Anionic Monosubstituted Cyclopentadienylsamarium Derivatives: Catalysts for a Stereospecific Isoprene Polymerization

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New alkyl and allyl complexes **1**–**3** {**1**: $[Cp'_2Sm(C_3H_5)]_n$, Cp′ = $Me_3CC_5H_4$; **2**: $[Me_4C_2(C_5H_4)_2]Sm(C_3H_5)_2Li(dme)$, dme = $(CH_3OCH_2CH_2OCH_3)$; **3**: $Cp'_2SmMe_2Li(dioxane)$} were synthesized from $(Cp'_2SmCl)_2$ and from the magnesium derivative $[Me_4C_2(C_5H_4)_2]SmCl \cdot MgCl_2(THF)_4$ (**4**). The ansa anionic complex **2** exhibited good activity for the stereospecific 1,4-*trans* polymerization of isoprene, whereas the neutral derivative **1** was inactive. In the same way, the anionic complex $[Cp'_2SmMe_2]Li(dioxane)$ (**3**) was found to be an ethylene polymerization catalyst of very short lifetime. The lack of reactivity of **1** is related to the associated structure of this coordinatively unsaturated complex: this fact was established by the formation of the carbene adduct $Cp'_2Sm(C_3H_5)[C(NiPr)_2(CMe)_2]$ (**1′**). Crystals of **1′** were isolated but this new compound undergoes a partial rearrangement into a tris-Cp′ species in solution. Similar behaviour is observed for the analogous complex $Cp'_2SmCl[C(NiPr)_2(CMe)_2]$ (**1′′**). The X-ray crystal structure revealed the formation of the adduct, as a toluene solvate, which exists in benzene solution in equilibrium with Cp'_3Sm and $Cp'SmCl_2[C(NiPr)_2(CMe)_2]_2$. The catalytic behaviour of **2** is compared with that of other early lanthanide derivatives.

Introduction

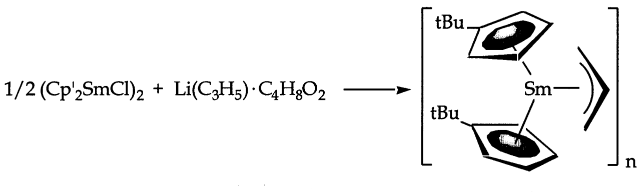
Isoprene polymerization, in relation to the chemistry of elastomers and adhesives, is of current interest[1]. Hydrido- or alkylmetallocenes of lanthanides are efficient catalysts for ethylene polymerization in the absence of the methyl aluminoxane reagent MAO[2][3]. However, the compounds Cp_2^*LnH or Cp^*_2LnR, $Cp^* = C_5Me_5$ or related bridged systems, are almost completely unreactive for the polymerization of α-olefins or dienes[4]. We were interested in the determination of the limits of stability of less hindered metallocene hydrides[5] of the early lanthanides and established that the hydride $[Cp'_2SmH]_2$, Cp′ = $Me_3CC_5H_4$, can be observed in solution, whereas the analogous neodymium hydride is only a transient species[6][7]. In this Cp′ series, or preferably in an analogous ansa cyclopentadienyl series [to avoid the easy redistribution leading to tris(cyclopentadienyl) derivatives], it was therefore necessary to synthesize alkyl or allyl derivatives that would be stable compounds capable of catalyzing the diene (and especially isoprene) polymerization without addition of a co-catalyst. The microstructure of a polymer is, to a large extent, controlled by the mode of coordination of the monomer to the catalyst: in a Cp'_2SmR moiety, even when R is a non-bulky alkyl or allyl ligand, only one vacant site will be readily accessible and, consequently, a stereospecific 1,4-*trans* polymerization is expected[8].

Results and Discussion

Synthesis of *tert*-Butylcyclopentadienyl Complexes

The methyl derivative $(Cp'_2SmMe)_2$[5] had been synthesized from $(Cp'_2SmCl)_2$[9] by addition of MeLi. The neutral allylic derivative $[Cp'_2Sm(C_3H_5)]_n$ (**1**) was obtained in a similar way using the dioxane adduct of allyl lithium[10] (Scheme 1).

Scheme 1



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Compound **1** was isolated in an analytically pure state as a red oil. Due to the fact that no ether ligand remained coordinated, it was inferred that this compound was dimeric or polymeric. Attempts to obtain a monomeric solvated form by crystallization in the presence of oxygenated solvents were unsuccessful. However, crystals could be obtained in the presence of another Lewis base, i.e. the stable carbene 1,3-diisopropylimidazoline-2-ylidene $C(NiPr)_2$-

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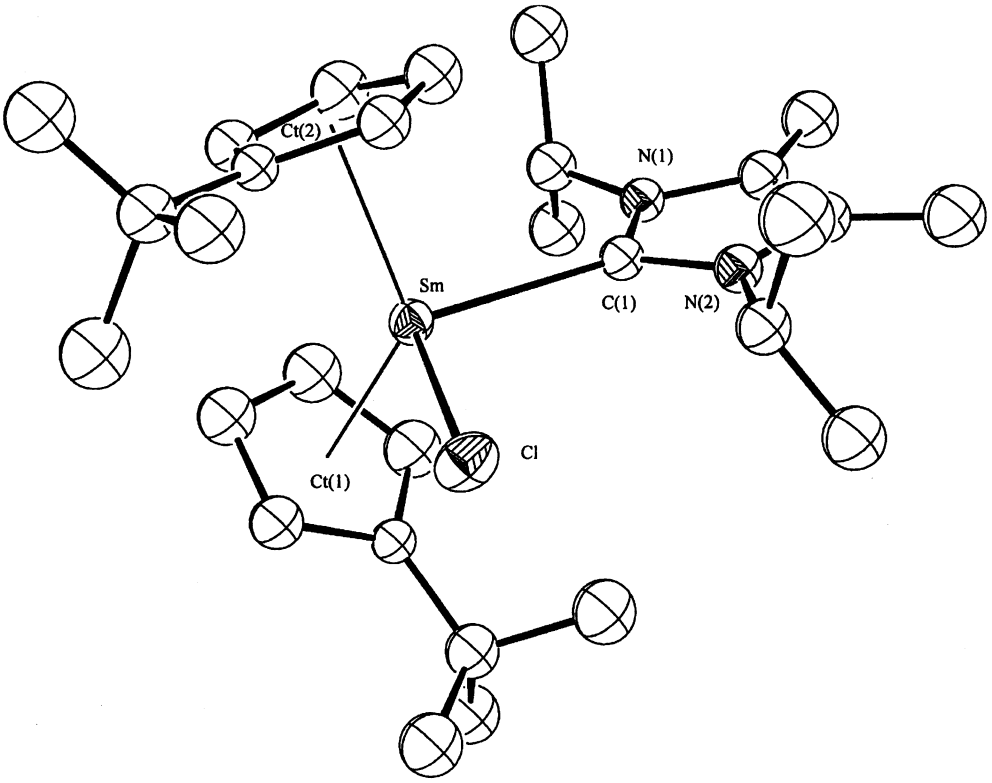
$(CMe)_2$[11], which has recently been used as a ligand in lanthanide compounds[12]. The nitrogen analysis of these thin red plates was consistent with the formula of a mono adduct $Cp'_2Sm(C_3H_5)[C(N\textit{i}Pr)_2(CMe)_2]$ (**1′**). The crystals were not suitable for X-ray structural analysis because the melting point was just above ambient temperature and, consequently, crystals melted in the sealed capillary. Surprisingly, the ^1H-NMR spectrum (C_6D_6 solution) of these monocrystals showed the known signals of Cp'_3Sm (ca. 10%) in addition to the set of signals due to the adduct (90%). A partial redistribution of the ligands could be involved, although no signals corresponding to the concomitant formation of a mono Cp′ derivative were detected.

Although we could not establish unambiguously the behaviour of $Cp'_2Sm(C_3H_5)[C(N\textit{i}Pr)_2(CMe)_2]$ (**1′**) in solution, this was possible in the case of another carbene adduct. Addition of one equivalent of the carbene $C(N\textit{i}Pr)_2(CMe)_2$ to a toluene solution of $(Cp'_2SmCl)_2$ allowed the isolation of yellow crystals [see ORTEP view (Figure 1) and Experimental Section] of an analytically pure toluene solvate of the adduct $Cp'_2SmCl[C(N\textit{i}Pr)_2(CMe)_2]$ (**1″**).

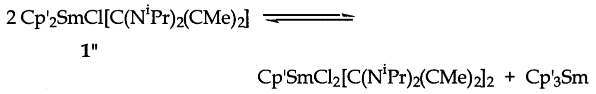
Figure 1. ORTEP view of the solid-state structure of $(Cp'_2SmCl[C(N\textit{i}Pr)_2(CMe)_2]$ (**1″**); for reasons of clarity, ellipsoids are set to the 30% probabity level and the toluene solvate molecule is not represented[a]



[a] Selected bond lengths [Å] and angles [°]: Sm–C(1) 2.62(2), Sm–Cl 2.648(4), Sm–Ct(1) 2.45(1), Sm–Ct(2) 2.44(1); Ct(1)–Sm–Ct(2) 128.6(14), Ct(1)–Sm–C(1) 106.3(9), Ct(1)–Sm–Cl 107.9(7), Ct(2)–Sm–C(1) 101.8(9), Ct(2)–Sm–Cl 105.6(6), C(1)–Sm–Cl 104.2(3).

After dissolution of these crystals in C_6D_6, the NMR spectrum showed the presence of three compounds: **1″**, a second adduct identified as $Cp'SmCl_2[C(N\textit{i}Pr)_2(CMe)_2]_2$ on the basis of the NMR data, and the unavoidable Cp'_3Sm. The integral values for the Cp signals of $Cp'SmCl_2[C(N\textit{i}Pr)_2(CMe)_2]_2$ and Cp'_3Sm were, as expected, in a 1:3 ratio. The percentage of the carbene adduct **1″** was a function of the concentration and it was found to be higher (nearly 80%) in dilute solution. This equilibrium (Scheme 2) is slow in the NMR timescale and Spin Saturation Transfer (SST) experiments could not be performed.

Scheme 2



Synthesis of Ansacyclopentadienyl Complexes

An ansa compound was synthesized from $SmCl_3(THF)_3$ and the Grignard reagent $[Me_4C_2(C_5H_4MgCl)_2](THF)_4$[13]. The X-ray crystal structure of two related samarium complexes $[\{Me_4C_2(C_5H_4)_2\}SmCl(THF)MgCl_2(THF)_3]$ and $[\{Me_4C_2(C_5H_4)_2\}SmCl(THF)]_2$ have been described elsewhere[14][15]. The reasons for the formation of one or other of these complexes were not clear given that the starting materials and the experimental procedures were quite similar. NMR data were not mentioned and, consequently, it was not established wether the two complexes could be distinguished in solution. The formation of a related monomeric complex, $[Me_4C_2(C_5H_4)_2]SmCl(THF)$, had also been reported, and this involved the oxidative addition of *tert*-

Table 1. ^{1}H-NMR data of complexes **1**−**4** [C_6D_6, δ vs. TMS, 298 K]

Complex	C_5H_4	CMe_3 or $(CMe_2)_2$	allyl or alkyl	carbene $C(NiPr)_2(CMe)_2$
$[Cp'_2Sm(C_3H_5)]_n$ **1**	13.21 (4 H) 9.21 (4 H)	−2.81 (18 H)	16.79 (1 H) 9.56 (2 H) 6.43 (2 H)	–
$Cp'_2Sm(C_3H_5),C(NiPr)_2(CMe)_2$ **1′**	12.72 (4 H) 9.21 (4 H)	−2.51 (18 H)	15.97 (1 H) 8.10 (4 H)	3.91 (m, 2 H); 1.72 (6 H); 1.47 (d, 12 H)
$Cp'_2SmCl,C(N^iPr)_2(CMe)_2$ **1″**	11.38; 10.45 8.15; 7.94 (2 H each)	1.18 (18 H)	–	3.95 (m, 2 H); 0.91 (6 H); 0.57 (12 H)
$Cp'SmCl_2,[C(NiPr)_2(CMe)_2]_2$ **1‴**	10.72 (2 H) 11.57 (2 H)	−0.5 (br 9 H)	–	1.51 (d, 24 H); 0.01 (s, 12 H); H signal not located
$[Me_4C_2(C_5H_4)_2]Sm(C_3H_5)_2$ Li(dme), **2**[a]	7.94 (4 H) 5.77 (4 H)	1.70 (12 H)	9.53 (m, 2 H) 8.61 (br., 4 H) 7.07 (br., 4 H)	3.35 (dme, 4 H) 3.19 (dme, 6 H)
Cp'_2SmMe_2Li(dioxane) **3**	9.77 (4 H) 9.07 (4 H)	−0.05 (18 H)	−5.12 (s, 6 H)	4.15 (dioxane, 8 H)
$[Me_4C_2(C_5H_4)_2]SmCl(THF)$ $MgCl_2(THF)_3$, **4**	15.31 (4 H) 8.05 (4 H)	1.25 (12 H)	–	3.73 (THF, 16 H) 1.34 (THF, 16 H)

[a] In C_4D_8O.

butyl chloride to the Sm^{II} compound $[Me_4C_2(C_5H_4)_2]Sm$. In this case NMR data were obtained[16].

Initially we tried to investigate the reaction on an NMR-scale preparation. By mixing stoichiometric amounts of $SmCl_3(THF)_3$ and $[Me_4C_2(C_5H_4MgCl)_2](THF)_4$ in C_6D_6, a yellow solution and a white precipitate of salts were obtained. The solution was transferred into another tube and the solvent removed under reduced pressure to remove the excess THF originating from the Grignard reagent. After redissolution in C_6D_6, the NMR spectrum showed the presence of four remaining THF molecules per $[Me_4C_2(C_5H_4)_2]Sm$ moiety and no further loss of THF was observed when the same process was repeated. This was interpreted in terms of the formation of the mixed samarium-magnesium compound, $[\{Me_4C_2(C_5H_4)_2\}SmCl(THF)MgCl_2(THF)_3]$ (**4**).

The synthesis was then performed on a larger scale, in THF, as described in the literature[15]. After the usual work-up, the NMR spectrum of the crude orange-yellow solid was very different from the one recorded in the previous synthesis (directly in the NMR tube) and could not be interpreted in terms of the formation of a well-defined pure compound. Further attempts were made using toluene as the solvent, but similar results were obtained. It was concluded that if evidence for the quantitative formation of a unique complex was provided by NMR experiments, then the handling of the mixture, leading to undefined materials, was not recommended.

The one-pot synthesis of an allylic derivative was therefore undertaken, initially on an NMR scale, by adding a stoichiometric amount of C_3H_5Li(dioxane) to the crude deuterated benzene solution obtained, as described previously, by mixing $SmCl_3(THF)_3$ and the Grignard reagent $[Me_4C_2(C_5H_4MgCl)_2](THF)_4$. A reaction occurred immediately and a pink-red precipitate deposited, which was partially soluble in the presence of the oxygenated solvents (7 THF + 2 dioxane). At 70°C the NMR spectrum showed a two-allyl signal pattern {2 H and 8 H per $[Me_4C_2(C_5H_4)_2]Sm$ moiety}, revealing a dynamic exchange process. The poor solubility, along with these integral values, indicated that the new complex was an anionic bis(allylic) complex. At ambient temperature the allylic signals coalesced and only the signals due to the ansa ligand could be detected. This could be interpreted as evidence for the partial dissociation of allyl ligands.

The synthesis was then performed on a bulk scale, in toluene, with two equivalents of $C_3H_5Li\cdot$dioxane. The crude compound contained THF and dioxane, which were exchanged by dissolution in DME. The red expanded oil obtained after removal of the solvents was washed with ether and finally gave a red powder of analytically pure **2**, $[Me_4C_2(C_5H_4)_2]Sm(C_3H_5)_2Li(DME)$. This new compound was not soluble in either toluene or benzene: its NMR spectrum was recorded in $[D_8]$THF and the allyl ligands exhibited a typical η^3 three-signal (1 H, 2 H, and 2 H) pattern.

The dianionic ansa cyclopentadienyl ligand $[Me_4C_2(C_5H_4)_2]^{2-}$ was chosen in order to avoid the disproportionation of the bis(cyclopentadienyl) derivatives of the lighter lanthanides[17][18]. Moreover, the stereoelectronic properties of a $[Me_4C_2(C_5H_4)_2]Sm$ moiety should be similar to those of a $(Me_3CC_5H_4)_2Sm$ unit, except that the angle between the metal center and the centroids of the rings would be slightly smaller in the case of an ethylene bridge[19] (the ring-centroid−Yb−ring-centroid angle is 121° and 121.3° in $[Me_4C_2(C_5H_4)_2]YbCl_2,Mg_2Cl_3\cdot 7$ THF[17] and $(Me_3CC_5H_4)_2YbCl\cdot$THF[20], respectively). In addition, in the ansa ligand the rotation of the Cp rings[21][22] is not possible and the effective size of the ligand is therefore smaller. The saturation of the coordination sphere of the metal atom therefore occurs in a different manner: in the Cp′ series, $Cp'_2YbCl\cdot$THF[20] is neutral whereas the homologous ansa complex $[Me_4C_2(C_5H_4)_2]YbCl_2 \cdot Mg_2Cl_3 \cdot 7\ THF$[17] is anionic.

In a similar manner, the reaction of an equimolar amount of C_3H_5Li with $(Cp'_2SmCl)_2$ leads to a dimer (or a polymer, although the high solubility of **1** in pentane suggests an oligomeric structure), showing that a neutral species is preferred. In the case of the ansa compound, a monomeric anionic complex **2** is formed.

In the presence of an excess of allyl ligand, no anionic compound was formed in the Cp′ series: a redistribution leading to a mixture of Cp'_3Sm[9] and $Sm(C_3H_5)_4Li$(dioxane)[23] was observed (Scheme 3).

Scheme 3

$$3\,Cp'_2Sm(C_3H_5) + Li(C_3H_5)\cdot C_4H_8O_2 \longrightarrow 2\,Cp'_3Sm + Sm(C_3H_5)_4Li\cdot C_4H_8O_2$$

Nevertheless, on using the small monohapto methyl ligand, a bis(alkyl)-anionic complex was obtained in the Cp′ series: treatment of $(Cp'_2SmMe)_2$ or $(Cp'_2SmCl)_2$ with one or two equivalents of MeLi, respectively, led to the same compound Cp'_2SmMe_2Li. After addition of one molar equivalent of $(Cp'_2SmCl)_2$ the neutral dimer could be recovered.

Scheme 4

$$Cp'_2SmMe_2Li + 1/2\,(Cp'_2SmCl)_2 \longrightarrow (Cp'_2SmMe)_2$$

The anionic bis(methyl) compound was isolated in an analytically pure form (pale yellow microcrystals) as a dioxane adduct: $Cp'_2SmMe_2Li \cdot$ dioxane.

Catalysis

Allylic lanthanide derivatives are known to catalyse the polymerization of dienes[24] and the new complexes **1** and **2** were tested in the polymerization of isoprene.

The anionic complex **2** was found to be efficient (the turn-over number amounts to ca. 260 mol of isoprene per mol of lanthanide catalyst per hour) and very stereospecific (95%) for 1,4-*trans* polymerization (see Table 2). Molecular weights are in the expected range for this type of polymerization test[1].

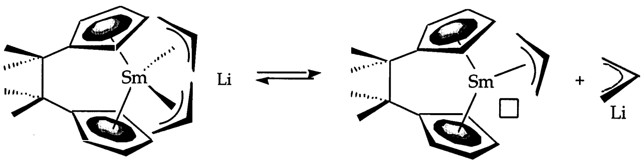
The neutral complex **1** was found to be inactive and its carbene adduct **1′** was found to be almost inactive. This implies that the $[Cp'_2Sm(C_3H_5)]_n$ compound remains strongly associated and isoprene does not possess a sufficiently strong ligand ability [unlike, for example, the nucleophilic carbene $C(NiPr)_2(CMe)_2$] to dissociate the starting material. Attempts to create a more accessible metallic center by addition of 1 equivalent of yttrium chloride as a Lewis acid led to a system of very low activity (yield of polyisoprene 2%).

In contrast, the dissociation of an allylic ligand in the anionic compound **2** is easy and allows the coordination of the diene. The precedent for this ligand dissociation was postulated for other anionic allyllanthanide compounds[8] tested in the polymerization of butadiene.

The tetraallylneodymium complex $Nd(C_3H_5)_4Li$(dioxane)$_{1.5}$ had been previously found to be a specific (86% of *trans*-1,4-polybutadiene) catalyst for butadiene polymerization[10]. We found that for the polymerization of isoprene, tetraallyllanthanide complexes are less specific (31% and 28% of *trans*-1,4-polyisoprene for neodymium and samarium, respectively). This reaction was thus very dependent on the steric hindrance of the monomer.

In the same way, C_3H_5Li(dioxane) leads to a high (ca. 53%) percentage of *cis* 1-4 polyisoprene; the participation of this species could be invoked for the polymerization obtained from the tetraallylic compounds and this has been discussed previously[8]. However, for the anionic bisallylic complexes (or systems) its role appears negligible because those systems led to an almost pure 1,4-*trans* polymer.

Scheme 5



The performances of other allylic systems towards isoprene polymerization are presented in Table 2 (**A**, the neodymium analogue of **2**, and **B**, an alkoxide derivative, tris-*tert*-butyloxy – "tritox" –). The catalysts are prepared in situ and may contain salts and an excess of oxygenated sol-

Table 2. Polymerization of isoprene (50°C, ratio isoprene/catalyst = 1500)

Catalyst	Yield (%)	$\bar{M}_w$	*trans*-1,4 (%)	*cis*-1,4 (%)	3,4 (%)	Reaction time [h]	T.O.[a] $[h^{-1}]$
$[Cp'_2Sm(C_3H_5)]_n$ **1**	0						
$[Me_4C_2(C_5H_4)_2]Sm(C_3H_5)_2Li(dme)$, **2**	62	8000	95	1	4	12	260
$(C_3H_5)Li$(dioxane)	100	–	27	53	20	2.5	110
$Sm(C_3H_5)_4Li$(dioxane)	55	24000	28	45	27	3	200
$Nd(C_3H_5)_4Li(dioxane)_{1.5}$[b]	75	1500	31	39	30	4	150
system A	30	37000	97	0	3	6	50
system B	30	46000	91	0	9	21	50

[a] T.O. = mol of monomer transformed/mol of catalyst/h. – [b] Was found to be inactive in the presence of 4 THF per Nd atom.

vents as ligands, which could modify the process of dissociation of the allylic ligand. Indeed, we found this to be the case for the tetraallylneodymium complex Nd$(C_3H_5)_4$Li(dioxane)$_{1.5}$, in which the activity decreases in the presence of 1 THF per molecule, and it becomes inactive with 4 THF per molecule. The turn-over values (Table 2) are lower than for **2**, nevertheless, the catalytic activity is well in evidence: in each case the same stereocontrol is observed, with predominant formation of 1,4-*trans*-polyisoprene.

The ansa and the tritox complexes possess more bulky ligands than the tetraallyl complexes. The isolated complexes are tetracoordinated, and in solution it also seems that no more than four coordination sites are accessible. After the decoordination of the allyl ligand, only one site will be vacant for the coordination of the monomer. As a consequence, a very high stereoselectivity (89 to 95% of 1,4-*trans* polymer) is observed.

The anionic complex **3**, Cp'_2SmMe_2Li(dioxane), was found to be very active (T.O. = 25000 mol of ethylene transformed/mol of catalyst/h) towards the polymerization of ethylene in the absence of MAO, but only within five minutes[25]. The rapid loss of activity was attributed to the ease of rearrangement leading to the inactive tris derivative.

The neutral dimer $(Cp'_2SmMe)_2$ had already been found to be very poorly active towards hydrogenolysis. This lack of reactivity was related to its dimeric structure[5].

Conclusion

New organometallic complexes of samarium have been synthesized, $[Cp'_2Sm(C_3H_5)]_n$ and its carbene adduct $Cp'_2Sm(C_3H_5)[C(N\textit{i}Pr)_2(CMe)_2]$, $[Me_4C_2(C_5H_4)_2]Sm(C_3H_5)_2Li$(dme), and Cp'_2SmMe_2Li(dioxane). The structures of these complexes are strongly dependent on steric factors: neutral monoallylic and anionic bis(allylic) complexes were characterized. Related complexes were prepared in situ. An X-ray structure analysis could be obtained for $Cp'_2SmCl[C(N\textit{i}Pr)_2(CMe)_2]$, which undergoes rearrangement in solution. The catalytic behaviour of all these new complexes towards polymerization was investigated. Anionic complexes are active: Cp'_2SmMe_2Li(dioxane) is an ethylene polymerization catalyst with a short lifetime and the ansa bis(allylic) complex is a stereospecific 1,4-*trans*-polymerization catalyst.

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Experimental Section

All manipulations were carried out under purified nitrogen in a Jacomex glove box or under argon using standard vacuum techniques. Solvents were distilled from the appropriate drying agent, stored over Na/benzophenone and vacuum-transferred to reaction vessels. ^{1}H- and ^{13}C-NMR spectra were recorded with AC 200 and DRX 500 Bruker spectrometers (297 K). − Polymer Analysis: Molecular weights and polydispersities were obtained by Steric Exclusion Chromatography (S.E.C.) on a Spectra-Physics chromatograph equipped with two detectors (a UV and a refractive index detector) connected in series. The calibration was carried out with PL-Lab polystyrene standards (EasiCal® PS-1, range $\bar{M}_w$ = 580−8.5 × 10^6). Each measurement was performed at 25°C in toluene as eluent, with a 1 ml/min flow rate. Two connected PL-Lab 5µ mixed-C 300 × 7.5 mm columns were used. The calculations for I_p and $\bar{M}_n$ were performed using GPC-Plus® software. Structural analysis of polyisoprene was conducted by ^{13}C- and ^{1}H-NMR spectroscopy and compared to commercially available samples. The isomeric purity was first evaluated by $^{13}C\{^1H\}$ sequences and then confirmed on the basis of ^{1}H-NMR data. − $SmCl_3(THF)_3$ and $NdCl_3(THF)_3$[26], $(Cp'_2SmCl)_2$ and $(Cp'_2SmMe)_2$[5] C_3H_5Li(dioxane)[10], 1,3-diisopropylimidazoline-2-ylidene $C(N\textit{i}Pr)_2(CMe)_2$[11], tritoxLi[27], $(C_3H_5)_4NdLi(dioxane)_{1.5}$[10], and $[Me_4C_2(C_5H_4MgCl)_2](THF)_4$[13] were prepared as described. $(C_3H_5)_4SmLi$(dioxane) was synthesized following the procedure described for its neodymium homologue and its NMR data were in accordance with the original synthesis[23]. Ethereal solutions of MeLi were purchased from Aldrich. The diene (isoprene 99%) was dried over molecular sieves and distilled twice to remove the stabiliser. Elemental analyses were performed with a Fisons EA 1108 CHONS apparatus.

$[Cp'_2Sm(C_3H_5)]_n$ (**1**): A solution of $(Cp'_2SmCl)_2$ (0.39 g, 0.91 mmol) was added at −78°C to a slurry of C_3H_5Li(dioxane) (0.13 g, 0.91 mmol) in toluene (20 ml). The mixture was stirred at −78°C for 30 min, and then warmed to room temperature for another 30 min. The solution turned red and LiCl was deposited. After filtration, the solvent was removed under reduced pressure and the residue extracted with pentane (3 × 30 ml). After evaporation of the pentane, a deep red oil was obtained (0.27 g, yield 68%). − $C_{21}H_{31}Sm$ (433.88): calcd. C 58.14, H 7.20; found C 58.27, H 7.33. − ^{1}H NMR (C_6D_6): δ = 16.79 (s, 1 H), 13.21 (s, 4 H), 9.56 (s, 2 H), 9.21 (s, 4 H), 6.43 (s, 2 H), −2.81 (s, 18 H).

A mixture of 10 mg (23 µmol) of **1** and 3 mg (22 µmol) of C_3H_5Li(dioxane) in C_6D_6 was stirred by sonification, and Cp'_3Sm and $(C_3H_5)_4SmLi$ slowly precipitated from the mixtute and these compounds were detected by NMR.

$Cp'_2Sm(C_3H_5)$, $C(NiPr)_2(CMe)_2$ (**1′**): A mixture of **1** (0.247 g, 0.57 mmol) and 1 equiv. (0.103 g) of $C(N\textit{i}Pr)_2(CMe)_2$ in 20 ml of toluene was stirred at room temperature for 12 h. The solvent was evaporated and the residue extracted with pentane (3 × 20 ml). After filtration and concentration, a dark red solid was obtained (0.273 g, yield 78%). The NMR analysis revealed the presence of the adduct **1′**: ^{1}H NMR (C_6D_6): δ = 15.97 (s, 1 H), 12.72 (s, 4 H), 9.21 (s, 4 H), 8.10 (s, 4 H), 3.91 (m, 2 H), 1.72 (s, 6 H), 1.47 (d, 12 H), −2.51 (s, 18 H). This compound was accompanied by 10% of Cp'_3Sm. To remove the yellow contaminant Cp'_3Sm, the solid was washed with cold pentane. Red/black crystals were obtained by a further dissolution in pentane (15 ml), followed by filtration and slow concentration to a volume of ca. 3 ml. These crystals seemed suitable for X-ray analysis and one was mounted in a capillary tube. However, the crystal had melted after only a few minutes of exposure. After dissolution in deuterated benzene, NMR showed the invariable presence of 10% of Cp'_3Sm. − $C_{32}H_{51}N_2Sm$ (614.18): calcd. N 4.56; found N 4.58.

Cp'_2SmCl, $C(NiPr)_2(CMe)_2$ (**1″**): To a mixture of $(Cp'_2SmCl)_2$ (0.36 g, 0.84 mmol) and $C(N\textit{i}Pr)_2(CMe)_2$ (0.255 g, 1.41 mmol) was added 30 ml of toluene. The mixture was stirred at room temperature overnight and then filtered. The yellow solution was concentrated slowly to ca. 5 ml. Yellow crystals were collected 12 h later. The crystals were washed with pentane (10 ml) and dried under vacuum. Total yield: 0.235 g, 40%. A crystal was found that was

suitable for X-ray structure analysis (see below for further details), which revealed the presence of one toluene molecule per samarium atom. − Toluene adduct $C_{36}H_{54}ClN_2Sm$ (700.70): calcd. C 61.71, H 7.71, N 4.00; found C 61.24, H 7.93, N 4.37.

^{1}H-NMR analysis of the dissolved crystals revealed the presence of three compounds in solution (C_6D_6): **1**″: δ = 11.38 (s, 2 H), 10.45 (s, 2 H), 8.15 (s, 2 H), 7.94 (s, 2 H), 3.95 (m, 2 H), 1.18 (s, 18 H), 0.91 (s, 6 H), 0.57 (d, 12 H); Cp_3Sm and $Cp'SmCl_2[C(N\textit{i}Pr)_2(CMe)_2]_2$; **1**‴: δ = 10.72 (s, 2 H), 11.57 (s, 2 H), 1.51 (d, 24 H), 0.01 (s, 12 H), −0.5 (br., 9 H).

$[Me_4C_2(C_5H_4)_2]Sm(C_3H_5)_2Li(dme)$ (**2**): (a) In an NMR tube a mixture of 9.17 mg (19.3 µmol) of $SmCl_3(THF)_3$ and 12 mg (19.3 µmol) of $[Me_4C_2(C_5H_4MgCl)_2](THF)_4$ was stirred by sonification in 0.4 ml of C_6D_6 and then the mixture was warmed at 60°C. First a pale yellow, and then an orange yellow colour developed, and after 20 min the reaction was complete; the ^{1}H-NMR spectrum recorded was consistent with $[Me_4C_2(C_5H_4)_2]SmClMgCl_2(THF)_n$. − NMR ($C_6D_6$) δ = 15.51 (s, 4 H), 8.16 (s, 4 H), 1.51 (s, 18 H). − After evaporation of the solvents, C_6D_6 (0.4 ml) was added. NMR analysis revealed the presence of $[Me_4C_2(C_5H_4)_2]SmCl(THF)MgCl_2(THF)_3$ (**4**) as the unique product. − NMR (C_6D_6): δ = 15.31 (s, 4 H), 8.05 (s, 4 H), 3.73 (s, 16 H), 1.34 (s, 16 H), 1.25 (s, 12 H). − 2 equivalents (5.28 mg) of $C_5H_3Li(C_4H_8O_2)$ were added, the solution became pink/red and a reddish precipitate was deposited that was partially soluble in the presence of the oxygenated solvents (7 THF + 2 dioxane molecules per Sm atom). − **2**: ^{1}H NMR (C_6D_6; 298 K): δ = 8.09 (s, 4 H), 5.97 (s, 4 H), 3.34 (dioxane + THF), 1.89 (s, 12 H), 1.25 (THF), the allylic signals could not be detected; (343 K): δ = 8.54 (s, 4 H), 7.99 (br., 2 H), 6.62 (s, 4 H), 5.76 (br., 8 H), 3.36 (dioxane + THF), 1.81 (s, 12 H), 1.32 (THF).

(b) A toluene solution of $[Me_4C_2(C_5H_4)_2]SmCl(THF)\cdot MgCl_2(THF)_2$ (**4**) was prepared following the published procedure[14] from 0.5 g (1.06 mol) of $SmCl_3(THF)_3$ and 0.66 g (1.06 mol) of $[Me_4C_2(C_5H_4MgCl)_2](THF)_4$ in 20 ml of toluene (instead of THF). Salts were removed by filtration and, at −30°C and with vigourous stirring, 0.29 g (2.12 mmol) of $C_3H_5Li(C_4H_8O_2)$ was added to the bright orange solution. The mixture turned pink within a few minutes and the temperature was allowed to rise to 20°C. Salts were removed by filtration and the solvent was evaporated under reduced pressure to give a red paste. This paste was dissolved in dimethoxyethane (20 ml) and the solvent was evaporated. The crude product was an expanded oil which was washed with ether (3 × 15 ml) to finally give a brick-red powder (yield 60%). − ^{1}H NMR (C_4D_8O): δ = 9.53 (m, 2 H), 8.61 (br., 4 H), 7.94 (s, 4 H), 7.07 (br., 4 H), 5.77 (s, 4 H), 3.35 (dme, 4 H), 3.19 (dme, 6 H), 1.70 (s, 12 H). − Crystals could be obtained as thin plates in a 75−25% mixture of dimethoxyethane and diethyl ether. − $C_{26}H_{40}LiO_2Sm$ (541.95): calcd. C 57.62, H 7.44; found C 57.20, H 7.29.

$Cp'_2SmMe_2Li(dioxane)$ (**3**): To a stirred solution of $(Cp'_2SmCl)_2$ (0.39 g, 0.91 mmol) in toluene (30 ml) was slowly added, at −78°C, a 1 M ethereal solution of MeLi (2.0 µl, 2.0 mmol). The mixture was stirred for 2 h and then warmed to room temperature and stirred for a further 30 min. The mixture turned pale yellow and LiCl was deposited. The solution was filtered and the solvent evaporated. The residue was extracted with toluene (2 × 10 ml). The clear solution was concentrated and microcrystals were formed. After evaporation of the toluene, the powder was washed with pentane (2 × 10 ml) and dried in vacuo; a pale yellow solid was obtained (0.25 g, yield 64%) that was sparingly soluble in aromatic solvents. − ^{1}H NMR (C_6D_6): δ = 9.16 (s, 4 H), 8.86 (s, 4 H), −0.01 (s, 18 H), −4.08 (s, 6 H). − The solid was dissolved in 30 ml of toluene, a slight excess of dioxane (50 µl) was added and the solution was stirred for 1 h at ambient temperature. Slow evaporation of the solvent under reduced pressure gave pale yellow crystals. − ^{1}H NMR (C_6D_6): δ = 9.77 (s, 4 H), 9.07 (s, 4 H), 4.15 (s, 8 H), −0.05 (s, 18 H), −5.12 (s, 6 H). − $C_{24}H_{40}SmLiO_2$ (517.92): calcd. C 55.66, H 7.79; found C 55.29, H 7.85.

Crystal Data for $Cp'_2ClSm\cdot C(N\textit{i}Pr)_2(CMe)_2$: $C_{29}H_{46}ClN_2Sm\cdot C_7H_8$, M = 700.6, monoclinic, space group $P2_1/c$, a = 13.351(2), b = 17.005(3), c = 16.443(2) Å, β = 101.011(12)°, V = 3664(1) Å^3, Z = 4, D_c = 1.27 gcm^{-3}, μ(Mo-K_α) = 1.7 mm^{-1}. A yellow crystal was mounted on a capillary on an Enraf-Nonius CAD4 diffractometer at 20°C. Unfortunately, the crystal underwent rapid decomposition under X-ray exposure and only the first shell of data with $17.90° < \theta < 20.58°$ was used to solve and refine the structure (decay = 82%). The solution was obtained by interpretation of the Patterson map[28] and refined on F^2 using all the 1228 independent reflections collected[29]. Due to the lack of data, only the samarium and chlorine atoms were anisotropically refined. Hydrogen atoms were included, when possible, at their calculated positions. The Cp rings were constrained to a regular pentagon and the toluene ring to a regular hexagon. The methyl group of the toluene solvate was not located. The final agreement indices are $R_w(F^2)$ = 0.124 and $R(F)$ = 0.102 for all data (1228 independent reflections) and 135 parameters; $R(F)$ = 0.047 for 822 data with $I > 2\sigma(I)$; goodness of fit = 0.94 and $\Delta\rho$ = 0.344 and −0.260 e A^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-101393. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: internat. +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

In situ Preparation of Catalytic Systems. − System A: In an NMR tube was placed 12 mg of $[Me_4C_2(C_5H_4MgCl)_2](THF)_4$, 9 mg of $NdCl_3(THF)_3$, and 5.3 mg of C_3H_5Li(dioxane). 0.5 ml of C_6D_6 was added and the mixture was stirred by sonification until the signals of the starting materials totally disappeared: a bright green colour developed and white salts precipitated. The benzene (and the excess THF and dioxane) was evaporated and the residue dissolved in toluene. The toluene solution was transferred into a flask and the solvents were evaporated. The green solid was used for polymerization.

System B: To a C_6D_6 solution of 8 mg of tris-*tert*-butylmethanol − "tritoxH" − (dried over molecular sieves), was added 10.3 mg of $(C_3H_5)_4NdLi(dioxane)_{1.5}$. The tube was heated (60°C) and the mixture stirred by sonification, which led to a green, sparingly soluble material; very large allylic signals with paramagnetic shifts in the range δ = −10 to −50 and a paramagnetic *tert*-butyl signal at δ = 10 were observed in the ^{1}H-NMR spectrum. The solvent was partially evaporated, THF was added and the solvents partially evaporated once again. The green solid was then soluble in benzene and the solution was transferred into the polymerization flask. The solvents were evaporated before isoprene was added.

Polymerization Experiments: (1) Diene polymerization: The catalyst (10 mg) was introduced into a flask connected to a vacuum line. The diene (3 ml) was then condensed on to it and the stirred solution was heated at 50°C during 5 h. Depending on the activity of the catalyst, the mixture can become highly viscous; the flask was opened to the air and the contents dissolved in the required volume (5−15 ml) of toluene. The toluene solution was poured into 200 ml of ethanol and the polymer precipitated. The liquors were decanted and the solid dried (12 Torr, 1−2 d) and weighed before sampling for analysis (^{1}H and ^{13}C NMR, molecular weight, polydispersity).

(2) Ethene polymerization: the reaction was conducted at 60°C and p(ethene) = 4 bar[25].

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