84(2)–2.97(2) Å bond distance range of those found in the analogous Sm(II) complexes with a heteroatom-containing monodentate anionic ligand, such as $[(C_5Me_5)Sm(ER)(C_5Me_5)K(THF)_2]_n$ (ER = $OC_6H_2{}^tBu_2$-2,6-Me-4, $SC_6H_2{}^iPr_3$-2,4,6, $N(SiMe_3)_2$).[10a] The Sm–$CH(SiMe_3)_2$ bond distance in **1a** (2.64(1) Å) is somewhat shorter than those of the Sm–C bonds found in the only other structurally characterized Sm(II) alkyl complex, $Sm\{C(SiMe_3)_2(SiMe_2OMe)\}_2(THF)$ (2.787(5) and 2.845(5) Å),[8c] but significantly longer than those found in Sm(III) alkyl complexes such as $(C_5Me_5)_2SmMe(THF)$ (2.48(1) Å).[14] The Eu–C_5Me_5 bond distances in **1b** (average 2.83(2), 2.91(2) Å) are comparable with those of the Sm–C_5Me_5 bonds in **1a** (average 2.85(2) and 2.86(2) Å), since both Eu(II) and Sm(II) have similar ion sizes.[15] The Eu–$CH(SiMe_3)_2$ bond distance in **1b** (2.65(1) Å), which is almost the same as that of the Sm–$CH(SiMe_3)_2$ bond in **1a** (2.64(1) Å), is slightly longer than the Eu–C bond distances found in $Eu\{C(SiMe_3)_3\}_2$ (2.605(6), 2.612(7) Å)[8d] and $Eu(C_6H_3Ph_2\text{-}2,6)_2(THF)_2$ (2.606(4), 2.623(4) Å)[8a] but much shorter than that in $Eu(C_6F_5)_2(THF)_5$ (2.822(3) Å).[8b] The Yb–C_5Me_5 bond distances in **1c** (average 2.74(3) and 2.79(3) Å) are comparable with those found in the mixed

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(12) The synthesis and structure of the Sm(II) alkyl complex (**1a**) has been briefly described in a previous communication.[7]

(13) In the previous communication,[7] a C_5Me_5 ring in **1a** was treated as a fixed Cp model (C–C = 1.420 Å), because of the poor quality of the crystal. This restraint was released in the present work.

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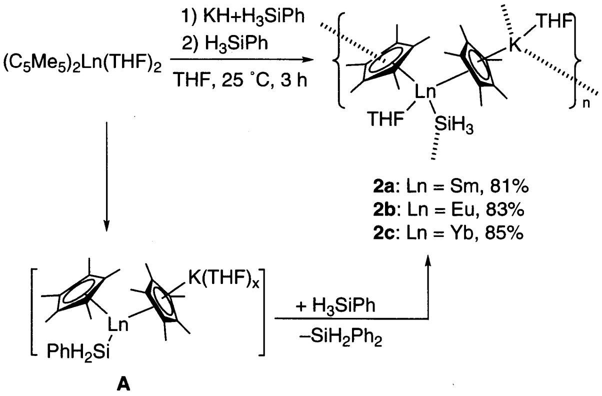
$C_5Me_5/N(SiMe_3)_2$-supported Yb(II) complex $(C_5Me_5)Yb(N(SiMe_3)_2)(C_5Me_5)Na(THF)_3$ (average 2.77(3) and 2.83(3) Å).[10a] The Yb−$CH(SiMe_3)_2$ bond distance in **1c** (2.56(1) Å) is in the 2.49−2.57 Å bond distance range of the Yb−C σ-bonds found in Yb(II) hydrocarbyl complexes such as $Yb\{C(SiMe_3)_3\}_2$ (2.490(8), 2.501(9) Å),[8f] $Yb(Tp^{t\text{-Bu,Me}})\{CH(SiMe_3)_2\}$ ($Tp^{t\text{-Bu,Me}}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate) (2.55(6) Å),[8g] $[Yb\{C(SiMe_3)_3\}(\mu\text{-OEt})(OEt_2)]_2$ (2.57(1) Å),[8e] and $Yb(C_6H_3\text{-}Ph_2\text{-}2,6)I(THF)_3$ (2.529(4) Å).[8a]

Synthesis and Structures of Lanthanide(II) Silyl Complexes. To synthesize an analogous phenylsilyl (SiH_2Ph) complex, the reaction of $(C_5Me_5)_2Ln(THF)_2$ with "$KSiH_2Ph$" was attempted. Since there was no literature available for the synthesis of $KSiH_2Ph$, the reaction of $PhSiH_3$ with KH was attempted analogously to the previous generation of the K(EAr) (E = O, S, NH, PH) species.[10a] The resultant THF-insoluble powder product was used as "$KSiH_2Ph$" without purification.[16] However, its reaction with $(C_5Me_5)_2Ln(THF)_2$ did not give an isolable Ln−SiH_2Ph complex. In the case of Yb, the Yb^{II}−SiH_3 complex $[(C_5Me_5)Yb(SiH_3)(THF)(C_5Me_5)K(THF)]_n$ (**2c**) was isolated as dark red crystals in ca. 15−20% yields. When 1 equiv of $PhSiH_3$ was added to the reaction mixture, the yield of **2c** increased to ca. 85% (eq 2). The analogous Sm(II) (**2a**) and Eu(II) (**2b**) complexes could also be obtained in a similar fashion, as shown in eq 2. The formation of **2a**−**c** in the present reactions apparently requires cleavage of the Si−Ph bond, which might occur through a Ln^{II}−SiH_2Ph intermediate such as **A** (eq 2).[17] Similar Si−Ph bond cleavage was observed previously by Tilley et al. in the reaction of $(C_5Me_5)_2SmCH(SiMe_3)_2$ with $PhSiH_3$.[6b,c] The Si−C bond cleavage also took place in the reaction of KH with an excess of $PhSiH_3$.[18]



(2)

Although structural characterization of the Sm complex **2a** was not successful because of poor quality of the crystal, its Eu (**2b**) and Yb (**2c**) analogues were successfully characterized by crystallographic studies. Complexes **2b**,**c** are isostructural and isomorphous with each other. Their basic structure unit is similar to those of **1a**−**c** and other analogous complexes (Figure 2 and Table 1). Moreover, in addition to the interaction between the K atom and a C_5Me_5 group, which forms a one-dimensional polymer structure as described previously, an "interchain" interaction between the SiH_3 group and the K atom was also observed in **2b**,**c**, which thus forms a two-dimensional layer structure as shown in Figure 3.

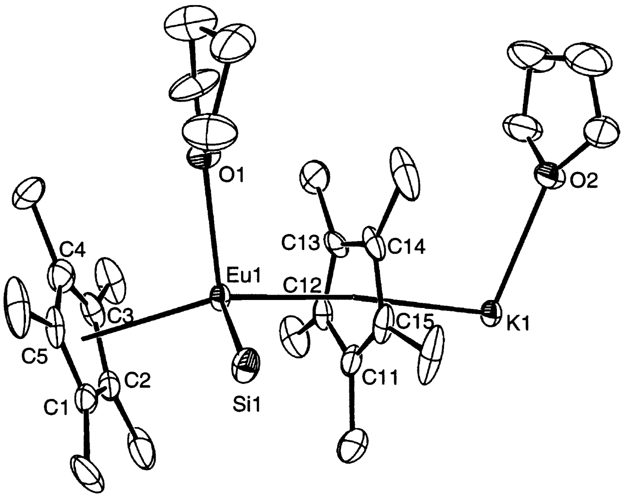


Figure 2. ORTEP drawing of a monomeric form of **2b** with 30% thermal ellipsoids. Complex **2c** is isostructural with **2b**.

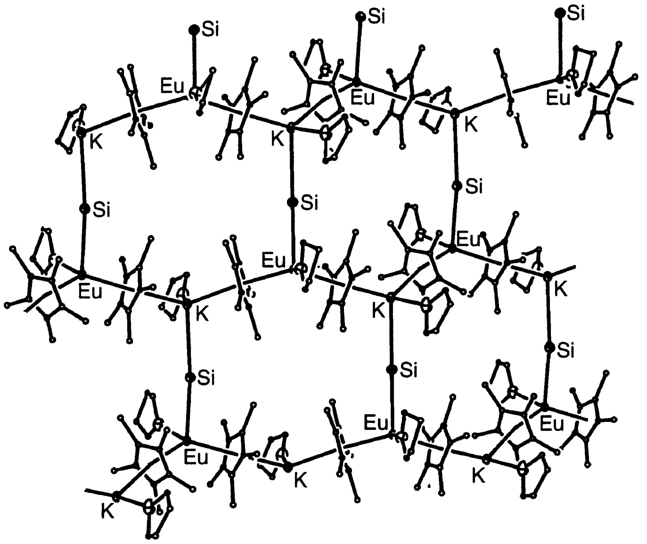


Figure 3. Two-dimensional layer structure of **2b**.

The Eu−C_5Me_5 bond distances in **2b** (average 2.85(1) and 2.86(1) Å) and the Yb−C_5Me_5 bond distances in **2c** (average 2.76(1) Å) can be compared with those found in **1b** (average 2.83(2), 2.91(2) Å) and **1c** (average 2.74(3) and 2.79(3) Å), respectively (Table 1). The bond distance of the Yb−Si bond in **2c** (3.091(3) Å) is comparable with those found in the Yb(II) silyl complexes $(C_5Me_5)Yb\{Si(SiMe_3)_3\}(THF)_2$ (3.032(3) Å)[9a] and $Yb(SiPh_3)_2(THF)_4$ (3.158(2) Å).[9b] Complex **2b** is the first structurally characterized europium silyl compound, and there are no Eu−Si bond data available for comparison. However, the Eu−Si bond distance in **2b**

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(16) The powder product might contain "$KSiH_3$", as described below.[18]

(17) Reaction of $(C_5Me_5)_2Ln(THF)_2$ with KH to give a Ln−H species was not observed in THF at room temperature.

(18) When KH was stirred with 2 equiv of $PhSiH_3$ in THF at room temperature for 36 h, a blue suspension was obtained, which after evaporation of the THF solvent and extraction of the residue with hexane gave a gray powder. From the hexane extract, a mixture of H_2SiPh_2, $HSiPh_3$, and $SiPh_4$ was obtained in a molar ratio of ca. 1:5:1, as shown by ^1H NMR. $SiPh_4$ was also confirmed by an X-ray analysis. Further purification or characterization of the gray powder was difficult, due to its poor solubility. Its reaction with $(C_5Me_5)_2Yb(THF)_2$ in THF produced **2c** in good yield (ca. 70%), which suggests that the gray powder could contain "$KSiH_3$".

Table 2. Polymerization of Ethylene[a]

run	cat.	time (min)	yield (g)	activity (g mmol^{-1} h^{-1}	M_n ($\times10^{-4}$)[b]	M_w/M_n[b]
1	**1a**	5	1.10	264	140	1.62
2	**1b**	60	trace			
3	**1c**	60	trace			
4	**2a**	10	0.78	94	11.3	3.51
5	**2b**	30	0.64	75	39.0	1.94
6	**2c**	30	0.08	9	10.8	3.39

[a] Reaction conditions: cat., 0.05 mmol; ethylene, 1 atm; toluene, 15 mL; 25 °C. [b] Determined at 135 °C against polystyrene standard by GPC.

Table 3. Polymerization of Styrene[a]

run	cat.	time	yield (%)	M_n ($\times10^{-4}$)[b]	M_w/M_n[b]
1	**1a**	5 min	100	14.0	3.20
2	**1b**	1 h	trace		
3	**1c**	1 h	trace		
4	**2a**	10 min	100	5.8	1.27
5	**2b**	1 h	91	7.0	1.28
6	**2c**	5 h	89	4.2	1.19

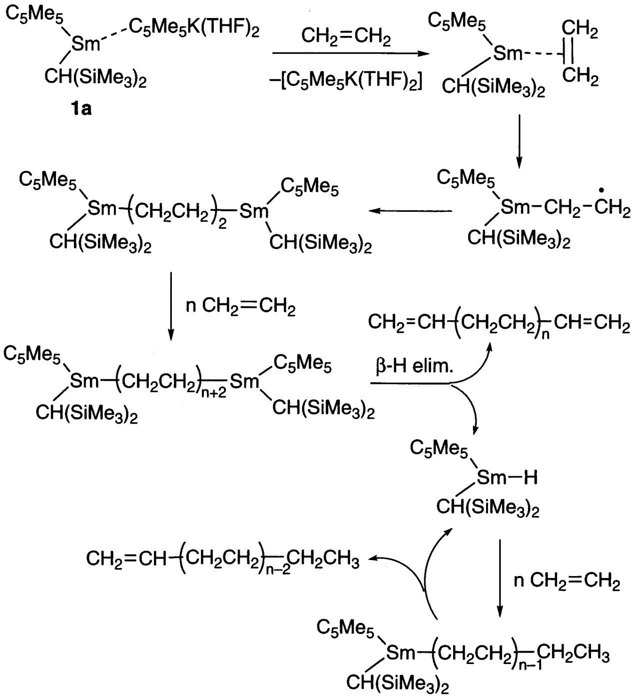
[a] Conditions: cat., 0.05 mmol; styrene, 4 mL (35 mmol); toluene, 10 mL; 25 °C. [b] Determined at 135 °C against polystyrene standard by GPC.

(3.239(3) Å) can be compared with that of the Yb–Si bond in **2c**, since Eu(II) is generally ca. 0.11–0.15 Å larger than Yb(II) in radius when both have the same coordination number.[15] The K–Si bond distances in **2b** (3.614(3) Å) and **2c** (3.684(3) Å) are in the 3.56–3.86 Å range of the Si–K interactions found in the polymeric $[\text{KSiH}_3]_n$[19] but significantly longer than those found in discrete potassium silanide molecules such as $\text{K(C}_6\text{D}_6)_3\text{-Si(}^t\text{Bu)}_3$ (3.378(1) Å)[20] and $[\text{K}\{\mu\text{-Si(SiMe}_3)_3\}]_2$ (3.368(1)–3.417(1) Å),[21] showing that the K···SiH_3 "interchain" interactions in **2b**,**c** are weaker than a normal K–silanide bond. These results also suggest that **2b**,**c** are truly $\text{Ln}^{\text{II}}\text{–SiH}_3$ compounds rather than "KSiH_3" adducts of $(\text{C}_5\text{Me}_5)_2\text{Ln}$.

Polymerization of Ethylene and Styrene. The results of ethylene polymerization by **1a**–**c** and **2a**–**c** are shown in Table 2, and those of styrene polymerization are given in Table 3.

The ethylene polymerization activity of the $\text{Sm}^{\text{II}}\text{–CH(SiMe}_3)_2$ complex **1a** (264 g mmol^{-1} h^{-1}) was much higher than that of conventional samarocene(II) complexes such as $(\text{C}_5\text{Me}_5)_2\text{Sm(THF)}$ (5 g mmol^{-1} h^{-1})[22] and also higher than those of analogous C_5Me_5/ER-ligated Sm(II) complexes such as $[(\text{C}_5\text{Me}_5)\text{Sm(ER)(C}_5\text{Me}_5)\text{K(THF)}_2]_n$ (ER = $\text{OC}_6\text{H}_2{}^t\text{Bu}_2$-2,6-Me-4, $\text{SC}_6\text{H}_2{}^i\text{Pr}_3$-2,4,6, $\text{NHC}_6\text{H}_2{}^t\text{Bu}_3$-2,4,6, or $\text{N(SiMe}_3)_2$) (58–194 g mmol^{-1} h^{-1}).[10a] Complex **1a** was also active for the polymerization of styrene. It quantitatively transformed 700 equiv of styrene into polystyrene at room temperature within 5 min, thus constituting the most active lanthanide catalyst ever reported for styrene polymerization.[3,10a] In striking contrast, the analogous, less reducing Eu^{II}– and $\text{Yb}^{\text{II}}\text{–CH(SiMe}_3)_2$ complexes **1b**,**c** were inactive for the polymerization of either ethylene or styrene under the same conditions.[23] These results strongly suggest that the polymerization by **1a** must be initiated through one-electron transfer from the $\text{C}_5\text{Me}_5/\text{CH(SiMe}_3)_2$-ligated Sm(II) center to a monomer (cf. Scheme 1), as reported for the analogous C_5Me_5/ER–Sm(II) complexes (ER = OAr, SAr, PHAr, NRR′).[10a] The possibility of polymerization initiation through a potassium species or through monomer insertion into the $\text{Sm–CH(SiMe}_3)_2$ bond could be excluded.[24]

Scheme 1. Possible Scenario for the Polymerization of Ethylene by 1a



Although the $\text{CH(SiMe}_3)_2$ complexes of Eu(II) (**1b**) and Yb(II) (**1c**) were inactive, the analogous SiH_3 complexes **2b**,**c** showed considerably high activity for the polymerization of ethylene and styrene. Also noteworthy is that the activity of the much less reducing Eu(II) complex **2b** for ethylene polymerization (75 g mmol^{-1} h^{-1}) is almost as high as that of the Sm(II) complex **2a** (94 g mmol^{-1} h^{-1}) and much higher than that of the Yb(II) complex **2c** (9 g mmol^{-1} h^{-1}) (runs 4–6, Table 2).[23] In the case of styrene a similar reactivity trend was also observed (runs 4–6, Table 3). Since electron transfer from Eu(II) or Yb(II) to an olefin monomer would be difficult, the polymerization by **2b**,**c** must be initiated through migration of the SiH_3 group to a monomer (Scheme 2),[25] and the higher activity of the Eu(II) complex **2b** as compared to that of the Yb(II) complex **2c** could probably be due to the larger ion size of Eu(II).[15] Polymerization by the $\text{Sm}^{\text{II}}\text{–SiH}_3$ complex **2a** could be initiated through either one-electron transfer from the Sm(II) center or migration of the SiH_3 to a monomer (or probably both).

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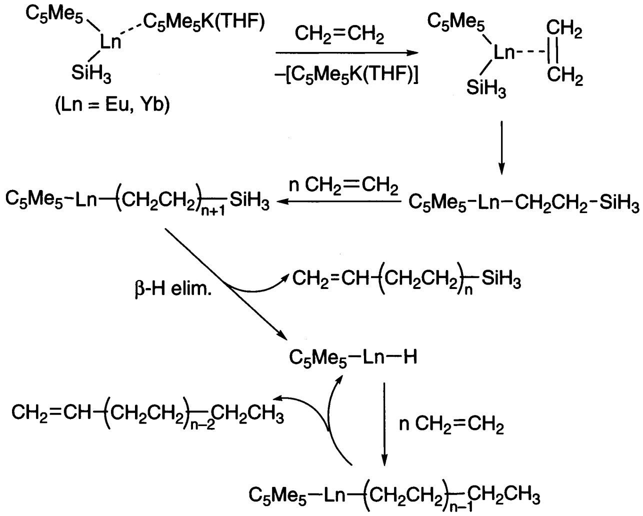
(23) Cf. the aqueous redox potentials vs NHE: $\text{Eu}^{3+}/\text{Eu}^{2+} = -0.35$ V, $\text{Yb}^{3+}/\text{Yb}^{2+} = -1.15$ V, $\text{Sm}^{3+}/\text{Sm}^{2+} = -1.55$ V. (a) Morss, L. R. *Chem. Rev.* **1976**, *76*, 827. (b) Imamoto, T. *Lanthanides in Organic Synthesis*; Academic: London, 1994; p 4.

(24) The inactivity of the $\text{Ln–CH(SiMe}_3)_2$ bond in lanthanide(III) metallocene complexes toward ethylene was known. See: Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(25) Attempts to observe the SiH_3 group in the polymer products by NMR were not successful, possibly owing to the high molecular weight of the polymers.

Scheme 2. Possible Scenario for the Polymerization of Ethylene by 2b,c



Complex **1a** was also active for the block-copolymerization of ethylene with styrene. In the presence of 0.05 mmol of **1a**, the reaction of styrene (3.64 g, 35 mmol) with ethylene (1 atm) at room temperature for 15 min afforded 1.38 g of styrene–ethylene block-copolymer ($M_n = 2.13 \times 10^5$, $M_w/M_n = 1.60$, polystyrene content 44%) and 2.14 g of homopolystyrene. These results are comparable with those reported previously for the C$_5$Me$_5$/ER–Sm^{II} analogues.[10a]

Conclusion

We have shown that the "C$_5$Me$_5$K" unit can generally serve as a neutral stabilization ligand for Sm(II), Eu(II), and Yb(II) complexes bearing mixed C$_5$Me$_5$/CH(SiMe$_3$)$_2$ or C$_5$Me$_5$/SiH$_3$ ligands, which are otherwise difficult to isolate owing to ligand redistribution problems. The C$_5$Me$_5$/CH(SiMe$_3$)$_2$-ligated Sm(II) complex **1a** showed high activity for the polymerization of ethylene and styrene through initiative one-electron transfer from the Sm(II) center to a monomer. The analogous Eu(II) (**1b**) and Yb(II) (**1c**) complexes showed no activity under the same conditions, owing to lower reducing power. In contrast with the inertness of the CH(SiMe$_3$)$_2$ complexes **1b**,**c**, the analogous SiH$_3$ complexes of Eu(II) (**2b**) and Yb(II) (**2c**) were active for the polymerization of ethylene and styrene, which might be initiated by migratory addition of the SiH$_3$ group to a monomer.

Experimental Section

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. The argon was purified by being passed through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4A) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O$_2$/H$_2$O Combi-Analyzer (Mbraun) to ensure both were always below 1 ppm. Samples of the lanthanide complexes for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H NMR spectra were recorded on a JNM-GSX 500 (FT, 500 MHz) or a JNM-EX 270 (FT, 270 MHz) spectrometer. Gel permeation chromatography (GPC) curves were recorded at 135 °C on an SSC-7100HT-GPC apparatus with an ACS 950/14 mass detector using *o*-dichlorobenzene as an eluent (Note that an RI detector is not suitable for the analysis of styrene–ethylene copolymers, since the signal for a polyethylene unit appears in a direction reverse to that for a polystyrene unit). Elemental analyses were carried out by the Chemical Analysis Laboratory of RIKEN. Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze–pump–thaw method (three times), and dried over fresh Na chips in the glovebox. Ethylene monomer was purified by being passed through a Dryclean column (4A molecular sieves) and a Gasclean GC-XR column (Nikka Seiko Co.). Styrene monomer was dried over CaH$_2$ overnight and vacuum-transferred before use. KCH(SiMe$_3$)$_2$ was synthesized by the reaction of LiCH(SiMe$_3$)$_2$[26] with KO^t-Bu according to the literature.[27] (C$_5$Me$_5$)$_2$Ln(THF)$_2$ (Ln = Sm, Eu, Yb) were prepared by reactions of LnI$_2$(THF)$_2$ with KC$_5$Me$_5$.[28]

[(C$_5$Me$_5$)Sm(CH(SiMe$_3$)$_2$)(C$_5$Me$_5$)K(THF)$_2$]$_n$ (1a). In the glovebox, a THF solution (5 mL) of KCH(SiMe$_3$)$_2$ (0.198 g, 1 mmol) was added to a purple THF solution (10 mL) of (C$_5$Me$_5$)$_2$Sm(THF)$_2$ (0.565 g, 1 mmol) in a 100 mL flask. The mixture was stirred at room temperature for 1 h and then transferred to another flask through a glass filter. After the solution was concentrated under reduced pressure, hexane was layered to give green platelike crystals of **1a** suitable for X-ray analysis. Leaving **1a** under vacuum (1 mmHg) at room temperature for 1 h removed one of the two THF ligands to give [(C$_5$Me$_5$)Sm(CH(SiMe$_3$)$_2$)(C$_5$Me$_5$)K(THF)]$_n$ (**1a′**; 0.636 g, 0.91 mmol, 91% yield), as shown by elemental analysis. ^{1}H NMR (THF-d_8, 22 °C): δ 10.20 (br s, 30 H, C$_5$Me$_5$), −0.02 (s, 18 H, CH(Si*Me*$_3$)$_2$). The methine proton in CH(SiMe$_3$)$_2$ could not be located, owing to the influence of the paramagnetic Sm(II) ion. Anal. Calcd for C$_{31}$H$_{57}$OSi$_2$KSm (**1a′**): C, 53.85; H, 8.31. Found: C, 53.73; H, 8.26.

[(C$_5$Me$_5$)Eu(CH(SiMe$_3$)$_2$)(C$_5$Me$_5$)K(THF)$_2$]$_n$ (1b). Complex **1b** was obtained as orange-red plates in a way identical with that described for **1a** by reaction of (C$_5$Me$_5$)$_2$Eu(THF)$_2$ with 1 equiv of KCH(SiMe$_3$)$_2$. Leaving **1b** under vacuum (1 mmHg) at room temperature for 1 h removed the two THF ligands to give [(C$_5$Me$_5$)Eu(CH(SiMe$_3$)$_2$)(C$_5$Me$_5$)K]$_n$ (**1b′**; 92% yield), as shown by elemental analysis. ^{1}H NMR (THF-d_8, 22 °C): δ 1.70 (br s, 30 H, C$_5$Me$_5$), −0.20 (br s, 18 H, CH(Si*Me*$_3$)$_2$). The methine proton in CH(SiMe$_3$)$_2$ could not be located, owing to the influence of the paramagnetic Eu(II) ion. Anal. Calcd for C$_{27}$H$_{49}$Si$_2$KEu (**1b′**): C, 48.76; H, 6.75. Found: C, 48.26; H, 6.69.

[(C$_5$Me$_5$)Yb(CH(SiMe$_3$)$_2$)(C$_5$Me$_5$)K(THF)$_2$]$_n$ (1c). Complex **1c** was obtained as green plates in a way identical with that described for **1a** by reaction of (C$_5$Me$_5$)$_2$Yb(THF)$_2$ with 1 equiv of KCH(SiMe$_3$)$_2$. Leaving **1c** under vacuum (1 mmHg) at room temperature for 1 h removed the two THF ligands to give [(C$_5$Me$_5$)Yb(CH(SiMe$_3$)$_2$)(C$_5$Me$_5$)K]$_n$ (**1c′**; 90% yield), as shown by elemental analysis. ^{1}H NMR (THF-d_8, 22 °C): δ 1.91 (br s, 30 H, C$_5$Me$_5$), −0.10 (s, 18 H, CH(Si*Me*$_3$)$_2$), −1.96 (s, 1 H, C*H*(SiMe$_3$)$_2$). Anal. Calcd for C$_{27}$H$_{49}$ Si$_2$KYb (**1c′**): C, 50.51; H, 7.69. Found: C, 50.43; H, 8.09.

[(C$_5$Me$_5$)Sm(SiH$_3$)(THF)(C$_5$Me$_5$)K(THF)]$_n$ (2a). To a THF solution (10 mL) of PhSiH$_3$ (0.13 g, 1.2 mmol) in a 100 mL flask was added KH (0.04 g, 1 mmol) at room temperature. The resultant green mixture was stirred overnight, and evolution of H$_2$ was evident. After the mixture was dried under reduced pressure, the residue was washed with hexane to give a greenish yellow powder,[16,18] to which a purple THF solution

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Table 4. Summary of Crystal Data

	1a	**1b**	**1c**	**2b**	**2c**
formula	$C_{35}H_{65}KO_2Si_2Sm$	$C_{35}H_{65}EuKO_2Si_2$	$C_{35}H_{65}KO_2Si_2Yb$	$C_{28}H_{49}EuKO_2Si$	$C_{28}H_{49}KO_2SiYb$
fw	763.50	765.11	786.19	636.82	657.90
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$C2$	$C2$	$C2$	$Pna2_1$	$Pna2_1$
a (Å)	34.204(6)	34.814(3)	34.574(10)	19.320(2)	19.321(3)
b (Å)	10.189(2)	10.3140(9)	10.083(3)	16.724(2)	16.496(2)
c (Å)	11.678(2)	11.8462(11)	11.702(3)	10.0278(12)	9.9264(15)
β (deg)	102.016(4)	102.617(2)	102.130(6)		
V (Å^3)	3980.5(12)	4150.9(6)	3988(2)	3240.0(7)	3163.7(8)
Z	4	4	4	4	4
D_{calcd} (g cm^{-3})	1.274	1.224	1.309	1.306	1.381
μ (mm^{-1})	1.666	1.694	2.535	2.121	3.145
no. of rflns collected	15 301	13 619	14 725	23 222	23 342
no. of indep rflns (R(int))	9883 (0.0481)	9371 (0.0254)	10 138 (0.0754)	8634 (0.0477)	8451 (0.0845)
no. of params	389	389	389	308	308
goodness of fit on F^2	1.077	1.267	0.983	1.056	1.014
final R indices ($I > 2\sigma(I)$)					
R1	0.0565	0.0491	0.0644	0.0463	0.0539
wR2	0.1116	0.0962	0.0862	0.0729	0.0718
R indices (all data)					
R1	0.0978	0.0922	0.1804	0.1326	0.1111
wR2	0.1198	0.1011	0.1053	0.0805	0.0772

(10 mL) of $(C_5Me_5)_2Sm(THF)_2$ (0.565 g, 1 mmol) and $PhSiH_3$ (0.108 g, 1 mmol) were added. The mixture was stirred at room temperature for 3 h and dried under reduced pressure. The residue was washed with hexane, dissolved in THF, and concentrated under reduced pressure. Layering of hexane afforded dark red microcrystals of **2a**. Leaving **2a** under vacuum (1 mmHg) at room temperature for 1 h removed the two THF ligands to give $[(C_5Me_5)Sm(SiH_3)(C_5Me_5)K]_n$ (**2a′**; 0.40 g, 0.81 mmol, 81% yield based on Sm), as shown by elemental analysis. ^1H NMR (THF-d_8, 22 °C): two broad signals for C_5Me_5 were observed at δ 2.48 and 1.67, respectively; a signal for the SiH_3 group was not observed, owing to the influence of the paramagnetic Sm(II) ion. IR (Nujol): 2128 (m, br, ν_{SiH}), 2088 (m, br, ν_{SiH}), 1305 (m), 1262 (m), 1158 (w), 1102 (w), 1032 (s), 920 (w), 880 (s), 800 (s), 724 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{33}SiKSm$ (**2a′**): C, 48.92; H, 6.77. Found: C, 48.51; H, 6.57.

$[(C_5Me_5)Eu(SiH_3)(THF)(C_5Me_5)K(THF)]_n$ (2b). Complex **2b** was obtained as orange-red blocks in a way identical with that described for **2a**. Leaving **2b** under vacuum (1 mmHg) at room temperature for 1 h removed the two THF ligands to give $[(C_5Me_5)Eu(SiH_3)(C_5Me_5)K]_n$ (**2b′**; 83% yield), as shown by elemental analysis. No clear ^1H NMR signal was observed for **2b** in either THF-d_8 or pyridine-d_5 at 22 °C, owing to the influence of the paramagnetic Eu(II) ion. IR (Nujol): 2136 (m, br, ν_{SiH}), 2090 (m, br, ν_{SiH}), 1310 (m), 1260 (m), 1160 (w), 1100 (w), 1032 (s), 920 (w), 890 (s), 800 (s), 724 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{33}SiKEu$ (**2b′**): C, 48.76; H, 6.75. Found: C, 48.26; H, 6.69.

$[(C_5Me_5)Yb(SiH_3)(THF)(C_5Me_5)K(THF)]_n$ (2c). Complex **2c** was obtained as dark red blocks in a way identical with that described for **2a**.[18] Leaving **2c** under vacuum (1 mmHg) at room temperature for 1 h removed the two THF ligands to give $[(C_5Me_5)Yb(SiH_3)(C_5Me_5)K]_n$ (**2c′**; 85% yield), as shown by elemental analysis. ^1H NMR (THF-d_8, 22 °C): δ 1.88 (br s, 30 H, C_5Me_5), 1.67 (s, 3 H, SiH_3). IR (Nujol): 2140 (m, br, ν_{SiH}), 2092 (m, br, ν_{SiH}), 1308 (m), 1260 (m), 1160 (w), 1100 (w), 1032 (s), 920 (w), 880 (s), 800 (s), 724 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{33}$ SiKYb (**2c′**): C, 46.76; H, 6.48. Found: C, 46.77; H, 7.04.

Polymerization of Ethylene. A typical procedure is as follows: in the glovebox, **1a′** (35 mg, 0.05 mmol), a magnetic stir bar, and toluene (15 mL) were placed in a 100 mL flask. The flask was taken outside the glovebox, set in a water bath (25 °C), and then connected to a Schlenk line, a well-purged ethylene line, and a mercury-sealed one-way stopper. Introduction of ethylene resulted in immediate formation (precipitation) of polyethylene. The mixture was stirred for 5 min, during which time a slightly positive ethylene pressure was maintained by the stopper. MeOH (20 mL) was added. The resultant mixture was poured into 300 mL of MeOH in a 1 L beaker and then stirred to further precipitate the polymer product. After filtration, the polymer product was dried under vacuum in an oven (80 °C) overnight, yielding 1.10 g of polyethylene (cf. run 1, Table 2).

Polymerization of Styrene. A typical procedure is as follows: in the glovebox, **1a′** (35 mg, 0.05 mmol), a magnetic stir bar, and toluene (10 mL) were placed in a 100 mL Schlenk flask which was equipped with a dropping funnel containing 4 mL of styrene (35 mmol). The flask was taken outside the glovebox and set in a water bath (25 °C). Styrene was dropped through the funnel under vigorous stirring to give a yellow viscous solution. After 5 min, 20 mL of MeOH was added. The resultant mixture was treated as in the case of ethylene to give 3.64 g of atactic polystyrene (100% yield) (cf. run 1, Table 3).

Copolymerization of Styrene and Ethylene. In the glovebox, **1a′** (35 mg, 0.05 mmol), a magnetic stir bar, and toluene (10 mL) was placed in a three-neck flask which was equipped with a dropping funnel containing 10 mL of styrene in 5 mL of toluene. The flask was taken outside the glovebox, set in a water bath (25 °C), and then connected to a Schlenk line, a well-purged ethylene line, and a mercury-sealed one-way stopper. As ethylene was introduced into the system, styrene was simultaneously added within 1 min under vigorous stirring. The mixture was stirred under the ethylene atmosphere for 15 min, during which time a yellow, viscous solution was gradually formed. MeOH (20 mL) was added, and the resultant mixture was then treated as in the case of ethylene homopolymerization, affording 3.55 g of a crude polymer product. This crude product was extracted repeatedly with THF at room temperature, until no polymer product was seen in the THF extract after addition of MeOH. The combined THF extracts yielded 2.14 g of atactic homopolystyrene after precipitation by addition of MeOH as described above. The THF-insoluble residue was then repeatedly extracted with toluene at 104−108 °C, which afforded 1.38 g of styrene−ethylene block-copolymer. Homopolyethylene (insoluble in toluene at 110 °C) was not observed. For more details on the separation and characterization of styrene−ethylene block-copolymers, see ref 10a.

X-ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glovebox under a microscope mounted on the glovebox window and were sealed in thin-walled glass capillaries. Data collections were performed at

293 K on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinements were performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystal data and processing parameters are summarized in Table 4.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for **1a**−**c** and **2b**,**c** and ORTEP drawings of **1b**,**c** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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