Alane complexes of divalent ytterbocenes.
Bimetallic mechanism of styrene polymerization

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Abstract

Heterometallic complexes of divalent ytterbocenes Cp'_2Yb ($Cp' = (tert\text{-}Bu)_2C_5H_3$, C_5Me_5) and alanes $AlH_3 \cdot L$ ($L = NEt_3$, C_4H_8O, Et_2O) have been obtained without changing the oxidation state of the lanthanide atom. The complexes $Cp'_2YbAlH_3 \cdot L$ have been shown to be moderately active for styrene polymerization, producing atactic polystyrene. Linear olefins have not been incorporated in the polymerization process. The results provide some evidence for the heterometallic mechanism of styrene polymerization.

Keywords: Ytterbium; Aluminium; Alane complexes of divalent lanthanides; Metallocenes; Olefins; Styrene polymerization

1. Introduction

The active species of different metallocene-based catalysts of olefin polymerization have similar monometallic structures and are cationic in the case of Group IV metals [1] or neutral in the case of lanthanides [2]. Consideration of their structural and electronic properties suggests that the key features required for olefin polymerization reactivity are (1) high electron deficiency of the metal center and (2) a readily accessible M–R bond for olefin double bond insertion.

As to heterometallic metallocene-based compounds, cationic complexes of zirconocenes and hafnocenes with alkylaluminium have been characterized by Bochmann and Lancaster [3] as temporarily inactive resting stages of polymerization catalysts or, in other words, as catalyst precursors. It has also been shown that heterometallic tetraalkylaluminates of trivalent samarocenes $[(C_5Me_5)_2Sm(\mu\text{-}R)_2AlR_2]$ [4] possess moderate activity in the ethylene polymerization, but real active species have not been determined. Later, similar complexes have been assumed to be precursors of active monometallic alkyl derivatives of lanthanidocenes [5]. Heterometallic adducts of trialkylaluminium and diva-

lent ytterbocenes [6] have just been mentioned once in passing as possible catalysts for ethylene and styrene polymerizations of low molecular weight, but details of these processes and their mechanism have not been described.

Aluminohydride complexes of metallocenes still remain unexplored. Trivalent titanocene aluminohydrides having a 17-electron configuration of the transition metal atom have been shown to possess high activity for the catalytic hydrogenation of olefins and double bond isomerization [7], but have not been studied in regard to olefin polymerization. In contrast, trivalent lanthanidocene aluminohydrides (lanthanides Sm, Yb, Lu, Y) have been assumed to form coordinatively saturated structures which turned out to be absolutely inert in reactions involving olefin double bonds [8–12].

Recently, we have briefly communicated [13] that divalent ytterbocenes form stable coordinatively unsaturated adducts with trialkylaminealane, $[(tert\text{-}C_4H_9)_2C_5H_3]_2YbAlH_3 \cdot NEt_3$, without change of the oxidation state of the lanthanide atom. These heterometallic complexes have exhibited high activity for homogeneous 1-hexene hydrogenation. These results prompted us to test these compounds in the olefin polymerization.

We report here the complete synthesis and characterization of the alane complexes of divalent ytterbocenes
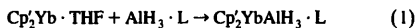
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and the first study of styrene polymerization induced by complexes of divalent lanthanidocenes.

2. Results and discussion

2.1. Preparation and characterization of ytterbocene alane complexes

For this study two readily soluble divalent lanthanidocenes $(C_5Me_5)_2Yb \cdot THF$ (I) [14] and [(*tert*-Bu)$_2C_5H_3]_2Yb \cdot THF$ (II) were chosen. Like its analogues, $[(SiMe_3)_2C_5H_3]_2Yb \cdot THF$ [15] and [(*tert*-Bu)$_2C_5H_3)_2Sm \cdot THF$ [16], complex II was obtained in the form of the green monosolvate [(*tert*-Bu)$_2C_5H_3]_2Yb \cdot THF$ by the reaction of YbI$_2$ with NaC$_5$H$_3$(*tert*-Bu)$_2$ followed by the crystallization from THF/toluene or THF/pentane (-50–30°C). In the IR spectrum of II (besides the many vibrations corresponding to the (*tert*-Bu)$_2C_5H_3$ fragment and THF molecule), a weak band is observed at $1600\,\mathrm{cm}^{-1}$ which is not present in the vibrational spectrum of I. Absorptions appearing in this region are usually assigned to the vibrations of M–H bonds. However, in the ^{1}H NMR spectrum of II we did not observe any M–H resonances. We therefore assigned this strange vibrational band to some interactions, occurring in the solid state only. It is worth noting that, unlike the compound [C$_5$H$_3$(SiMe$_3$)$_2$]$_2$Ln · THF [15], the complex II can be sublimed without decomposition upon heating to 130°C (5×10^{-3} torr). However, we cannot exclude the possibility of dissociation during heating followed by recombination on the cooling surface. In spite of the fact that II can be crystallized in the form of distinctive hexagonal plates, our efforts to determine its structure by X-ray diffraction were not fruitful owing to its totally amorphous nature.

Addition of alanes AlH$_3$ · L (L = NEt$_3$ (a), C$_4$H$_8$O (b), Et$_2$O (c)) to I and II in such solvents as toluene, benzene, pentane or ether does not lead to the oxidation of the ytterbium atom as was observed for Sm complexes [4,9–12]. Independently of the solvent type and order of reagent addition, interaction of alanes with the red solution of I or green solution of II leads to dark-cherry or green–brown solutions of the complexes III and IV respectively (Eq. (1)). Reaction (1) is not accompanied by H$_2$ and/or Al release.

$$Cp'_2Yb \cdot THF + AlH_3 \cdot L \rightarrow Cp'_2YbAlH_3 \cdot L \qquad (1)$$

$$Cp' = C_5Me_5 \ (\mathbf{III}), \ (tert - C_4H_9)_2C_5H_3 \ (\mathbf{IV});$$

$$L = NEt_3 \ (\mathbf{a}), \ THF \ (\mathbf{b}), \ Et_2O \ (\mathbf{c})$$

A property of the complexes III and IV is their high solubility in all solvents used, so that they could not be crystallized from solution. Complete removal of solvents in vacuo gave brown solids III and IV which were characterized by spectral methods.
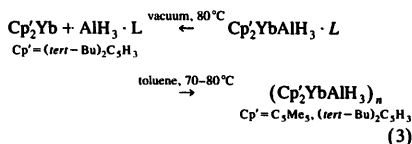
As expected, the quadrupolar moment of the aluminium atom does not allow us to observe resonances of hydrogen atoms in the NMR spectra of III and IV. Because of numerous vibrational bands corresponding to both cyclopentadienyl fragments and the Lewis base in the IR spectra of the complexes III(a–c) and IV(a–c), only a broad band at $1800\,\mathrm{cm}^{-1}$ and a narrow singlet at $1660\,\mathrm{cm}^{-1}$ could be directly assigned to M–H bond vibration. In the vibrational spectra of the deuterated analogues, these bands were shifted to 1270 and $1200\,\mathrm{cm}^{-1}$ respectively. Comparing these data with those for well characterized aluminohydride metallocene complexes [7–12], we assigned these bands to the terminal Al–H bonds of a five-coordinate aluminium atom ($1800\,\mathrm{cm}^{-1}$) and to bridging Al–H–Al and/or Yb–H–Al bonds ($1660\,\mathrm{cm}^{-1}$). These data are not sufficient to predict reliably the structure of the complexes III and IV. On the basis of the spectral and structural data reported for aluminohydride complexes of titanocenes [7,17] and lanthanidocenes [8–12,18] as well as catalytic properties of the complexes III and IV (see below), however, their most probable structure in the solid state might be supposed to be a dimer with a bridging Al$_2$H$_4$ moiety which is well documented for the structures of metallocene aluminohydrides of transition metals. At the same time, we believe that the dissociation of a dimeric molecule is possible in solution to yield two monomers (Eq. (2)).

$$(2)$$
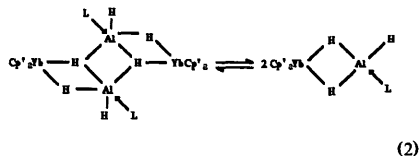
A similar monomeric alane complex, [(*tert*-C$_4$H$_9$)$_2$-C$_5$H$_3$]$_2$SmAlD$_3$ · TMEDA, has been reported as an intermediate in the oxidation of divalent samarocene by alanes. For the trivalent lutetium complex [Cp'$_2$LuAlH$_4$ · NEt$_3$]$_2$, similar dissociation has been observed in a crystal under X-ray irradiation [18].

The complex [(*tert*-C$_4$H$_9$)$_2$C$_5$H$_3$]$_2$YbAlH$_3$ · NEt$_3$ (IVa) in the solid state dissociates upon heating at 80°C in vacuum to give non-solvated ytterbocenes [(*tert*-C$_4$H$_9$)$_2$C$_5$H$_3$]$_2$Yb and alane (Eq. (3)). This is consistent with relatively weak Yb–H binding in this adduct in comparison with aluminohydride complexes of the trivalent ytterbocene, [Cp'$_2$YbAlH$_4$NEt$_3$]$_2$ [9]. The latter commences to decompose above 110°C, at first losing an amine molecule followed by complete decomposition of the AlH$_4$ group [9]. Heating the complex (C$_5$Me$_5$)$_2$YbAlH$_3$NEt$_3$ (IIIa) to 95°C does not lead to

its dissociation to metallocene and alane. However, at elevated temperatures the triethylamine is released and a black insoluble solid is formed as the complex decomposes. The difference in thermal behavior of the complexes III and IV may be related to the difference in electronic properties of the C_5Me_5 and (tert-$C_4H_9)_2C_5H_3$ ligands. In accordance with Ref. [19], C_5Me_5 ligands increase somewhat the electron density on the metal center, which may result in strengthening of the Yb–H linkage. However, other reasons for this strengthening are also possible since the relationship between the electronic properties of Cp' ligands and the strength of an M–X bond was found to be negligible [20].

$$Cp_2'Yb + AlH_3 \cdot L \xrightarrow[\leftarrow]{\text{vacuum, 80°C}} Cp_2'YbAlH_3 \cdot L$$
$$Cp' = (tert-Bu)_2C_5H_3$$

$$\xrightarrow{\text{toluene, 70–80°C}} (Cp_2'YbAlH_3)_n$$
$$Cp' = C_5Me_5, (tert-Bu)_2C_5H_3$$
$$(3)$$

Upon heating at 70–80°C in toluene solution, the complexes III and IV irreversibly lose a molecule of the Lewis base (Eq. (3)), but oxidation of Yb is still not observed. In the IR spectra of the products obtained after cooling and removal of the solvent in vacuum, there are no bands in the region $1700-2000\,cm^{-1}$, which might be attributed to the terminal Al–H bonds. A very broad band in $1650\,cm^{-1}$ can be definitely assigned to the numerous bridging Al–H bonds. In the proton NMR spectra of these materials, there are no signals corresponding to the Lewis base. On the basis of such data the most probable structure of those compounds appears to be polymeric. The similar processes of irreversible desolvation leading to polymerization have been previously described for the aluminohydride

complexes of trivalent lanthanides $[Cp_2LnAlH_4 \cdot L]_2$ (Ln = Y [21], Lu [22]).

2.2. Polymerization of styrene

The alane complexes of ytterbocenes were found to be moderately active for the polymerization of styrene performed in toluene, but addition of THF killed the polymerization. The results are summarized in Table 1. All of the polystyrene samples were quite atactic. The polydispersity indexes of the obtained polymers varied from 1.45 to 2.48, and molecular weights of the samples did not correlate with the conversion, being in the range $(100-170) \times 10^3$, indicating that the polymerization has no living character. The conversion of styrene never exceeded 68% (Fig. 1).

Runs 5–7 demonstrate the dependence of catalytic activity on the donor properties of the Lewis base to the Al atom. For the complexes IV(a–c), having the same cyclopentadienyl ligand but different L ligands, the activity increases from IVa to IVc, which correlates with decreasing donor power of the ligand from NEt_3 to Et_2O.

The activity of the investigated catalysts is extremely dependent on temperature. Thus, polymerization was practically non-existent at 0°C (run 8) but catalytic activity increased up to 65°C (runs 8, 7, 9). Above 65°C, the Et_2O complexes IIIc and IVc did not exhibit any catalytic activity (runs 4 and 11); only autopolymerization of styrene (run 12) was found under these conditions. The complex containing triethylamine (IVa) lost its activity at 80°C. These temperatures coincide with those of complex desolvation and their difference is in agreement with the lesser strength of the Al–OEt_2 bond compared with the Al–NEt_3 bond. Thus, the loss of activity at elevated temperatures can be explained by

Table 1
Polymerization conditions, activity and molecular weights for the polymerization of styrene by alane complexes of ytterbocenes [a]

Run	Catalyst	T (°C)	Conversion (%)	$M_n(\times 10^{-3})$ [b]	$M_w(\times 10^{-3})$ [b]	PDI
1	II	50	6	87.1	159.9	1.84
2	IIIc	25	15	46.5	83.8	1.80
3	IIIc	65	53	50.2	84.9	1.69
4	IIIc	70	2	22.3	41.7	1.87
5	IVa	25	8	135.3	240.0	1.77
6	IVb	25	11	102.8	200.7	1.95
7	IVc	25	21	156.7	226.8	1.45
8	IVc	0	5	79.7	176.0	2.21
9	IVc	65	66	170.3	342.7	2.01
10	IVa	70	27	162.5	402.9	2.48
11	IVc	70	2	18.9	54.5	2.88
12	—	70	2	19.2	66.7	3.38

[a] 50 ml toluene; [st] = 0.4 mmol ml^{-1}; st/cat(mol/mol) = 1000; time 60 h.
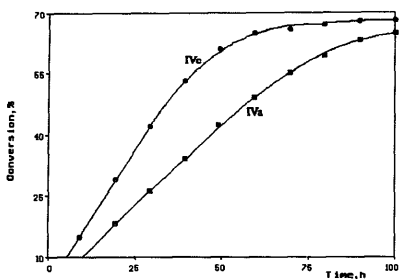[b] From GPC relative to polystyrene standards.

Fig. 1. Relation between styrene conversion and polymerization time for the complexes [(*tert*-Bu)$_2$C$_5$H$_3$]$_2$YbAlH$_3$·Et$_2$O (IVc) and [(*tert*-Bu)$_2$C$_5$H$_3$]$_2$YbAlH$_3$·NEt$_3$ (IVa) (50 ml of toluene; [st] = 0.4 mmol ml^{-1}; st/cat(mol/mol) = 1000; 65°C).

irreversible desolvation of the aluminium component leading to catalytically inactive polymeric structures.

The polymerization depends greatly on the electronic properties and/or the geometry of the Cp' ligand. Thus, the complexes containing C$_5$Me$_5$ were less active than their analogues having ^{t}C$_4$H$_9$ substituents and did not produce polystyrenes of high molecular weight (run pairs 2/7 and 3/9).

Besides styrene, such olefins as propylene, 1-hexene and cyclohexene were tested as monomers and co-monomers. These olefins did not polymerize by the complexes Cp$_2'$Yb·AlH$_3$·L and, moreover, the presence of these co-monomers completely suppressed the styrene polymerization.

2.3. Discussion of the polymerization mechanism

The catalytic action of divalent lanthanidocenes has been thoroughly studied in regard to the polymerization of different olefins [23,24]. In all those cases, the color of the catalytic system changed to yellow, which is typical for Ln(+3) complexes (Ln = Sm, Yb). The active species have been assumed to be trivalent metallocene complexes arising from oxidation of the lanthanide atom by olefins.
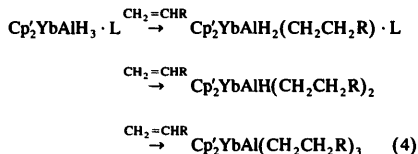
The monometallic complexes I and II slowly react with styrene to form yellow solutions of trivalent ytterbocene derivatives which reveal low activity in the polymerization (run 1), at a level nearly ten times less than that for the complex IVc (run 9). In contrast, none of the bimetallic systems investigated (III and IV) changed color during the course of polymerization. The active species are therefore considered to be heterometallic complexes containing the divalent lanthanide. If dissociation of bimetallic adducts occurred by the action of monomer and the catalytically active

species were monometallic, we would observe the same color change in solution and the same values of activity as for I and II.

The most intriguing question is whether the aluminium component of catalysts remains in hydride form during the polymerization or preliminary hydrometalation leads to alkylaluminium derivatives. In order to elucidate the mode of alane participation in the described process, a reaction was performed in toluene–ether at 65°C with complex II:AlH$_3$·Et$_2$O:styrene ratios of 1:100:150. Every 10 h of reaction, a 5 ml aliquot (containing 0.1 mmol of Al) of the reaction mixture was hydrolyzed by acidified methanol and analyzed by GC/MS for ethylbenzene. It is worth noting that no high molecular weight polystyrene was formed under these conditions; only autopolymer traces were found. Noticeable amounts of C$_6$H$_5$C$_2$H$_5$ in the hydrolyzed samples appeared after ca. 30 h of reaction (Fig. 2). This time nearly corresponds to the linear section termination of the complex [(*tert*-C$_4$H$_9$)$_2$C$_5$H$_3$]$_2$YbAlH$_3$·Et$_2$O kinetic curve (Fig. 1). After ca. 80 h of reaction, the amounts of ethylbenzene corresponded to almost complete conversion of AlH$_3$ to Al(CH$_2$CH$_2$Ph)$_3$. This period of time coincides with the point of polymerization stagnation (top curve in Fig. 1).

From this point of view, the suppression of styrene polymerization in the presence of linear olefins becomes explicable. The same experiment as described above was carried out at 25°C with complex II:AlH$_3$·Et$_2$O:hexene-1 ratios of 1:100:100. After 10 min of reaction, hydrolysis of aliquots gave n-hexane corresponding to 100% conversion of AlH$_3$ to Al(C$_6$H$_{13}$)$_3$.

Thus, alkylaluminium derivatives of divalent ytterbocenes do not promote the polymerization of styrene and their formation (Eq. (4)) is a reaction of the catalyst degradation. Before this process has begun, polystyrene can be precipitated with pentane or hexane and the transparent supernatant solution can be separated by decantation. Removal of alkane in vacuum results in a brown toluene–styrene solution of the catalyst which may be used again.

$$Cp_2'YbAlH_3·L \xrightarrow{CH_2=CHR} Cp_2'YbAlH_2(CH_2CH_2R)·L$$

$$\xrightarrow{CH_2=CHR} Cp_2'YbAlH(CH_2CH_2R)_2$$

$$\xrightarrow{CH_2=CHR} Cp_2'YbAl(CH_2CH_2R)_3 \quad (4)$$

The lower activity of C$_5$Me$_5$ containing complexes (III) in comparison with ^{t}Bu$_2$C$_5$H$_3$ containing analogues (IV) is in agreement with the data on the thermal behavior of these complexes and is likely consistent with the firmer Yb–H bonding in the complexes III.
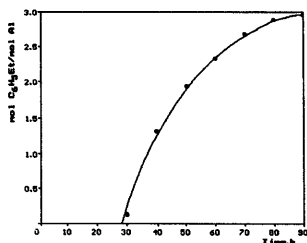
Fig. 2. Alkylation degree of the aluminium component as a function of time in the system [(tert-Bu)₂C₅H₃]₂Yb:AlH₃·Et₂O:styrene 1:100:150 (by GC/MS analysis of hydrolyzed samples).

The donor power of the ligand at the aluminium atom has a similar effect. Thus, a stronger Lewis base leads to a less electron-deficient YbH_2Al moiety and stronger Yb–H bonding. This explains the increasing polymerization rates in the series $NEt_3 < C_4H_8O < Et_2O$ (runs 5–7). Fig. 1 shows that the initial linear sections of the kinetic curves for the complexes [(tert-Bu)₂C₅H₃]₂YbAlH₃·NEt₃ (**IVa**) and [(tert-Bu)₂C₅H₃]₂YbAlH₃·Et₂O (**IVc**) are not parallel. This fact is obviously connected with the permanent participation of the aluminium component in polymer formation.

In accord with these data, the role of the aluminium component is (1) to form a bridging Yb–H bond readily accessible for olefin double bond insertion and (2) to create the necessary electronic situation in the coordination sphere of the transition metal atom for growth of the polymer chain. A similar approach to Ziegler–Natta catalysis was proposed earlier by Olivé and coworker [25], but is not widely recognized.

An NMR study of those systems is in progress and will be reported shortly.

3. Conclusions

Styrene polymerization induced by heterometallic alane complexes of divalent ytterbocenes represents an example of bimetallic catalysis in olefin polymerization. Two processes are possible in this system, namely polymer chain growth and alane component alkylation. The latter leads to catalyst deactivation arising from formation of inactive trialkylaluminium derivatives of divalent ytterbocene. Although these adducts are moderately active for styrene polymerization, they cannot be used for the polymerization of α-olefins because of rapid hydroalumination.

4. Experimental part

4.1. General considerations

All operations were performed under argon using standard Schlenk techniques. Styrene was washed twice with a 5% aqueous solution of KOH, five times with water, then dried over Na_2SO_4, CaH_2 for four days and 3 Å activated molecular sieves for a week. Finally, styrene was distilled over $LiAlH_4$ before use. Toluene, benzene, pentane and hexane were all washed with H_2SO_4, five times with water, then dried over $CaCl_2$ and further refluxed over $LiAlH_4$ for 3 h. Benzene and alkanes were distilled before use. Toluene was distilled from $LiAlH_4$, the distillate was refluxed over Na/K alloy for 3 h and afterwards distilled before use. Tetrahydrofuran was refluxed over KOH for 2 h, the distillate was refluxed with sodium benzophenone ketyl until the solution became violet, the distillate was refluxed over Na/K alloy and was distilled before use. Diethyl ether and NEt_3 were distilled over $LiAlH_4$ before use. Deuterated solvents were distilled over LiD before use. $AlCl_3$ was twice sublimed in a sealed tube. Alanes were prepared by the Schlesinger reaction [26] and were used as solutions in benzene ($AlH_3·NEt_3$, $AlD_3·NEt_3$, $AlH_3·THF$) or in ether ($AlH_3·Et_2O$). ¹H NMR spectra were recorded on a Varian Gemini-200 spectrometer (200 MHz). IR spectra (suspension in Nujol) were recorded in the $400–4000 \, cm^{-1}$ region with a UR-20 spectrophotometer. Gel permeation chromatographic analyses were run on a Hewlett-Packard 1050 using 10⁵Å, 10⁴Å and 10Å Styragel columns in THF. GC/MS analyses were run on a Hewlett-Packard 5890 chromatograph using capillary columns Ultra 2 (0.2 mm × 25 m) and a Hewlett-Packard 5971 mass spectrometer as detector. The molecular weights of polymers were determined using polystyrene standards.

4.2. Synthesis of (C₅Me₅)₂Yb·THF (I)

$(C_5Me_5)_2Yb·THF$ (**I**) was prepared as previously described [14].

4.3. Synthesis of [(tert-C₄H₉)₂C₅H₃]₂Yb·THF (II)

To the gray–green suspension of YbI_2 (31 mmol; obtained from Yb powder (5.900 g, 34.1 mmol) and I_2 (7.868 g, 62 mmol)) in THF (200 ml) a solution of [(tert-C₄H₉)₂C₅H₃]Na [27,28] (65 mmol) in THF (100 ml) was slowly added with vigorous magnetic stirring. The mixture became dark green immediately. The solution was stirred overnight and THF was further removed under vacuum. The residue was extracted with 200 ml of pentane and the residue of NaI and Yb was removed by filtration. Evaporation of the solvent gave a green solid which was dried in vacuum at 70 °C for 5 h

to yield 14.885 g (91%) of **II**. Anal. Found: C, 60.83; H, 8.30; Yb, 30.75. $C_{30}H_{50}OYb$ Calc.: C, 60.07; H, 8.40; Yb, 30.45%.

¹H NMR (THF-d_8, δ ppm): 6.20 d (2H, J_{H-H} = 2.6 Hz), 5.70 tr (1H, J_{H-H} = 2.5 Hz), 1.34 s (18H).

¹H NMR (toluene-d_8, δ ppm): 6.17 d (2H, J_{H-H} = 2.5 Hz), 5.74 tr (1H, J_{H-H} = 2.5 Hz), 3.65 br s (4H), 1.40 s (22H).

IR (Nujol, KBR cm⁻¹): 1600, 1420, 1380, 1305, 1250, 1225, 1200, 1170, 1140, 1085, 1075, 1050, 1020, 925, 890, 875, 840, 825, 805, 790, 750, 730, 695, 665, 485.

4.4. Preparation of heterometallic alane complexes of ytterbocenes

All the procedures of preparation were similar to those described for [$(tert$-$C_4H_9)_2C_5H_3]_2$YbAlH₃ · NEt₃ (**IVa**) and were as follows.

To the green solution of **II** (0.6 g, 1 mmol) in 50 ml of toluene was added dropwise 2 ml of benzene solution of AlH₃NEt₃ (1 mmol) with magnetic stirring. The color of the solution immediately changed to green–brown. The resulting solutions were used in the polymerization of styrene. Lyophilization of frozen solutions gave a brown amorphous solid.

¹H NMR (toluene-d_8, δ ppm): 5.95 br d (2H), 5.58 br tr (1H), 2.61 br q (6H, NCH₂CH₃), 1.18 s (18H), 1.05 s (9H, NCH₂CH₃).

IR (Nujol, KBR cm⁻¹): 1800, 1660, 1420, 1380, 1305, 1250, 1225, 1200, 1170, 1140, 1085, 1075, 1050, 1020, 925, 890, 875, 840, 825, 805, 780, 750, 730, 695, 665, 485.

4.5. Transformation of heterometallic alane complexes of ytterbocenes

Brown **IVa** (0.536 g, 0.854 mmol) was placed in a standard 50 ml Schlenk flask fitted with a cold finger (−78 °C). The system was evacuated to 5×10^{-3} torr and then heated to 80 °C for 1 h. The cold finger carrying 0.100 g (0.762 mmol) of AlH₃ · NEt₃ was removed under argon and the resulting light-green solid was identified as [$(tert$-$C_4H_9)_2C_5H_3]_2$Yb (0.530 g, 0.850 mmol). Anal. Found: C, 59.41; H, 8.35; Yb, 32.12. $C_{26}H_{42}$Yb Calc.: C, 59.18; H, 8.02; Yb, 32.79%.

¹H NMR (toluene-d_8, δ ppm): 6.23 d (2H, J_{H-H} = 2.5 Hz), 5.90 tr (1H, J_{H-H} = 2.5 Hz), 1.25 s (18H).

IR (Nujol, KBR cm⁻¹): 1610, 1420, 1380, 1315, 1250, 1225, 1190, 1170, 1140, 1085, 1075, 1050, 1010, 875, 840, 825, 805, 790, 760, 730, 695, 665.

The green–brown solution of **VIa** was heated to 80 °C for 30 min. During this period the solution slowly became dark brown. The mixture was allowed to cool down and toluene was removed under vacuum. The resulting dark-brown solid was identified as [$(tert$-

$C_4H_9)_2C_5H_3]_2$YbAlH₃. Anal. Found: C, 56.15; H, 8.21; Yb, 30.90; Al, 4.82. $C_{26}H_{45}$YbAl Calc.: C, 55.99; H, 8.13; Yb, 31.03; Al, 4.88.

¹H NMR (toluene-d_8, δ ppm): 6.05 br d (2H), 5.70 br tr (1H), 1.21 s (18H).

IR (Nujol, KBR cm⁻¹): 1650, 1420, 1380, 1305, 1250, 1225, 1200, 1170, 1140, 1085, 1075, 1050, 1020, 875, 840, 825, 805, 780, 750, 730, 695, 665.

4.6. Polymerization of styrene initiated by heterometallic ytterbocenes

The procedures were as follows. To a toluene solution (50 ml) of styrene (20 mmol) was added at once a toluene solution (2 ml) of one of the complexes **III** or **IV** (0.02 mmol) with vigorous magnetic stirring at the required temperature. After the solution was held for 60 h at this temperature the polymerization was quenched with acidified methanol. The resulting polymer was twice precipitated from CH₂Cl₂ into methanol and dried at 65 °C in vacuum. The polymer microstructure was characterized by ¹H and ¹³C NMR.

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