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C_5Me_5/ER-Ligated Samarium(II) Complexes with the Neutral “C_5Me_5M” Ligand (ER = OAr, SAr, NRR′, or PHAr; M = K or Na): A Unique Catalytic System for Polymerization and Block-Copolymerization of Styrene and Ethylene

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Abstract: Reactions of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of K(ER) in THF gave in high yields the Sm(II) complexes $[(C_5Me_5)Sm(THF)_m(ER)(\mu\text{-}C_5Me_5)K(THF)_n]_\infty$ (m = 0 or 1; n = 1 or 2; ER = $OC_6H_2{}^tBu_2$-2,6-Me-4 (**1a**), $OC_6H_3{}^iPr_2$-2,6 (**1b**), $SC_6H_2{}^iPr_3$-2,4,6 (**1c**), $NHC_6H_2{}^tBu_3$-2,4,6 (**1d**), or $N(SiMe_3)_2$ (**1e**)), in which the “$(C_5Me_5)K(THF)_n$” unit acts as a *neutral* coordination ligand bonding to the Sm(II) center with the “C_5Me_5” part. The similar reaction of $(C_5Me_5)_2Yb(THF)_2$ with 1 equiv of $KN(SiMe_3)_2$ yielded the corresponding Yb(II) complex $[(C_5Me_5)Yb(N(SiMe_3)_2)(\mu\text{-}C_5Me_5)K(THF)_2]_\infty$ (**1f**) in 90% yield. These complexes all adopt a similar polymeric structure via “intermolecular” interactions between the K atom and a C_5Me_5 ligand. The analogous reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of KPHAr afforded $[(C_5Me_5)Sm(THF)(\mu\text{-}PHAr)K(C_5Me_5)(THF)]_\infty$ (**1g**, Ar = $C_6H_2{}^tBu_3$-2,4,6), in which the “C_5Me_5K” unit is bonded to the phosphide site with its K atom. The reaction of the silylene-linked bis(tetramethylcyclopentadienyl) samarium(II) complex $Me_2Si(C_5Me_4)_2Sm(THF)_2$ with 1 equiv of KOAr in THF yielded $[Me_2Si(C_5Me_4)(\mu\text{-}C_5Me_4)K(THF)_nSm(OAr)]_\infty$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4 (**1h**, n = 2) or $C_6H_3{}^tBu_2$-2,6 (**1i**, n = 1)), which can be viewed as a C_5Me_4/OAr-ligated Sm(II) species coordinated by the silylene-linked, neutral “C_5Me_4K” ligand. The use of $NaN(SiMe_3)_2$ in place of $KN(SiMe_3)_2$ in the reactions with $(C_5Me_5)_2Ln(THF)_2$ afforded the “$C_5Me_5Na(THF)_3$”-coordinated, “monomeric” Ln(II) complexes $(C_5Me_5)Ln(N(SiMe_3)_2)(\mu\text{-}C_5Me_5)Na(THF)_3$ (Ln = Sm (**1j**) or Yb (**1k**)). Reactions of the polymeric complexes **1a**,**e** with 2 equiv of HMPA (per Sm) in THF yielded the corresponding HMPA-coordinated, monomeric Sm(II) complexes $(C_5Me_5)Sm(ER)(HMPA)_2$ (ER = $OC_6H_2{}^tBu_2$-2,6-Me-4 (**2a**), $N(SiMe_3)_2$ (**2e**)). This type of C_5Me_5/ER-ligated Sm(II) complexes, particularly **1a**−**c**, showed unique reactivity toward styrene and ethylene, which can not only polymerize styrene and ethylene but also copolymerize them into *block* styrene−ethylene copolymers under the presence of both monomers. The less reducing Yb(II) complex **1f** or the silylene-linked cyclopentadienyl Sm(II) complex **1h** did not show an activity for the polymerization of ethylene under the same conditions, suggesting that the polymerization reaction in the present systems is initiated by dissociation of the neutral “C_5Me_5M” ligand (M = K or Na) from the Sm(II) center, followed one-electron transfer from the resultant C_5Me_5/ER-ligated Sm(II) species to an incoming monomer. As a leaving group, “C_5Me_5K” seemed more suitable than “C_5Me_5Na”. Among the ER ligands, the thiolate ligand $SC_6H_2{}^iPr_3$-2,4,6 (**1c**) showed the highest selectivity for the block copolymerization of styrene and ethylene, while the aryloxide $OC_6H_2{}^tBu_2$-2,6-Me-4 (**1a**) and the silylamide $N(SiMe_3)_2$ (**1e**) gave the highest activity for the polymerization of ethylene and that of styrene, respectively. Possible mechanisms for the polymerization and copolymerization reactions are proposed.

Introduction

Changing the ligand environment of a metal complex to modify its properties is an important strategy for the development of more efficient or selective catalysts. In the past two decades, extensive studies have been carried out on lanthanide complexes bearing two substituted or unsubstituted cyclopentadienyl ligands, and a variety of such lanthanide metallocene complexes have been synthesized and structurally characterized.[1,2] Particularly, divalent samarium metallocene complexes of types **A**[3] and **B**[4] (Figure 1) and trivalent lanthanide metallocene alkyl or hydride complexes of types **C**[5] and **D**[6] have received much interest as homogeneous catalysts or precatalysts for various useful transformations such as hydrogenation,[7] hydrosilylation,[8] and cyclization[9] of olefins as well as polymerization and copolymerization of ethylene,[4,5a,6a,10] butadiene,[11] acrylates,[2b,d,e,12] and lactones.[13] Some of the lanthanide catalytic

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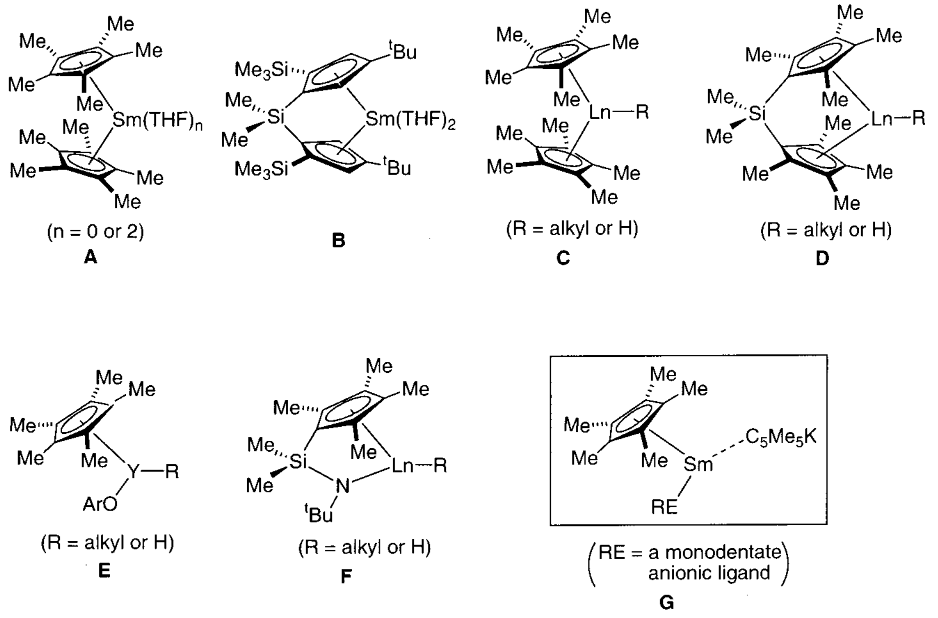

Figure 1. Some representative lanthanide metallocene complexes.

systems display advantages over analogous d-block transition metal-based catalysts such as extremely high activity and stereoselectivity, good living character in polymerization, and no requirement for a cocatalyst or activator. However, the olefin polymerization efficiency of the lanthanide metallocene catalysts has been largely limited to sterically unhindered monomers because of the high degree of steric saturation required to stabilize the large and highly reactive metal centers.[14] Polymerization of styrene by the lanthanide metallocene complexes has proved to be more difficult.[10c,15,16] The reaction of $(C_5Me_5)_2Sm$ with an excess of styrene in toluene yielded a stable bimetallic complex which was inert toward styrene.[15a] Polymerization of ethylene by $(C_5Me_5)_2SmH$ in the presence of styrene incorporated, at maximum, no more than two molecules of styrene per polyethylene chain while successive insertion of styrene was not observed,[10c] owing to the steric hindrance of the two bulky C_5Me_5 ligands. Linking the cyclopentadienyl rings with a silylene group provided a more open ligand sphere (type **D**)[6a] and enabled random incorporation of more styrene into ethylene oligomers,[17] but the activity as well as the molecular weight of the resultant copolymers was low.

Complexes supported by mixed C_5Me_5/ER ligands (ER = a monodentate anionic ligand) (types **E**[18] and **F**[19]) are anticipated to offer a further more open ligand sphere and thus to show

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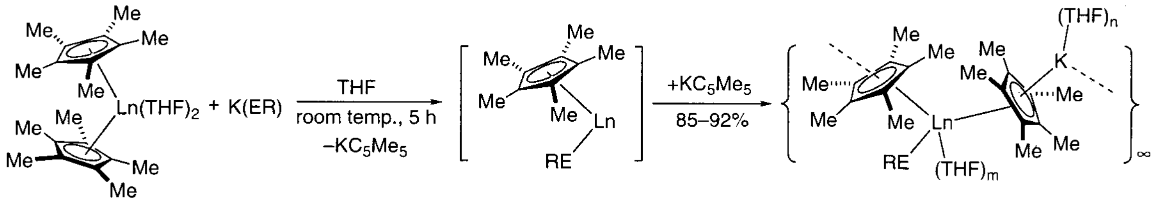
Scheme 1. Synthesis of the C_5Me_5/ER-Ligated Lanthanide(II) Complexes with the Neutral "C_5Me_5K" Ligand



1a: Ln = Sm; ER = $OC_6H_2{}^tBu_2$-2,6-Me-4; m = 0; n = 2
1b: Ln = Sm; ER = $OC_6H_3{}^iPr_2$-2,6; m = 1; n = 2
1b′: Ln = Sm; ER = $OC_6H_3{}^iPr_2$-2,6; m = 0; n = 1
1c: Ln = Sm; ER = $SC_6H_2{}^iPr_3$-2,4,6; m = 1; n = 1
1c′: Ln = Sm; ER = $SC_6H_2{}^iPr_3$-2,4,6; m = 0; n = 1
1d: Ln = Sm; ER = $NHC_6H_2{}^tBu_3$-2,4,6; m = 0; n = 2
1e: Ln = Sm; ER = $N(SiMe_3)_2$; m = 0; n = 2
1f: Ln = Yb; ER = $N(SiMe_3)_2$; m = 0; n = 2

higher activity toward sterically demanding monomers. However, only a few of this type of half-sandwich lanthanide complexes have been synthesized and have had their reactivity studied. One such a complex, $[Me_2Si(C_5Me_4)(N{}^tBu)Y(\mu\text{-}C_6H_{13})(THF)_x]_2$ ($x < 1$), has been recently reported to initiate styrene polymerization to give atactic polystyrenes with narrow molecular weight distributions, but its activity remained low because of the presence of the strongly coordinating THF ligand which obstructs the access of a monomer to the metal center.[19f] Divalent lanthanide complexes with mixed C_5Me_5/ER ligands are more rare, owing to easy ligand redistribution to yield the corresponding homoleptic compounds.[20] It is apparent that to create a C_5Me_5/ER-supported, highly reactive lanthanide system, the use of an additional, easily dissociable stabilizing ligand is desired.

During our previous studies on lanthanide(II) aryloxide complexes,[20,21] we serendipitously found that the "C_5Me_5K" unit could act as a good neutral coordination ligand to stabilize Sm(II) complexes with mixed C_5Me_5/OAr ligands (Ar = $C_6H_2{}^tBu_2$-2,6-X-4; X = H, Me, or ^{t}Bu) (type **G**, ER = OAr).[20] This type of complexes showed high activity not only for polymerization of styrene and ethylene but also for copolymerization of these two monomers, possibly as a result of dissociation of the "C_5Me_5K" ligand from the C_5Me_5/OAr-ligated Sm(II) center.[22] To see if this unusual "C_5Me_5K" ligation could be generally utilized to stabilize analogous lanthanide(II) complexes with other monodentate anionic ligands and to probe the ligand effects on the reactivity of the mixed-ligand-supported Ln(II) species, we have examined various monodentate anionic ligands including aryloxides, thiolates, amides, and phosphides. In this paper, we present a full account of the synthesis, structural features, and styrene/ethylene polymerization and copolymerization reactions of a series of C_5Me_5/ER-supported lanthanide(II) complexes with the neutral "C_5Me_5M" ligand (ER = $OC_6H_2{}^tBu_2$-2,6-Me-4, $OC_6H_3{}^iPr_2$-2,6, $SC_6H_2{}^iPr_3$-2,4,6, $NHC_6H_2{}^tBu_3$-2,4,6, $N(SiMe_3)_2$, or $PHC_6H_2{}^tBu_3$-2,4,6; M = K or Na). Insights into the mechanistic aspects of the polymerization/copolymerization reactions are also described. A portion of this work has been communicated previously.[22,23]

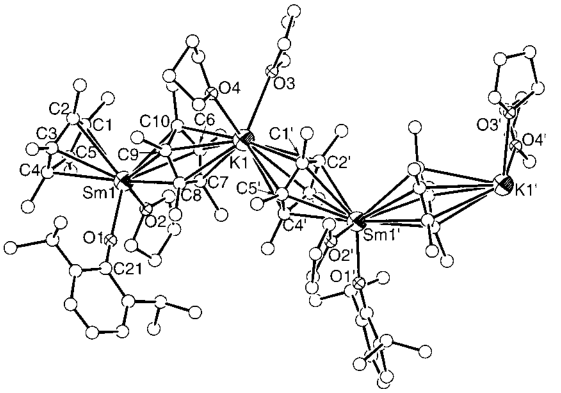


Figure 2. Extended X-ray structure of **1b**.

Results and Discussion

C_5Me_5/ER-Ligated Lanthanide(II) Complexes with the "C_5Me_5K" Ligand. As previously reported,[20] the reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of KOAr in THF provided the most efficient route to the C_5Me_5/OAr-ligated Sm(II) complex with the neutral "$C_5Me_5K(THF)_2$" ligand (**1a**, Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) (Scheme 1). The use of the smaller aryloxide $KOC_6H_3{}^iPr_2$-2,6 in place of the bulkier $KOC_6H_2{}^tBu_2$-2,6-Me-4 in this reaction afforded the $C_5Me_5/OC_6H_3{}^iPr_3$-2,6-supported Sm(II) complex **1b**, which also contains the "$C_5Me_5K(THF)_2$" unit as a stabilizing ligand. The overall structure of **1b** is essentially the same as that of **1a**, except that **1b** bears an extra THF ligand on the Sm(II) center owing to the smaller bulkiness of the $OC_6H_3{}^iPr_2$-2,6 ligand (Figure 2). Upon evacuation, two of the three THF ligands in **1b** were removed to give **1b′**,[24] as shown by elemental analyses. Analogous reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of KSAr yielded the corresponding C_5Me_5/SAr-supported Sm(II) complex **1c** (Ar = $C_6H_2{}^iPr_3$-2,4,6), which bears one THF and the "$C_5Me_5K(THF)$" unit as additional stabilizing ligands (Scheme 1 and Figure 3). One of the two THF ligands in **1c** could also be removed under

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(24) The accurate structures of **1b′**,**c′**,**j′**,**k′** were not determined. Their formulations were based on elemental analyses.

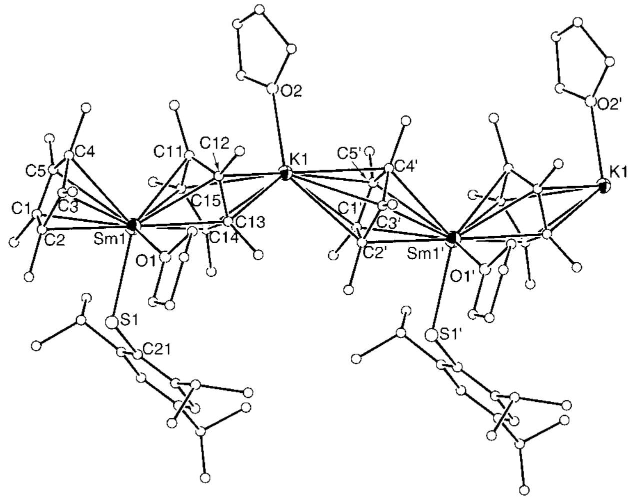
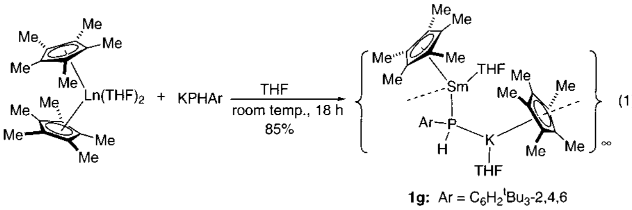


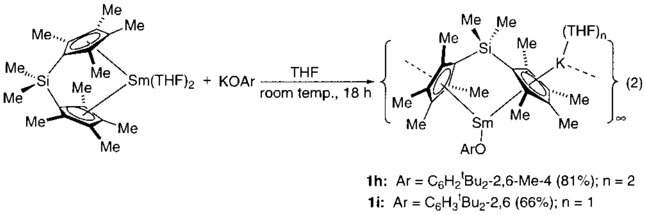
Figure 3. Extended X-ray structure of **1c**.

vacuum to give **1c′**.[24] Similarly, the reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of KNHAr or $KN(SiMe_3)_2$ in THF afforded the C_5Me_5/NHAr-ligated Sm(II) complex **1d** (Ar = $C_6H_2{}^tBu_3$-2,4,6) or the $C_5Me_5/N(SiMe_3)_2$-ligated Sm(II) complex **1e**, respectively. In an analogous way the reaction of $(C_5Me_5)_2Yb(THF)_2$ with 1 equiv of $KN(SiMe_3)_2$ yielded the corresponding Yb(II) complex **1f** (Scheme 1).[25] Complexes **1a**−**e** all adopt a similar polymeric structure via "intermolecular" interactions between the K atom and a C_5Me_5 ligand. Some selected bond lengths and angles are summarized in Table 1. These structural data can be compared with those previously reported for the related Sm(II) compounds, such as $(C_5Me_5)_2Sm(THF)_2$,[3a] $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4),[21b,26a] $[Sm(SAr)(\mu\text{-}SAr)(THF)_3]_2$ (Ar = $C_6H_2{}^iPr_3$-2,4,6),[26b] $Sm(N(SiMe_3)_2)_2(THF)_2$,[26c] and $[(C_5Me_5)Sm(OAr)(\mu\text{-}C_5Me_5)K(THF)_2]_\infty$ (Ar = $C_6H_3{}^tBu_2$-2,6).[20] As far as we are aware, complex **1c** represents the first example of a lanthanide(II) complex bearing mixed cyclopentadienide/thiolate ligands, and **1d**−**f** are the first examples of lanthanide(II) complexes with mixed cyclopentadienide/amide ligands.

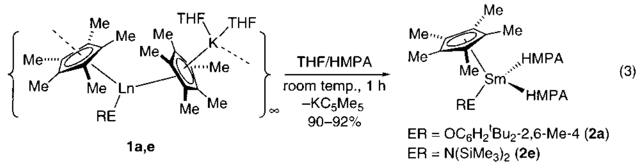
The analogous reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of KPHAr afforded the C_5Me_5/PHAr-ligated Sm(II) complex **1g** (Ar = $C_6H_2{}^tBu_3$-2,4,6) (eq 1).[27] In contrast with the aryloxide, thiolate, and amide complexes **1a**−**f**, in which the "C_5Me_5K" unit is bonded to the Ln(II) center with the C_5Me_5 part, the "C_5Me_5K" unit in **1g** is bonded to the phosphide site with its K atom (Figure 4),[28] which is probably due to the stronger electron-donating ability of the phosphide ligand. The Sm−C_5Me_5 bond distances in **1g** (av 2.862(9) and 2.923(8) Å) are comparable with those found in **1a**−**e** (2.83−2.98 Å) (Table 1), while the Sm−P bond in **1g** (3.234(2) Å) is significantly longer than those found in samarium(II) bis(phosphide) complexes such as $Sm(PAr_2)_2(THF)_4$ (3.139(3) Å for Ar = Ph[29a] and 3.034(2) Å for Ar = $C_6H_2Me_3$-2,4,6)[29b] and $Sm(\eta^1\text{-}PC_{12}H_8)(THF)_4$ (3.1908(6) Å),[29c] probably owing to the interaction between the phosphide ligand and the K atom in **1g**. The K−P bond distance in **1g** (3.350(3) Å) is comparable with those found in the polymeric potassium phosphide compound $[KPH(C_6H_2{}^tBu_3\text{-}2,4,6)]_\infty$ (3.181(2)−3.357(2) Å).[30]



The "C_5Me_5K" ligation could also be applied to samarium(II) complexes with linked-cyclopentadienyl ligands. The reaction of $Me_2Si(C_5Me_4)_2Sm(THF)_2$ with 1 equiv of KOAr (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4 or $C_6H_3{}^tBu_2$-2,6) in THF yielded **1h** or **1i**, respectively (eq 2). Complexes **1h**,**i** can be viewed as a C_5Me_4/OAr-ligated Sm(II) species stabilized by the silylene-linked "C_5Me_4K" unit. Similar to the unlinked analogue **1a**, complexes **1h**,**i** also form a polymeric structure via the K$\cdots$Cp′ interactions (Figure 5). It is also noteworthy that the OAr ligands in **1h** (∠Sm−O−Ar: 110.3(3)°, Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) and **1i** (∠Sm−O−Ar: 108(1)°, Ar = $C_6H_3{}^tBu_2$-2,6), as that in **1a** (∠Sm−O−Ar: 126.7(5)°, Ar = $C_6H_2{}^tBu_2$-2,6-Me-4),[20] adopt a bent structure, which is in contrast with the "linear" ones in the analogous samarium(II) aryloxide complexes $[(C_5Me_5)Sm(OAr)(\mu\text{-}C_5Me_5)K(THF)_2]_\infty$ (∠Sm−O−Ar: 175(1)°, Ar = $C_6H_3{}^tBu_2$-2,6)[20] and **1b** (∠Sm−O−Ar: 165(1)°, Ar = $C_6H_3{}^iPr_2$-2,6), showing that the aryloxide ligands are of excellent flexibility.



Similar to **1a** which yielded **2a** upon reaction with hexamethylphosphoric triamide (HMPA),[20] the reaction of the polymeric **1e** with 2 equiv of HMPA (per Sm) in THF afforded the corresponding HMPA-coordinated, monomeric Sm(II) complex **2e** (eq 3, Figure 6), indicating that the "C_5Me_5K" ligand in this type of complexes could be replaced by an appropriate coordinative ligand.



$C_5Me_5/N(SiMe_3)_2$-Ligated Lanthanide(II) Complexes with the "C_5Me_5Na" Ligand. "C_5Me_5Na" could also act as a

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(25) The cell parameters for **1f** are almost the same as those for **1e** (see Table 5), although **1f** could not be fully refined owing to poor quality of the crystal: monoclinic, $a = 34.914(7)$ Å, $b = 10.155(6)$ Å, $c = 11.661(3)$ Å, $\beta = 103.72(2)°$, $V = 4017(3)$ Å^3.

(26) (a) Qi, G.-Z.; Shen, Q.; Lin, Y.-H. *Acta Crystallogr., Sect. C* **1994**, *50*, 1456. (b) Mashima, K.; Nakayama, Y.; Fukumoto, H.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2523. (c) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575.

(27) Although **1g** in the polymeric solid state could also be viewed as a "KPHAr" adduct of the samarocene species "$(C_5Me_5)_2Sm(THF)$" via Sm$\cdots$P bonding, its behavior in polymerization reactions (different from that of "$(C_5Me_5)_2Sm$", see Tables 2 and 3) suggests that it should best be considered as a "$(C_5Me_5)Sm(PHAr)$" species connected with a "C_5Me_5K" unit through the P$\cdots$K interaction.

(28) An interaction between the C(1) atom of the phosphide unit and the K atom in **1g** was also observed (C(1)−K(1): 3.124(6) Å).

(29) (a) Rabe, G.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1995**, *34*, 4521. (b) Nief, F.; Ricard, L. *J. Organomet. Chem.* **1997**, *529*, 347. (c) Nief, F.; Ricard, L. *J. Organomet. Chem.* **1994**, *464*, 149.

(30) Rabe, G.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1997**, *36*, 1990.

Table 1. Summary of Selected Bond Lengths (Å) and Angles (deg) for Cp*/ER-Ligated Lanthanide(II) Complexes of the Types of "(Cp*^{1})Ln(ER)(Cp*^{2}M)" (**1a**−**k**) and Cp*^{1}Ln(ER)(HMPA)$_2$ (**2a**,**e**) (cf. Scheme 1, eqs 1−4, and Figures 2−7)

	1a[a]	**1b**	**1c**	**1d**	**1e**	**1g**	**1h**	**1i**	**1j**	**1k**	**2a**[b]	**2e**
Ln =	Sm	Sm	Sm	Sm	Sm	Sm	Sm	Sm	Sm	Yb	Sm	Sm
M =	K	K	K	K	K	K	K	K	Na	Na		
ER =	OAr(^{t}Bu)	OAr(^{i}Pr)	SAr(^{i}Pr)	NHAr(^{t}Bu)	N(SiMe$_3$)$_2$	PHAr(^{t}Bu)	OAr(^{t}Bu)	OAr(^{t}Bu)′	N(SiMe$_3$)$_2$	N(SiMe$_3$)$_2$	OAr(^{t}Bu)	N(SiMe$_3$)$_2$
Ln-Cp*^{1} (av)	2.876(8)	2.92(2)	2.902(10)	2.87(3)	2.97(3)	2.862(9)	2.84(2)	2.893(5)	2.86(3)	2.77(3)	2.860(7)	2.86(2)
Ln-Cp*^{2} (av.	2.911(7)	2.95(2)	2.891(9)	2.90(3)	2.83(3)	2.923(8)	2.87(2)	2.852(4)	2.92(3)	2.83(3)		
Ln-ER	2.330(6)	2.37(1)	2.936(3)	2.48(2)	2.49(1)	3.234(2)	2.37(1)	2.375(3)	2.50(2)	2.41(2)	2.345(4)	2.55(1)
M-Cp*^{2} (av)	3.142(7)	3.14(2)	3.059(9)	3.11(3)	3.08(2)	3.006(8)	3.19(2)	3.134(4)	2.73(3)	2.74(3)		
M-Cp*$^{1'}$ (av)	3.157(8)	3.21(2)	3.024(10)	3.14(3)	3.24(2)		3.20(2)	3.194(5)				
M-ER						3.350(3)						
∠Cp*^{1}−Ln−Cp*^{2}	137.6(3)	131(1)	134.1(3)	138(1)	135(1)	133.7(7)	118(1)	117.8(2)	135(1)	134(1)		
∠Cp*^{1}−Ln−ER	101.9(3)	108(1)	103.1(3)	102(1)	109(1)	102.0(5)	106(1)	135.1(2)	114(1)	115(1)	116.1(2)	118.7(8)
∠Cp*^{2}−Ln−ER	120.4(2)	114(1)	113.9(3)	118(1)	116(1)	118.4(5)	136(1)	107.1(2)	111(1)	112(1)		
∠Ln−E−R	126.7(5)	165(1)	124.9(3)	127(2)	120(1) 114(1)	123.9(2)	108(1)	110.3(3)	119(1) 112(1)	120(1) 113(1)	163.6(4)	119.9(8) 115.7(7)

[a] Reference 20. [b] References 20, 21b.

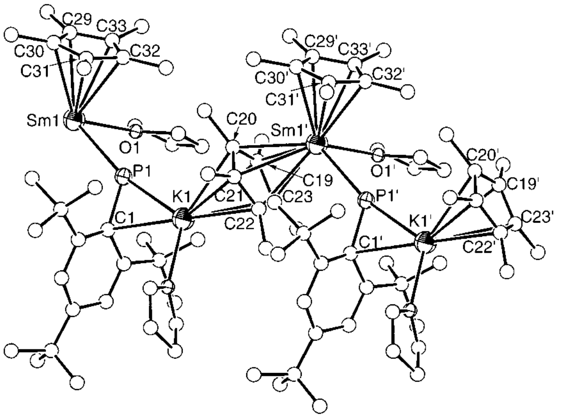


Figure 4. Extended X-ray structure of **1g**.

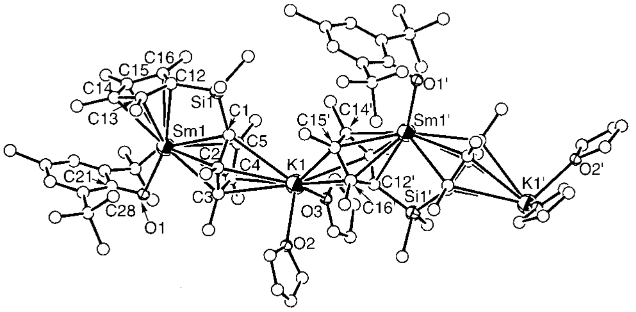


Figure 5. Extended X-ray structure of **1h**.

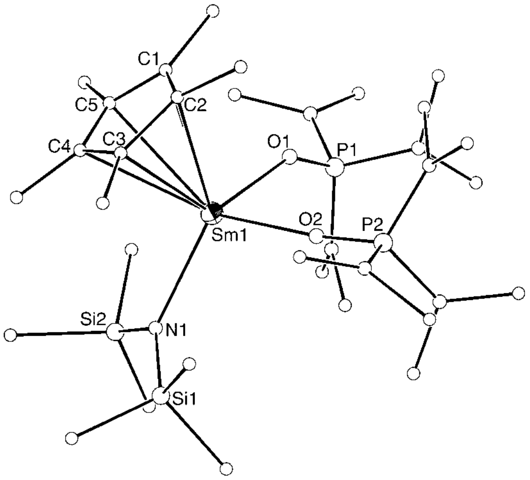


Figure 6. X-ray structure of **2e**.

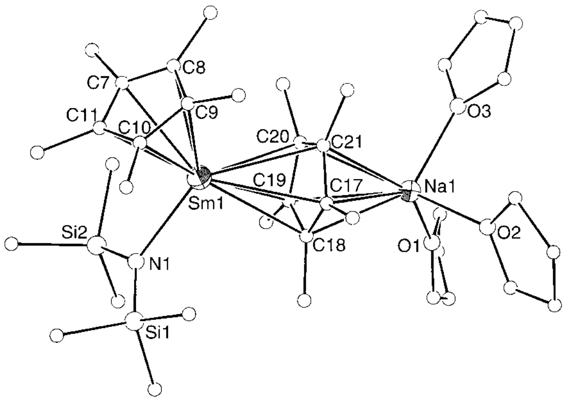
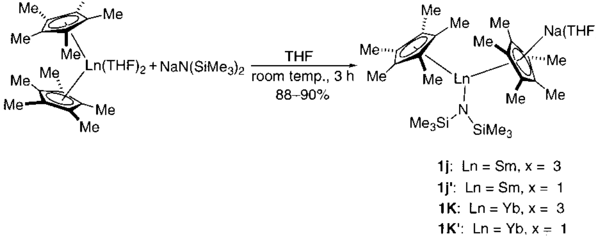


Figure 7. X-ray structure of **1j**.

stabilizing ligand for the C_5Me_5/N(SiMe$_3$)$_2$-ligated lanthanide(II) complexes. The use of NaN(SiMe$_3$)$_2$ in place of KN(SiMe$_3$)$_2$ in the reactions with $(C_5Me_5)_2$Ln(THF)$_2$ afforded the "C_5Me_5Na(THF)$_3$"-coordinated Ln(II) complexes **1j** (Ln = Sm) and **1k** (Ln = Yb), respectively (eq 4). In contrast with the "C_5Me_5K"-coordinated complexes **1a**−**f**,**h**,**i**, which adopt a polymeric structure through intermolecular K···C_5Me_5 interactions, the "C_5Me_5Na"-coordinated complexes **1j**,**k** adopt a "monomeric" form, owing to coordination of more THF ligands to the Na atom (eq 4 and Figure 7), showing that the Na atom in **1j**,**k** prefers the coordination of THF rather than intermolecular interaction with C_5Me_5. These results are in agreement with the previous observation that C_5Me_5Na tends to form a monomeric structure: C_5Me_5Na(Py)$_3$, while C_5Me_5K prefers a polymeric form: [C_5Me_5K(Py)$_2$]$_\infty$.[31] Upon evacuation, two of the three THF ligands on the Na atom in **1j**,**k** could be removed to give **1j′**,**k′**, respectively.[24]



(4)

Polymerization of Ethylene. To assess the ability of this new class of lanthanide(II) complexes as a catalytic system for

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(31) Rabe, G.; Roesky, H. W.; Stalke, D.; Pauer F.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *403*, 11.

Table 2. Polymerization of Ethylene by Lanthanide(II) Complexes[a]

run	cat	time	yield (g)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]
1	$(C_5Me_5)_2Sm(THF)$[c]	1 h[c]	0.42[c]	<2.50[d]	2.28[d]
2	$Sm(OAr)_2(THF)_3$	1 h	0	–	–
3	**1a**	10 min	1.62	43.4	2.22
4	**1b′**	10 min	1.00	33.0	2.49
5	**1c′**	10 min	0.99	58.0	1.79
6	**1d**	10 min	0.48	49.7	2.90
7	**1e**	30 min	0.55	309.9	2.83
8	**1f**	1 h	0	–	–
9	**1g**	10 min	1.36	81.8	1.64
10	**1h**	1 h	0	–	–
11	**1j′**	30 min	1.15	86.5	2.30
12	**2a**	1 h	0	–	–
13	$[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$	1 h	0	–	–
14	$[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$[e]	10 min	0.27	32.6	2.37

[a] Reaction conditions: cat., 0.05 mmol; ethylene, 1 atm; toluene, 15 mL, 25 °C (water bath). [b] Determined at 135 °C against polystyrene standard by GPC. [c] 0.083 mmol of the catalyst was used. These data were taken from ref 10d. [d] See ref 4. [e] THF (5 equiv per Sm) was also added.

polymerization reactions, their reactivity toward ethylene was first examined. As shown in Table 2, the C_5Me_5/ER-ligated Sm(II) complexes **1a**,**b′**,**c′**,**d**,**e**,**g**,**j′**, which are stabilized by the "C_5Me_5M" ligand (M = K or Na), all showed high activity for the polymerization of ethylene at 25 °C under 1 atm, yielding linear polyethylene with M_n up to 3×10^6 (based on polystyrene standard). Compared to the samarocene(II) complexes $(C_5Me_5)_2Sm(THF)_n$ ($n = 0-2$) (run 1, Table 2),[4,10a,d,e] these mixed-ligand-supported complexes are more active and afford polymers with much higher molecular weight. Moreover, the reactivity of this type of complexes appeared to be ER-ligand dependent. The 4-Me-2,6-$^tBu_2C_6H_2O$-ligated complex **1a** showed the highest activity (run 3, Table 2), while the $(Me_3Si)_2N$-ligated complex **1e** gave the highest molecular weight of polyethylene (run 7, Table 2).

In contrast with the highly reactive **1a**, the analogous complex **1h**, which bears the silylene-linked cyclopentadienyl ligands, was inactive for the polymerization of ethylene (run 10, Table 2). This is probably due to the silylene bridge in **1h**, which could prevent complete dissociation of the "C_5Me_4K" unit from the Sm(II) center and thus hamper the access of an ethylene monomer to the metal center. In consistence with this result, complex **2a** was also inert toward ethylene because of the strongly coordinating HMPA ligands (run 12, Table 2).[32] Similarly, the dimeric complex $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) did not show an activity for ethylene polymerization in pure toluene probably owing to the strong and bulky μ-OAr-bridges (run 13, Table 2).[20] Upon addition of a small amount of THF, however, this dimeric complex became active, yielding polyethylene with $M_n = 3.26 \times 10^5$ and $M_w/M_n = 2.37$ (run 14, Table 2), possibly as a result of the formation of a THF-coordinated, monomeric Sm(II) species such as "$(C_5Me_5)Sm(OAr)(THF)_x$". All of these results strongly suggest that dissociation of the neutral "C_5Me_5M" ligand to generate a sterically unsaturated, C_5Me_5/ER-ligated Sm(II) species must be an essential step in the polymerization reactions promoted by complexes **1a**,**b′**,**c′**,**d**,**e**,**g**,**j′**. On the other hand, the analogous, less reducing Yb(II) complex **1f** showed no activity for the polymerization of ethylene under the same conditions (run 6, Table 2), suggesting that one-electron transfer from the Ln(II) center to an ethylene monomer plays a critically important role in the initiation of the polymerization reactions.[2e,4,10c]

Table 3. Polymerization of Styrene by Lanthanide(II) Complexes[a]

run	cat	time	yield (%)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]
1	$(C_5Me_5)_2Sm(THF)_2$	24 h	0	–	–
2	$Sm(OAr)_2(THF)_3$	24 h	0	–	–
3	$Sm(N(SiMe_3)_2)_2(THF)_2$	24 h	0	–	–
4	**1a**	30 min	89	34.7	1.73
5	**1a**	40 min	100	34.0	1.76
6	**1b′**	30 min	100	24.5	1.93
7	**1c′**	2.5 h	79	17.1	1.45
8	**1d**	20 min	100	14.4	2.16
9	**1e**	10 min	100	8.2	2.45
10	**1f**	24 h	0	–	–
11	**1g**	24 h	trace	–	–
12	**1g**	3.5 h[c]	36	2.7	1.51
13	**1h**	30 min	59	32.5	1.59
14	**1h**	2 h	100	32.2	1.97
15	**1j′**	2 h	23	8.2	2.28
16	**2a**	24 h	0	–	–
17	$[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$	24 h	0	–	–

[a] Conditions: cat., 0.05 mmol; styrene, 4 mL (35 mmol); toluene, 10 mL; 25 °C (water bath). [b] Determined at 135 °C against polystyrene standard by GPC. [c] 50 °C.

Polymerization of Styrene. The C_5Me_5/ER-ligated Sm(II) complexes **1a**,**b′**,**c′**,**d**,**e** showed high activity also for the polymerization of styrene at room temperature (runs 4−9, Table 3), in striking contrast with the homoleptic type Sm(II) complexes $(C_5Me_5)_2Sm(THF)_n$ (n = 0 or 2),[10c,15] $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4), and $Sm(N(SiMe_3)_2)_2(THF)_2$, which were inactive for styrene polymerization under the same conditions. In most cases, a quantitative conversion was achieved in less than 1 h, affording atactic polystyrenes with M_n ranging from 8.2×10^4 to 3.5×10^5 and $M_w/M_n = 1.45-2.45$. The ER-ligand dependence of the activity was also observed in this case. Complex **1b′**, which bears the less sterically demanding 2,6-$^iPr_2C_6H_3O$ ligand, was more active than the 4-Me-2,6-$^tBu_2C_6H_2O$-ligated complex **1a** (run 4 vs run 6, Table 3). The more electron-donating amide complexes **1d**,**e** showed higher activity than the aryloxide and thiolate complexes **1a**,**b′**,**c′** (runs 4−9, Table 3).

Compared to ethylene polymerization, the polymerization of styrene appeared to be more susceptible to the changes in the ligand environment of a complex. In contrast with the active aryloxide, thiolate, and amide complexes **1a**,**b′**,**c′**,**d**,**e**, the phosphide complex **1g** was almost inactive for styrene polymerization at room temperature (run 11, Table 3), although it showed high activity for ethylene polymerization. The lower activity of **1g** than those of **1a**,**b′**,**c′**,**d**,**e** toward styrene could probably be due to the strong interaction between the phosphide ligand and the "C_5Me_5K" unit in **1g** (cf. eq 1 and Figure 4).[28] In the case of **1g**, dissociation of the "C_5Me_5K" unit from the Sm(II) center would lead to formation of a species such as "$(C_5Me_5)Sm(\mu\text{-}PHAr)K(C_5Me_5)$", which is apparently more crowded than the analogous species "$(C_5Me_5)Sm(ER)$" generated in the case of **1a**,**b′**,**c′**,**d**,**e**, and could therefore retard the access of the sterically demanding styrene monomer to the central samarium atom. The "C_5Me_5M" ligand also showed much influence on the polymerization of styrene. The "C_5Me_5Na"-coordinated complex **1j′** (run 13, Table 3) showed a much lower activity than the analogous "C_5Me_5K"-coordinated complex **1e** (run 9, Table 3). This could be due to the difference in structural preference between C_5Me_5K and C_5Me_5Na.[31]

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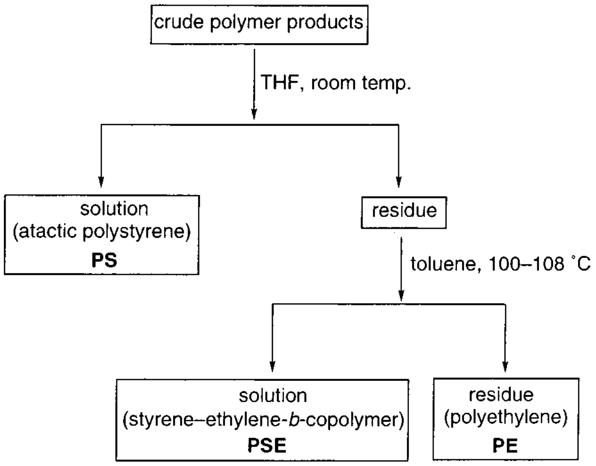
(32) It is well-known that HMPA usually forms a very strong coordination bond with lanthanide ions. For examples, see: (a) Hou, Z.; Zhang, Y.; Wakatsuki, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 149. (b) Hou, Z.; Wakatsuki, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1205. (c) Hou, Z.; Kobayashi, K.; Yamazaki, H. *Chem. Lett.* **1991**, 265.

Scheme 2. A Flowchart for Separation of Block Styrene−Ethylene Copolymers from Atactic Homopolystyrenes and Homopolyethylenes



As in the case of ethylene, the Yb(II) complex **1f** again did not show an activity for styrene polymerization. Neither did the HMPA-coordinated complex **2a** or the dimeric complex $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) in toluene or toluene/THF. Unexpectedly, the silylene-linked cyclopentadienyl complex **1h** initiated styrene polymerization at room temperature (runs 13,14, Table 3), although its activity was lower than that of the unlinked analogue **1a**.[33]

Block Copolymerization of Styrene and Ethylene. Since complexes **1a**,**b′**,**c′**,**d**,**e**,**g**,**j′** were active for the polymerization of both ethylene and styrene, copolymerization of the two monomers by these complexes was investigated. The copolymerization reactions were carried out in toluene at 25 °C under an atmosphere of ethylene with varying amounts of styrene monomer. The crude polymer products, precipitated by addition of MeOH, were first repeatedly washed with THF at room temperature to remove homopolystyrene, and then extracted with toluene at 100−108 °C to collect the copolymers (Scheme 2). Since the homopolystyrenes formed in the present reactions are atactic and very soluble in THF at room temperature while the homopolyethylenes are insoluble in refluxing toluene (110 °C), the styrene−ethylene copolymers, which are soluble in hot toluene, can be easily separated from the homopolymers by the above extractions. Some representative results are summarized in Table 4 and Figures 8 and 9.

The aryloxide and thiolate complexes **1a**,**b′**,**c′** showed good activity and selectivity for the copolymerization reactions under the presence of both monomers, affording styrene−ethylene copolymers with M_n around 2×10^5 and $M_w/M_n < 2$ in most cases (runs 1−8,10−13, Table 4). Besides the major copolymer products, homopolystyrene was also obtained as a byproduct while homopolyethylene was almost not observed, except when a very small amount of styrene monomer was fed, which led to formation of homopolyethylene as a dominant product (cf. run 9, Table 4). Among these complexes, the thiolate complex **1c′** showed the highest selectivity for the copolymerization reaction, which could reach up to as high as 96% (run 10, Table 4). As the feeding amount of styrene monomer was raised under 1 atm of ethylene, the selectivity for styrene−ethylene copolymers generally decreased for all these three complexes owing to increased formation of homopolystyrene (Table 4 and Figure 8). The polystyrene content in the copolymers, however, increased almost linearly as the feeding amount of styrene was raised (Figure 9). In each styrene feeding, the styrene incorporation increased in the order of **1b′** > **1a** > **1c′** (Figure 9), reflecting the activity trend of these complexes shown for styrene homopolymerization reactions (see also Table 3).

In contrast with the aryloxide and thiolate complexes **1a**,**b′**,**c′**, the amide complexes **1d**,**e**, which had shown much higher activity for styrene polymerization (cf. Table 3), preferred the homopolymerization of styrene, yielding homopolystyrene as the only or a major product under the presence of both monomers (runs 14 and 15, Table 4). On the other hand, the phosphide complex **1g** and the "C_5Me_5Na"-coordinated complex **1j′**, which had shown much lower activity for styrene polymerization (cf. Table 3), afforded only homopolyethylene under the similar conditions (runs 16 and 17, Table 4). These results again show that the present copolymerization reactions are closely related to the activity of a complex shown for the homopolymerization reactions and are strongly influenced by the ligand environment around the central metal atom.

^{13}C NMR analyses have revealed that the copolymer products obtained in the present reactions are *block* styrene−ethylene copolymers rather than random or alternating ones (for an example see Figure 10). To further confirm that the copolymer products do not contain homopolymers, an artificial mixture of homopolyethylene ($M_n = 5.7 \times 10^4$, $M_w/M_n = 1.11$), homopolystyrene ($M_n = 24.5 \times 10^4$, $M_w/M_n = 1.93$, obtained in run 6, Table 3), and a copolymer ($M_n = 15.1 \times 10^4$, $M_w/M_n = 1.92$, PS content = 68 mol %, obtained in run 7, Table 4) was extracted in the same way as the crude product was done (cf. Scheme 2). Each of these three polymers was thus recovered quantitatively, which suggests that this copolymer does not contain homopolystyrenes with $M_n \leq 24.5 \times 10^4$ or homopolyethylenes with $M_n \geq 5.7 \times 10^4$.[34] Since the GPC curve of the copolymer showed a unimodal narrow molecular weight distribution and that of its mixture with the homopolystyrene ($M_n = 24.5 \times 10^4$) or the homopolyethylene ($M_n = 5.7 \times 10^4$) was bimodal, the content of homopolystyrenes with $M_n > 24.5 \times 10^4$ or homopolyethylenes with $M_n < 5.7 \times 10^4$ in this copolymer should also be negligible. The TEM (transmission electron microscopy) images of the copolymer products showed good uniform phases, which are in sharp contrast with that of a mixture of the immiscible homopolystyrene and homopolyethylene. Viscoelasticity studies further confirmed that the copolymers are mechanically much stronger and more flexible than the mixtures of homopolystyrenes and homopolyethylenes. All of these results clearly show that the copolymer products obtained in the present reactions are true block styrene−ethylene copolymers rather than mixtures of the homopolymers.

The selective formation of block styrene−ethylene copolymers in the present reactions is in striking contrast with what was observed in the case of the silylene-linked bis(cyclopentadienyl) lanthanide complexes $Me_2Si(C_5Me_4)_2LnCH(SiMe_3)_2$ (Ln = Nd or Sm)[17a] and in group 4 metal-catalyzed styrene−ethylene copolymerization reactions.[35] The latter two systems always yielded random or alternating styrene−ethylene copolymers under the presence of both monomers. As far as we are aware, selective formation of block styrene−ethylene copolymers under the presence of both monomers is unprecedented. These reactions are not only of great fundamental interest, but

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[33] The mechanism of styrene polymerization by **1h** was not clear. It might proceed to some extent through an "anionic" process. However, the polymerization did not take place in a THF solution.

[34] In fact, atactic polystyrenes with $M_n > 24.5 \times 10^4$ are also soluble in THF at room temperature and can therefore be removed by the extraction with THF. The solubility of polyethylene, however, decreases greatly as the molecular weight increases.

Table 4. Block-Copolymerization of Styrene and Ethylene by Samarium(II) Complexes Bearing Mixed C_5Me_5/ER Ligands[a]

			yield (g)						
run	cat.	styrene (mL)	THF-sol (**PS**)[d]	tol-sol (<108 °C) (**PSE**)[d]	tol-Insol (108 °C) (**PE**)[d]	PSE selectivity (wt %)	PS cont (mol %)[b]	M_n ($\times 10^{-4}$)[c]	M_w/M_n[c]
1	**1a**	3	0.65	1.59	trace	71	31	20.3	1.60
2	**1a**	5	1.18	1.62	trace	58	44	20.6	1.69
3	**1a**	7	1.54	2.04	trace	57	61	24.0	1.74
4	**1a**	10	1.81	2.12	trace	54	79	27.6	1.68
5	**1b′**	3	0.46	2.14	trace	82	34	15.9	1.97
6	**1b′**	5	1.29	2.83	trace	69	48	14.6	1.82
7	**1b′**	7	1.37	2.94	trace	68	68	15.1	1.92
8	**1b′**	10	2.40	3.99	trace	62	81	13.1	1.84
9	**1c′**	2	trace	0.29	0.19	–	<2	13.6	2.49
10	**1c′**	3	0.06	1.31	trace	96	13	11.3	2.21
11	**1c′**	5	0.23	2.55	trace	92	37	10.7	2.01
12	**1c′**	7	0.27	2.74	trace	91	43	13.7	1.73
13	**1c′**	10	0.34	2.82	trace	89	60	14.6	1.66
14	**1d**	3	2.36	0.78	trace	25	15	11.3	1.99
15	**1e**	5	4.55	trace	trace	–	–	–	–
16	**1g**	7	trace	trace	0.51	–	–	–	–
17	**1j′**	5	trace	trace	0.17	–	–	–	–

[a] Conditions: cat., 0.05 mmol; ethylene, 1 atm; the total volume of styrene and toluene, 25 mL, 25 °C (water bath), 30 min. [b] Polystyrene content in the copolymers, determined by ^{13}C NMR in *o*-dichlorobenzene/$CDCl_2CDCl_2$ at 125 °C. [c] Determined at 135 °C against polystyrene standard by GPC. [d] **PS** = atactic polystyrene, **PSE** = styrene–ethylene block copolymer, **PE** = polyethylene.

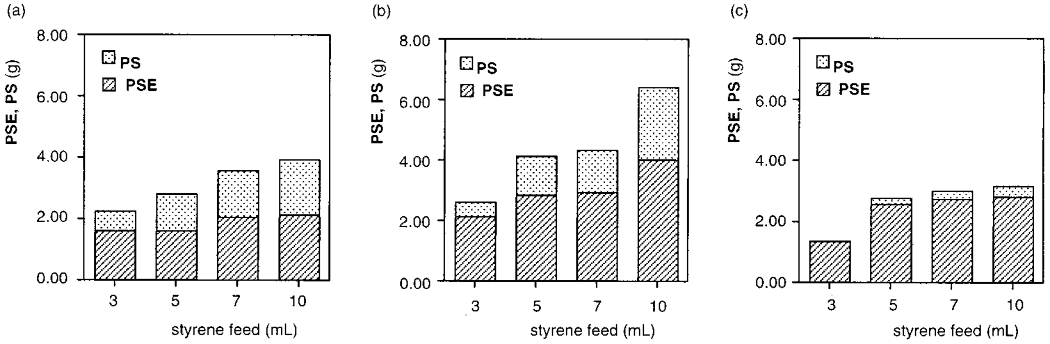

Figure 8. Yields (g) of **PSE** and **PS** vs styrene monomer feed (mL) for styrene–ethylene copolymerization reactions with (a) **1a**, (b) **1b′**, or (c) **1c′** as a precatalyst (see also Table 4).

could also be of practical usefulness as a convenient route to a new class of important polymer materials.[36,37]

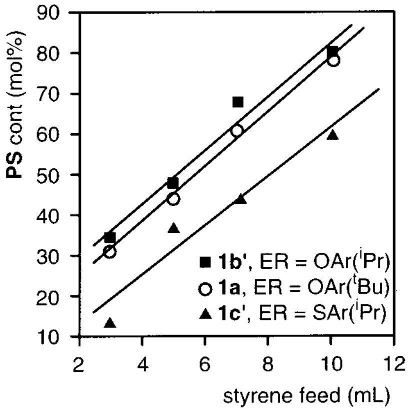

Figure 9. Polystyrene content (mol %) in styrene–ethylene copolymers vs styrene monomer feed (mL) for reactions with **1a**,**b′**,**c′** as precatalysts (see also Table 4).

Polymerization Mechanisms. (i) Homopolymerization Reactions. It is well-known that the polymerization of ethylene by the samarocene(II) complexes $(C_5Me_5)_2Sm(THF)_n$ ($n = 0-2$) is initiated by a one-electron transfer from the Sm(II) center to an ethylene monomer to give a Sm(III) alkyl species.[2e,4,10c] In the present systems, a similar mechanism could also be operative. Since ER-ligand dependence of the polymerization reactions was observed in all cases, a bonding interaction

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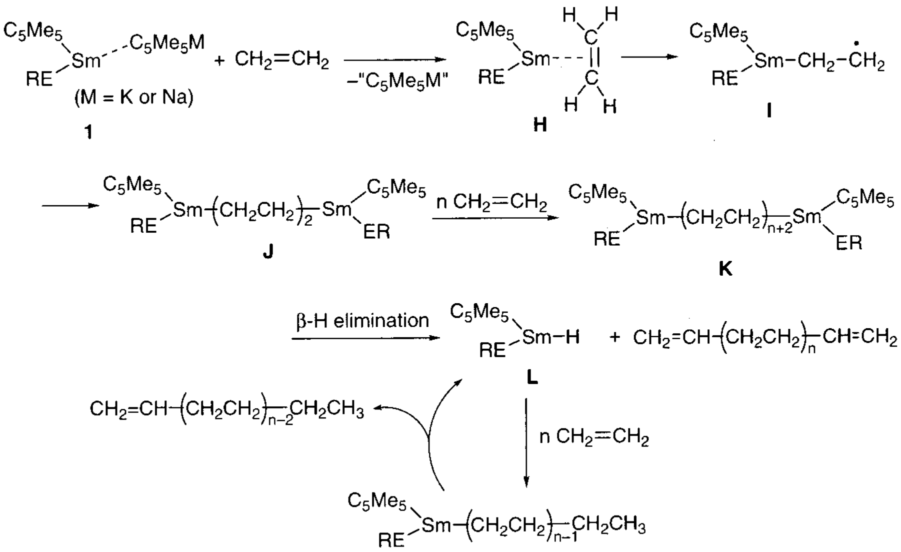
(35) For examples see: (a) Xu, G. *Macromolecules* **1998**, *31*, 2395. (b) Xu, G.; Lin, S. *Macromolecules* **1997**, *30*, 685. (c) Arai, T.; Ohtsu, T.; Suzuki, S. *Macromol. Rapid Commun.* **1998**, *19*, 327. (d) Sernetz, F. G.; Mülhaupt, R.; Fokken, S.; Okuda, J. *Macromolecules* **1997**, *30*, 1562. (e) Sernetz, F. G.; Mülhaupt, R.; Waymouth, R. M. *Macromol. Chem. Phys.* **1996**, *197*, 1071. (f) Oliva, L.; Mazza, S.; Longo, P. *Macromol. Chem. Phys.* **1996**, *197*, 3115. (g) Pellecchia, C.; Pappalarrdo, D.; D'Arco, M.; Zambelli, A. *Macromolecules* **1996**, *29*, 1158. (h) Aaltonen, P.; Seppala, J.; Matilainen, L.; Leskela, M. *Macromolecules* **1994**, *27*, 3136. (i) Miyatake, T.; Mizunuma, K.; Kagugo, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 203. (j) Longo, P.; Grassi, A.; Oliva, L. *Makromol. Chem.* **1990**, *191*, 2387.

(36) Generally, block copolymers have uniquely different chemical, physical, and mechanical properties compared to their random or alternating copolymeric analogues, and particularly show great emulsifying or compatibilizing effect in the blending of the corresponding homopolymers. Since polystyrene and polyethylene are among the most widely used polymer materials, the effective blending of these two immiscible homopolymers could result in various commercial applications. For a recent review on compatibilization of polymer blends, see: Koning, C.; Van Duin, M.; Pagnoulle, C.; Jerome, R. *Prog. Polym. Sci.* **1998**, *23*, 707.

(37) Conventional sequential "living" polymerization methods are not suitable for the synthesis of styrene–ethylene block copolymers, since there is no "living system" which is able to polymerize both styrene and ethylene owing to the different natures of these two monomers. Attempts to obtain a block styrene–ethylene copolymer by sequential copolymerization of styrene with ethylene by group 4 metal-based catalysts produced the corresponding homopolymers as major products. See: (a) Inoue, N.; Jinno, M.; Shiomura, T. JP 0687937, 1994; *Chem. Abstr.* **1994**, *121*, 109890h. (b) Naganuma, A.; Tazaki, T.; Machida, S. JP 04130114, 1992; *Chem. Abstr.* **1993**, *118*, 7536t.

Scheme 3. A Possible Mechanism for Ethylene Polymerization by the C_5Me_5/ER-Ligated Sm(II) Complexes with the Neutral "C_5Me_5M" Ligand



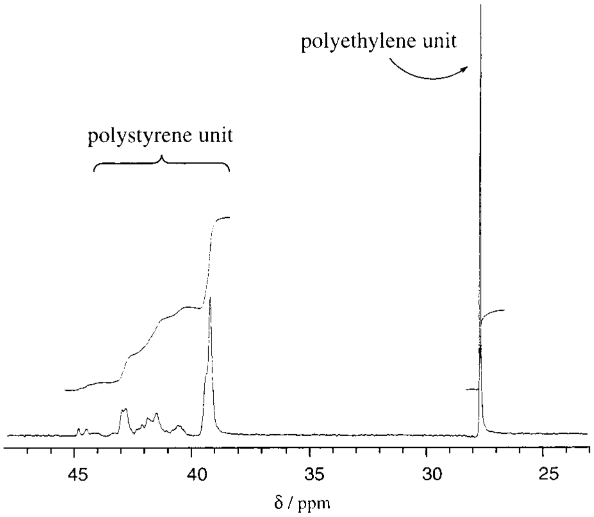


Figure 10. Aliphatic region of the ^{13}C NMR spectrum of a block styrene–ethylene copolymer (run 7, Table 4) in *ortho*-dichlorobenzene/$CDCl_2CDCl_2$ at 125 °C.

between the ER ligand and the Sm atom in a catalytic species must remain during the polymerization reactions. A possible mechanism for the polymerization of ethylene by the present systems is shown in Scheme 3. Dissociation of the "C_5Me_5M" unit from the Sm(II) center in **1** (either dissociative or associative) followed by coordination of an ethylene molecule would yield **H**. Rapid electron transfer from the Sm(II) center to the ethylene ligand in **H** and the subsequent dimerization of the resultant radical species **I** would afford the Sm(III) alkyl species **J**. Successive insertion of ethylene into the Sm-alkyl bond in **J** and the following β-hydrogen elimination from the resulting polymeric compound **K** could release polyethylene and the hydride species **L**. The C_5Me_5/ER-ligated Sm(III) hydride species **L** is probably a true catalytic species in the present systems, which could constitute a catalytic cycle by the subsequent ethylene insertion/β–H elimination reactions (Scheme 3). The polymerization of styrene could take place via an analogous mechanism. The more open ligand sphere provided by the mixed C_5Me_5/ER ligands could explain why the present systems are more active than the metallocene complexes $(C_5Me_5)_2Sm(THF)_n$ ($n = 0-2$).[38]

(ii) Copolymerization Reactions. For complexes active toward both ethylene and styrene, the polymerization of ethylene and that of styrene could start independently in the presence of both monomers. The selective formation of block rather than random styrene–ethylene copolymers in the present systems strongly suggests that the reactivity of the propagation site of polyethylene unit and that of polystyrene unit are critically different from each other, one being able to incorporate both ethylene and styrene, while the other only the identical monomer. To gain more information on the copolymerization reactions, sequential polymerization reactions of styrene with ethylene were carried out by use of **1b′** as a precatalyst. The reaction of 1 mL of styrene (0.9 g) with 0.05 mmol of **1b′** was first carried out at 25 °C in toluene (10 mL) for 1 h. Quenching this reaction mixture with MeOH yielded 0.88 g (98% yield) of polystyrene with $M_n = 8.8 \times 10^4$ and $M_w/M_n = 1.34$, showing that the polymerization reaction was almost completed under the present conditions. Addition of another 1 mL of styrene to this reaction mixture, followed by further stirring of the resultant mixture for 1 h, afforded 1.75 g of polystyrene whose M_n increased to 13.9×10^4 while M_w/M_n (1.37) remained almost unchanged, which shows that the completed styrene-polymerization solution was still "living" and able to incorporate and polymerize styrene. Exposure of this "living" styrene-polymerization solution to an atmosphere of ethylene with stirring for 30 min, however, did not give a styrene–ethylene copolymer, but instead yielded 0.85 g of polystyrene ($M_n = 8.6 \times 10^4$, $M_w/M_n = 1.35$) and 0.76 g of polyethylene ($M_n = 43.2 \times 10^4$, $M_w/M_n = 1.67$) after being quenched with MeOH and separated by THF/toluene extractions (cf. Scheme 2). These results suggest that the propagation site of the polystyrene unit in the present system does not allow insertion of ethylene, although it can generate a species (possibly a Sm(III) hydride) active for ethylene homopolymerization. In contrast, when the introduction of ethylene to this styrene polymerization mixture was immediately followed by addition of 7 mL of styrene, a block styrene–ethylene copolymer product (0.42 g, M_n = 8.7

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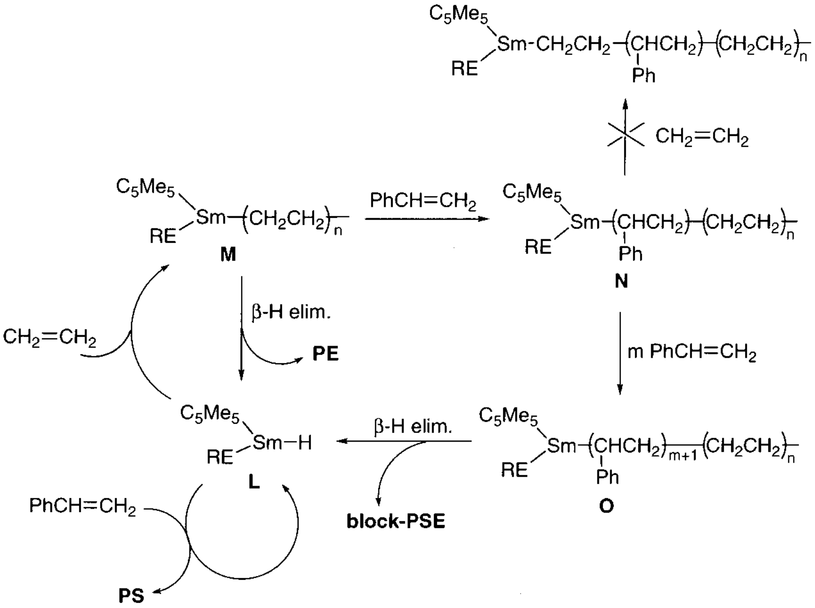
[38] The inactivity of the Sm(II) complexes with two ER ligands such as $Sm(OAr)_2(THF)_3$ or $Sm(N(SiMe_3)_2)_2(THF)_2$ for the polymerization of ethylene or styrene is probably due to the weak electron-donating ability of the ER ligands,[40] with which the Sm(II) center is not able to transfer an electron to an olefin monomer to initiate the polymerization reaction, although these complexes are less sterically demanding than $(C_5Me_5)_2Sm(THF)_n$.

Scheme 4. A Possible Mechanism for Block Copolymerization of Styrene and Ethylene



× 10^4, $M_w/M_n = 1.54$, PS content = 48 mol %) together with 1.11 g of homopolystyrene ($M_n = 9.4 \times 10^4$, $M_w/M_n = 1.34$) was obtained after the resultant mixture was stirred under the ethylene atmosphere for 30 min, whereas homopolyethylene was almost not observed. All these results strongly suggest that the present copolymerization reactions must be initiated by polymerization of ethylene followed by successive incorporation of styrene. Since the copolymerization reactions were also ER-ligand dependent and the molecular weight distributions of the resulting copolymers were relatively narrow (see also Table 4), the possibility that the copolymerization reactions proceeded via a radical process could be excluded. A possible mechanism for reactions starting with the C_5Me_5/ER-ligated Sm(III) hydride species **L** is shown in Scheme 4.[39]

Thus, the reactions initiated by styrene polymerization would afford only homopolystyrene (**PS**), while those by ethylene polymerization could end up with the formation of block styrene−ethylene copolymers (**PSE**) through the intermediates **M**, **N**, and **O**, if there is a sufficient amount of styrene monomer in the reaction systems (Scheme 4). These reaction paths could explain why homopolystyrene was always obtained as a byproduct while homopolyethylene was almost not observed in most of the copolymerization reactions by **1a**,**b′**,**c′** (Table 4). When a very small amount of styrene monomer was employed, the initiation of styrene polymerization and the incorporation of styrene into the polyethylene unit in **M** would be significantly slowed, and homopolyethylene (**PE**) thus formed as a dominant product (cf. run 9, Table 4). Obviously, a complex must show a well-balanced activity toward each monomer to selectively achieve the copolymerization reaction under the presence of both monomers. If the activity of a complex for styrene polymerization is much higher than that for ethylene, the formation of homopolystyrene would become dominant and *vice versa* (cf. **1d**,**e** and **1g**,**j′**).

The difference in selectivity for styrene−ethylene copolymerization reactions observed between the present C_5Me_5/ER-supported systems and the lanthanidocene complexes $Me_2Si(C_5Me_4)_2LnCH(SiMe_3)_2$ (Ln = Nd or Sm)[17a] must result from the difference in ancillary ligands between these two types of complexes. Since the ER ligand is less electron donating than "C_5Me_4",[40] the metal center supported by the mixed C_5Me_5/ER ligands would be electron-poorer than that supported by the two silylene-linked-"C_5Me_4" ligands. This could be a reason the C_5Me_5/ER-supported polystyrene-propagation site distinguished styrene from ethylene and thus led to formation of block styrene−ethylene copolymers under the presence of both monomers.[41] These results well demonstrate that replacement of one of the two cyclopentadienyl ligands in an ordinary lanthanide metallocene complex with an appropriate monodentate anionic ligand can effectively modify the steric and electronic properties of the metal center and thus create a brand-new catalytic system.

Concluding Remarks

By use of "C_5Me_5M" (M = K or Na) as a neutral stabilization ligand, a new series of C_5Me_5/ER-supported lanthanide(II) complexes have been successfully synthesized and structurally characterized. The "C_5Me_5K"-coordinated Ln(II) complexes, which bear one or two THF ligands on the K atom, prefer formation of a polymeric structure through intermolecular K···C_5Me_5 interactions when ER is an aryloxide, thiolate, or amide ligand (**1a**−**f**,**h**,**i**). In contrast, the analogous "C_5Me_5-Na"-coordinated complexes (**1j**,**k**) adopt a "monomeric" form, owing to the coordination of more (three) THF ligands to the Na atom. When ER = PHAr (**1g**), the "C_5Me_5K" unit prefers to bond to the phosphide ligand with the K atom, and a polymeric structure through intermolecular C_5Me_5···Sm interactions is formed. Dissociation of the "C_5Me_5M" ligand from the central lanthanide metal can yield a sterically unsaturated Ln(II) species which is supported by the mixed C_5Me_5/ER ligands. As a dissociable stabilization ligand, "C_5Me_5K" is unique and more suitable than "C_5Me_5Na", possibly owing to its tendency to adopt a polymeric, insoluble form. Since the

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[39] Reactions starting with the Sm(II) species would follow a similar mechanism and end up with the formation of the Sm(III) hydride species **L** as in the case of the homopolyerization reactions (cf. Scheme 3).

[40] Using the "neutral ligand formalism", an ER ligand (ER = OAr, SAr, NR_2, etc.) can donate, at most, three electrons to the central metal, two electrons fewer than a *pentahapto* cyclopentadienyl ligand.[19a]

[41] The propagation site of the polystyrene unit in the present case might be to some extent "anionic" and thus more reactive toward styrene than toward ethylene. Further studies are, however, required to understand the details.

Table 5. Summary of Crystallographic Data

compound	**1b**	**1c**	**1d**	**1e**	**1g**·C_6H_6
formula	$C_{44}H_{71}KO_4Sm$	$C_{43}H_{69}KO_2SSm$	$C_{46}H_{76}KNO_2Sm$	$C_{34}H_{64}KNO_2Si_2Sm$	$C_{49}H_{79}KO_2PSm$
formula weight	853.54	839.59	864.61	764.56	920.63
crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P-1$ (No. 2)	$C2/c$ (No. 15)	$C2$ (No. 5)	$P-1$ (No. 2)
a (Å)	14.867(6)	10.139(6)	42.125(6)	35.013(10)	14.043(5)
b (Å)	18.269(2)	14.180(6)	10.238(9)	10.306(5)	18.638(5)
c (Å)	17.362(6)	17.465(5)	27.706(6)	11.684(4)	10.291(1)
α (deg)		105.79(3)			92.05(1)
β (deg)	103.190(7)	93.83(3)	125.17(1)	104.00(3)	99.46(2)
γ (deg)		70.70(4)			106.92(2)
V (Å^3)	4591(2)	2279(2)	9767(8)	4091(3)	2531(1)
Z	4	2	8	4	2
D_c (g cm^{-1})	1.24	1.22	1.18	1.24	1.21
μ (cm^{-1})	14.08	14.64	13.23	16.25	13.09
no. of reflns collcd	8415	11410	7362	5187	10392
no. of reflns with $I_o > 3\sigma(I_o)$	4800	7299	3409	4479	8547
no. of variables	411	433	460	369	487
R_{int}		0.051		0.055	
R	0.096	0.055	0.109	0.065	0.061
R_w	0.120	0.074	0.122	0.083	0.082

compound	**1h**	**1i**	**1j**	**1k**	**2e**
formula	$C_{43}H_{69}KO_3SiSm$	$C_{38}H_{59}KO_2SiSm$	$C_{38}H_{72}NNaO_3Si_2Sm$	$C_{38}H_{72}NNaO_3Si_2Yb$	$C_{28}H_{69}N_7O_2P_2Si_2Sm$
formula weight	851.60	765.47	820.56	843.20	804.43
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	14.222(3)	15.080(4)	17.716(6)	17.627(4)	19.205(4)
b (Å)	18.04(1)	15.566(2)	18.188(5)	18.130(3)	21.877(4)
c (Å)	17.978(2)	17.295(9)	14.379(4)	14.300(2)	10.283(2)
α (deg)					
β (deg)	102.317(6)	105.40(4)q	94.13(3)	94.32(1)	92.89(1)
γ (deg)					
V (Å^3)	4506(2)	3913(2)	4621(2)	4556(1)	4315(1)
Z	4	4	4	4	4
D_c (g cm^{-1})	1.26	1.30	1.18	1.23	1.24
μ (cm^{-1})	14.58	16.69	13.62	21.36	15.17
no. of reflns collcd	9154	8179	6573	6321	10801
no. of reflns with $I_o > x\sigma(I_o)$	4934 ($x = 5$)	6477 ($x = 3$)	3849 ($x = 3$)	3437 ($x = 3$)	4744 ($x = 3$)
no. of variables	442	388	415	415	379
R_{int}			0.066	0.062	0.058
R	0.097	0.043	0.078	0.060	0.064
R_w	0.135	0.080	0.094	0.087	0.094

ER ligand is less sterically demanding and less electron-donating than the C_5Me_5 ligand, the mixed C_5Me_5/ER ligand system provides a sterically and electronically unique environment for the lanthanide metal center. This mixed ligand system is particularly effective for the Sm(II) species, which constitutes the first lanthanide catalytic system which is active not only for polymerization of styrene and ethylene but also for copolymerization of these two monomers. Furthermore, the subtle interplay between the steric and electronic effects of the mixed C_5Me_5/ER ligands has enabled the metal center to discern styrene from ethylene in reactivity, and thus resulted in formation of block styrene−ethylene copolymers under the presence of both monomers, a unique reaction which has never been reported for any other kind of catalytic systems. The reactivity difference observed among the C_5Me_5/ER-ligated Sm(II) complexes **1a**,**b′**,**c′**,**d**,**e**,**g**,**j′** and that between these mixed-ligand-supported complexes and the ordinary lanthanide metallocene complexes clearly show that the reactivity of a lanthanide complex can be fine-tuned by changing the ancillary ligands.

Experimental Section

See Supporting Information for experimental details. The crystal data of complexes **1b**−**e**, **g**−**k**, **2e** are summarized in Table 5.

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Supporting Information Available: Experimental details, tables of atomic coordinates, thermal parameters, and bond distances and angles for complexes **1b**−**e**, **g**−**k**, **2e**, X-ray structures of complexes **1d**, **e**, **i**, **k**, and TEM images, GPC profiles, and hysteresis curves of some typical polymer materials (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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