Group 3 and 4 metal alkyl and hydrido complexes containing a linked amido-cyclopentadienyl ligand: "constrained geometry" polymerization catalysts for nonpolar and polar monomers

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Abstract

In order to understand the nature of the putative cationic 12-electron species $[M(\eta^5:\eta^1-C_5R_4SiMe_2NR')R'']^+$ of titanium catalysts supported by a linked amido-cyclopentadienyl ligand, several derivatives with different cyclopentadienyl C_5R_4 and amido substituents R' were studied systematically. The use of tridentate variants $(C_5R_4SiMe_2NCH_2CH_2X)^{2-}$ $(C_5R_4 = C_5Me_4, C_5H_4, C_5H_3{}^tBu; X = OMe, SMe, NMe_2)$ allowed the NMR spectroscopic observation of the titanium benzyl cations $[Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2X)(CH_2Ph)]^+$. Isoelectronic neutral rare earth metal complexes $[Ln(\eta^5:\eta^1-C_5R_4SiMe_2NR')R'']$ can be expected to be active for polymerization. To arrive at neutral 12-electron hydride and alkyl species of the rare earth metals, we employed a lanthanide tris(alkyl) complex $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Y, Lu, Yb, Er, Tb), which allows the facile synthesis of the linked amido-cyclopentadienyl complex $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$. Hydrogenolysis of the linked amido-cyclopentadienyl alkyl complex leads to the dimeric hydrido complex $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$. These complexes are single-site, single-component catalysts for the polymerization of ethylene and a variety of polar monomers such as acrylates and acrylonitrile. Nonpolar monomers such as α-olefins and styrene, in contrast, give isolable mono-insertion products which allow detailed studies of the initiation process. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Single-site polymerization catalysts; Polar monomer polymerization; Alkyl complexes; Hydride complexes; Amido ligands

1. Introduction

In the late 1980s Bercaw and co-workers [1] introduced the linked amido-cyclopentadienyl ligands with the single-site, single-component catalysts $[Sc(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)X]$ (X = H, alkyl). These electronically more unsaturated and sterically more accessible 12-electron analogs of *ansa*-scandocene complexes $[Sc(\eta^5-C_5Me_5)_2X]$ were found to be capable of initiating the living oligomerization of the α-olefins propylene, 1-butene, and 1-pentene. In these complexes the steric constraint [2] of Brintzinger-type *ansa*-metallocenes is alleviated by the replacement of one 5-electron cyclopentadienyl ligand by a 3-electron amido ligand NR'. To explore sterically demanding derivatives of this novel dianionic ligand $(C_5R_4ZNR')^{2-}$, iron and titanium complexes were synthesized shortly thereafter [3]. Based on these

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bridged amido-cyclopentadienyl ligands, a flurry of development occurred independently in the research laboratories of Dow Chemical and Exxon Chemical and culminated in their patent applications filed within two weeks of each other in 1990 [4]. The great interest in the group 4 metal complexes containing the linked amido-cyclopentadienyl ligand stems from their unprecedented potential as a new generation of homogeneous olefin polymerization catalysts (so-called "constrained geometry catalyst") [5]. In particular, the possibility of producing ethylene copolymers with new rheological properties and good processability at high temperatures, has stimulated intense activity in synthesizing and testing such complexes [6]. Efficient copolymerization of ethylene with bulky monomers such as 1-alkene [6a,6b], styrene [6c], norbornene [6d], and even isobutylene [6e] became possible when methylaluminoxane (MAO)- and $B(C_6F_5)_3$-activated group 4 metal catalysts based on linked amido-cyclopentadienyl ligand $(C_5R_4SiMe_2NR')^{2-}$ were used. We summarize here our efforts at establishing structure–activity relationships for this class of catalysts and at expanding the applicability of the linked amido-cyclopentadienyl ligand to rare earth metals other than scandium.

2. Results and discussion

2.1. Titanium alkyl cation formation and ethylene polymerization

In contrast to the 14-electron group 4 metallocenium polymerization catalysts $[M(\eta^5\text{-}C_5R_5)_2R'']^+$, but in analogy to Bercaw's scandium catalysts $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)X]$, the 12-electron alkyl cation of the type $[M(\eta^5:\eta^1\text{-}C_5R_4ZNR')R'']^+$ is thought to be the active species for the group 4 metal linked amido-cyclopentadienyl catalysts [7]. It can be generated either by the treatment of the dichloride $[M(\eta^5:\eta^1\text{-}C_5R_4ZNR')Cl_2]$ with MAO, or by the reaction of a dialkyl complex $[M\eta^5:\eta^1\text{-}C_5R_4ZNR')R''_2]$ with a Lewis acid such as $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$. Activity–structure relationships [5] indicate that these catalysts form, depending on the nature of the ligand framework, high-molecular weight polyethylene with long-chain branching, resulting from the incorporation of oli-

Table 1
Ethylene polymerization by MAO-activated titanium catalysts[a]

Catalyst precursor	Activity (kg PE/mol Ti h mol/l)
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^iPr)Cl_2$	100
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2CH_2N^iPr)Cl_2$	330
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Cl_2$	950
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2CH_2N^tBu)Cl_2$	1320
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NAd)Cl_2$	460
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2Ph)Cl_2$	3090
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2CH_2NCH_2Ph)Cl_2$	120
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2CH_2^tBu)Cl_2$	72
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Ph)Cl_2$	54
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2Ph)Cl_2$	15
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$	12
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2NMe_2)Cl_2$	53
$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2SMe)Cl_2$	265

[a] Polymerization conditions: ethylene 3 bar, cat. 25 µmol/l in toluene, Ti:Al(MAO) molar ratio 1:500, reaction time 2 h, temperature 23 °C.

goethylene chains formed by β-hydride elimination. Also, superior properties as copolymerization catalysts were recognized, allowing efficient and uniform incorporation of higher α-olefins such as 1-octene [6].

The pronounced ability of these catalysts to incorporate bulky monomers can be ascribed to their coordination sphere being sterically more open than that of conventional metallocene systems. The nature of the ligand substituents R in the C_5R_4 ring, R' of the amido substituent NR', and the length of the bridge Z was found to influence the catalytic activity. Since catalyst precursors with the short bridge $Z = SiMe_2$ were found to give the best polymerization characteristics, the bite angle of the chelating ligand (angle Cp(centroid)–Ti–N) was proposed to be a crucial geometrical criterion for a catalyst to perform well ("constrained geometry catalysts") [8]. However, there is still no transparent universal structure–activity relationship and we and others [8] have noticed that the activity values for ethylene polymerization are also remarkably sensitive to the nature of the amido substituent R' (Table 1) [9].

As confirmed by several authors, the *tert*-amido substituent invariably gives the highest activity, although the benzyl cation $[Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2Ph)]^+$ $[PhCH_2B(C_6F_5)_3]^-$ was reported to be not detectable. Careful experimentation revealed that the thermal instability of the benzyl cation

is indeed dramatically dependent on the nature of the amido substituent NR′. When the titanium dibenzyl complexes [Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$-CH$_2$X)(CH$_2$Ph)$_2$] (X = OMe, NMe$_2$) were reacted with equimolar amounts of B(C$_6$F$_5$)$_3$ in bromobenzene at room temperature, the clean formation of [Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$CH$_2$NMe$_2$)(CH$_2$Ph)]$^+$ [PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ stable for several hours, was observed. On the basis of NMR spectroscopic evidence, we assume a solvent-separated ion pair rather than a contact ion pair (**B** favored over **A** in Scheme 1). The anion shows ^{19}F NMR spectroscopic features that indicate a free [PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ ion [10]. The methylene protons of the benzyl group bonded to the boron appear at δ 3.27 as a broad singlet and all aromatic protons are recorded well below δ 6.5, excluding the possibility of any strong interaction of the aromatic ring with the cationic metal center. There is no evidence for agostic or dihapto bonding of the benzyl group attached to the cationic titanium center [11]. From NMR spectroscopic evidence, including variable-temperature NMR spectroscopy, the

side-chain is assumed to be engaged in fluxional ("weak") bonding at room temperature without halting the nitrogen inversion. Apparently the strongly electrophilic, formally 12-electron cation is sufficiently stabilized by this mode of fluxional coordination.

Polymerization of ethylene and 1-hexene was observed with these cations, but with erratic, irreproducible results. We therefore set out to study the ethylene polymerization using MAO-activated [Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$CH$_2$X)Cl$_2$] (X = Ph, NMe$_2$, OMe, SMe). Compared to similar complexes containing the bidentate ligand such as the prototypical [Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$N^{t}Bu)Cl$_2$] under identical conditions, it is evident that the side-chain modification results in significantly lower activities (12 vs. 950 kg polyethylene/mol Ti h) [12]. We ascribe this to the occupation of one additional site at the metal that blocks the π-complex formation of ethylene. When the titanium catalysts with the softer donor group [Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$CH$_2$SMe)Cl$_2$]/MAO were studied, the activity of this thioether derivative was increased (by a factor of over 20 compared with
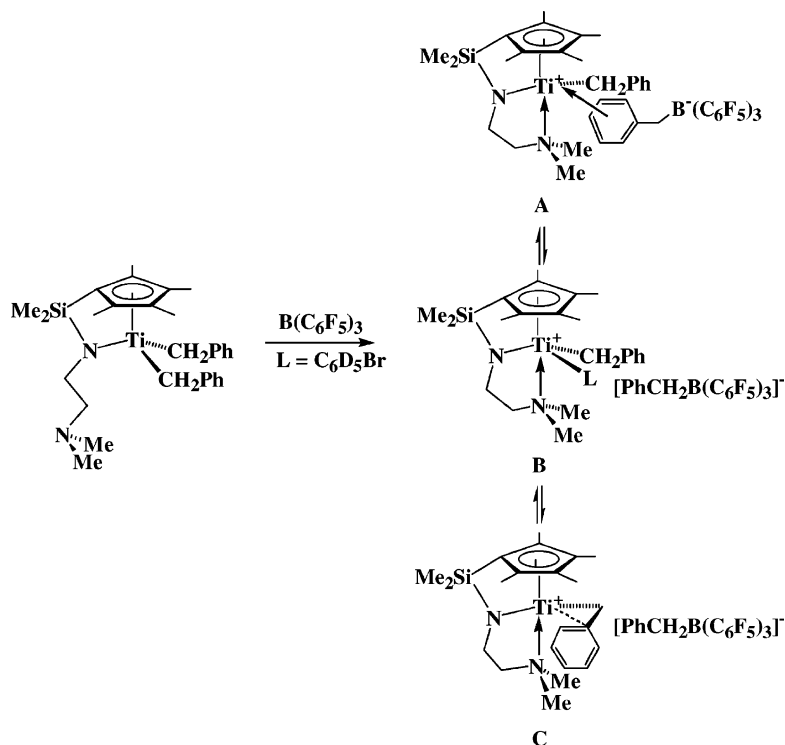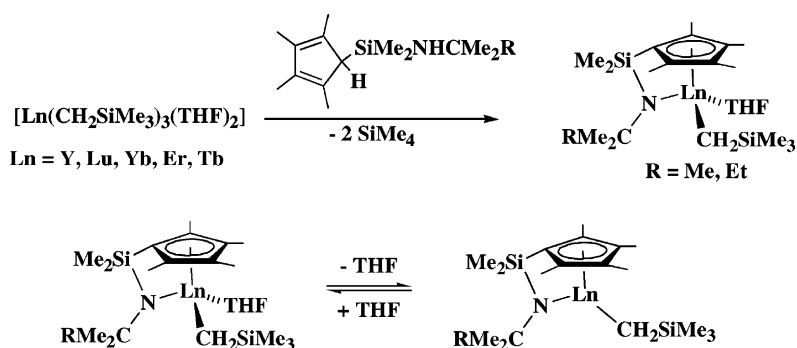

Scheme 1.

the ether-functionalized system), in agreement with weaker bonding of the donor group at the hard cationic titanium center [13]. Such a "mismatched" hard–soft interaction appears to be particularly well suited to stabilize an electrophilic metal center.

## 2.2. Rare earth metal catalysts and polar monomer polymerization

Isoelectronic neutral 12-electron hydride and alkyl species of group 3 metals are expected to be active for polymerization without any cocatalysts, as was already shown for Bercaw's scandium complexes $[Sc(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(PMe_3)(\mu-H)]_2$ and $[Sc(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(\mu-CH_2CH_2R)]_2$ [1]. We were interested in finding out whether the homologous complexes with the larger rare earth metals would lead to more active single-component polymerization catalysts. Conventional synthesis of mono(cyclopentadienyl) rare earth complexes $[Ln(\eta^5-C_5R_5)X_2(L)_n]$, where at least one X ligand is a hydride or an alkyl, is often hampered by ate-complex formation due to the high Lewis acidity and electrophilicity of the rare earth metal center [14]. A further complication lies in the uncontrolled formation of the thermodynamically more stable metallocene derivatives [15]. Thus, σ-bond metathesis of an appropriate cyclopentadiene derivative, in particular of a linked amido-cyclopentadiene $(C_5R_4H)SiMe_2NHR'$ [3a,6f,6g], and a lanthanide alkyl appeared to be a highly attractive synthetic pathway for the preparation of lanthanide complexes with only one supporting ring ligand [16].

To circumvent the problems associated with salt metathesis, we employed a lanthanide tris(alkyl) complex $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Y, Lu, Yb, Er, Tb), which allows the facile synthesis of the linked amido-cyclopentadienyl complex $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ under mild conditions in high yield (Scheme 2). These alkyl complexes are rather sensitive and cannot be stored for prolonged periods of time [17]. The choice of $[Ln(CH_2SiMe_3)_3(THF)_2]$, which is significantly more reactive than $[Ln\{CH(SiMe_3)_2\}_3]$, was a trade-off against the problematic presence of THF which is fortunately highly labile [17]. Hydrogenolysis of the linked amido-cyclopentadienyl alkyl complex cleanly leads to the dimeric hydrido complex $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$ (Scheme 3).

The diamagnetic hydrido complexes of yttrium and lutetium were fully characterized by X-ray diffraction in the solid state and by variable-temperature NMR spectroscopy in solution. They are highly fluxional with respect to THF dissociation, monomer–dimer equilibrium, and rotation about the metal–metal axis. Two diastereomers can be detected at lower temperatures. The presence of the monomeric species can be inferred from various scrambling reactions [17b]. Thus, mixing a benzene solution of $[Y(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$ with that of the lutetium analog $[Lu(\eta^5:\eta^1-C_5Me_4SiMe_2NC-Me_3)(THF)(\mu-H)]_2$ at room temperature instantaneously gave a statistical 1:2:1 mixture containing the homo and heterometallic complexes $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$ (Ln = Y, Lu)

Scheme 2.
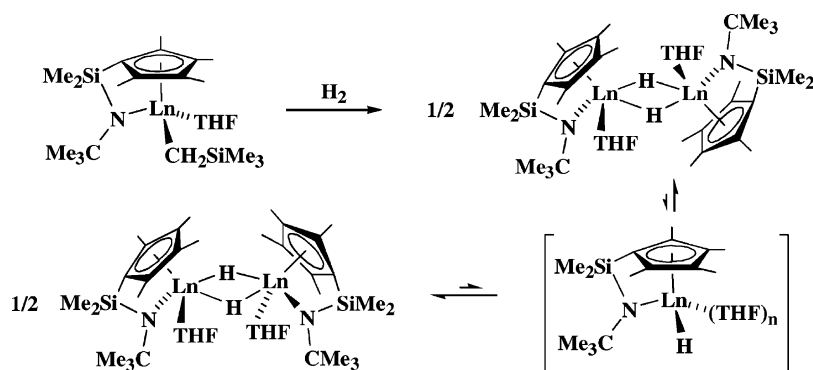
Scheme 3.

and [YLu(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)$_2$(THF)$_2$(μ-H)$_2$].

The hydrido complex [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NC-Me$_3$)(THF)(μ-H)]$_2$ smoothly reacts with a variety of olefinic substrates (Scheme 4). Ethylene undergoes sufficiently slow sequential insertion at low temperatures (<−30 °C) to give a mixture of *n*-alkyl complexes [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$){μ-(CH$_2$-CH$_2$)$_n$H}]$_2$, which can be independently synthesized by the reaction of the dimeric hydride with the even-carbon number 1-alkenes. Initially it was somewhat surprising that the crystals obtained from these reactions were THF-free. However, single-crystal

structural analyses of a series of *n*-alkyl complexes revealed the presence of a β-agostic interaction which appears to alleviate the high Lewis acidity of the rare earth metal center. Few related structures of *n*-alkyl complexes have been reported in the literature [18]. The THF-free dimeric alkyl complexes dissolve in THF or DME to give the monomeric *n*-alkyl complex [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$){(CH$_2$CH$_2$)$_n$H}-(THF)].

Whereas ethylene is slowly polymerized by the hydrido complex at room temperature to give linear polyethylene (T_m = 136 °C), none of α-olefins, dienes, or styrene are polymerized. In all these cases stable
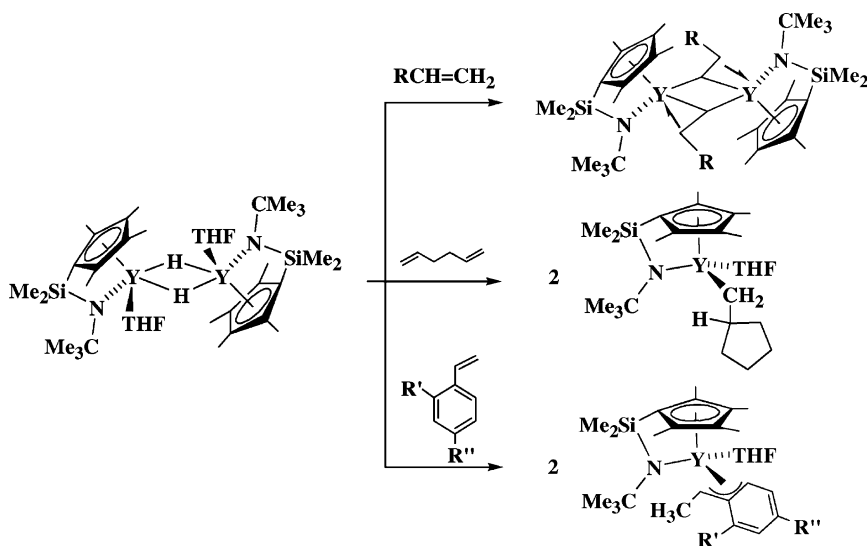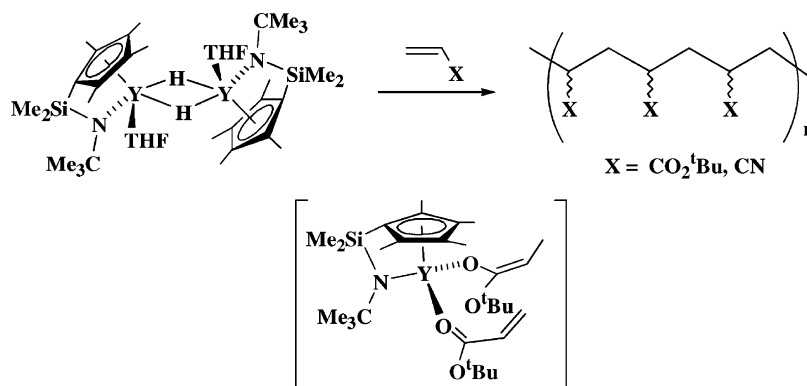
Scheme 4.
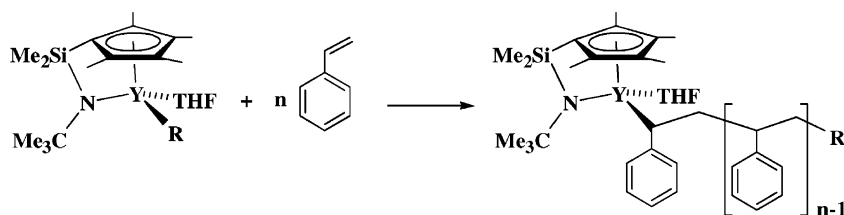
Scheme 5.

mono(insertion) products can be isolated. In particular, styrenes with not more than one *ortho*-substituent give bright yellow 1-phenethyl complexes. An X-ray diffraction study of [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_2$ − Et)(CHMeC$_6$H$_4$^{t}Bu-4)(THF)] confirmed that the insertion occurred in a Markovnikov(2,1)-fashion and that the phenyl ring is engaged in a dynamic η^3-coordination. Variable-temperature NMR spectroscopy further revealed fluxional behavior that includes THF dissociation, phenyl ring coordination, and rotation about the *ipso-* and α-carbon atom. These results are relevant to the mechanism of syndiospecific styrene polymerization by mono(cyclopentadienyl)-titanium complexes [19].

The polymerization of styrene, however, cannot be initiated efficiently by the hydrido complex or the styrene insertion product, probably because the THF present in the resulting mono(insertion) complex cannot be displaced by the weakly bonding styrene. However, the *n*-alkyl complex [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$){(CH$_2$CH$_2$)$_n$H}(THF)] polymerizes styrene in a controlled manner to give atactic polystyrene

with low polydispersity (Scheme 5). Thus, 50 equiv. of styrene gives polystyrene with $M_n = 24\,100$ and $M_w/M_n = 1.10$; $mm = 0$, $mr = 29.5$, $rr = 70.5\%$. This polymerization is sufficiently controlled to allow diblock copolymerization, although only a fraction of the yttrium complex appears to be active (efficiency 21%).

The yttrium hydrido complex [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)(THF)(μ-H)]$_2$ as well as the alkyl complex [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)(CH$_2$SiMe$_3$)(THF)] are found to polymerize the polar monomers *tert*-butyl acrylate and acrylonitrile (Scheme 6). *tert*-Butyl acrylate is polymerized at temperatures as low as −30 °C (i.e., well below the decomposition temperature of the complexes) to give poly(*tert*-butyl acrylate) in high yields and with molecular weights $M_n > 20\,000$ and efficiencies of 19 to 61%. The molecular weight distributions of the resulting polymers are in the range of $M_w/M_n = 1.5$–2.0 and the polymer microstructure as determined by ^{13}C NMR spectroscopy is predominantly atactic (Table 2).

Scheme 6.

Table 2

Polymerization of *tert*-butyl acrylate by [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)(CH$_2$SiMe$_3$)(THF)] (runs 1–3) and [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)-(THF)(μ-H)]$_2$ (run 4)[a]

Run no.	t (h)	T (°C)	$[M_0]/[Y]$	Yield (%)	M_n	M_w	M_w/M_n
1	2	25	95	85	24900	38900	1.56
2	18	−30	79	98	30000	59000	1.97
3	18	−30	201	90	38100	61200	1.61
4	3	25	181	11	13200	22300	1.69

[a] Polymerization conditions: 25 μmol of yttrium complex, 5 ml of toluene.

Table 3

Polymerization of acrylonitrile by [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)(CH$_2$SiMe$_3$)(THF)] (runs 1–3) and [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)-(THF)(μ-H)]$_2$ (run 4)[a]

Run no.	t (h)	T (°C)	$[M_0]/[Y]$	Yield (%)	M_n	M_w	M_w/M_n
1	18	25	152	43	5700	30600	5.4
2	16	25	328	24	4500	59000	8.2
3	48	−30	198	48	4200	11300	27
4	24	25	185	24	6700	94000	14

[a] Polymerization conditions: 12 μmol of yttrium complex, 5 ml of toluene.

Recently, Collins and co-workers [20] reported the isospecific polymerization of methyl methacrylate by a cationic zirconium enolate complex supported by the linked *tert*-butylamido-cyclopentadienyl ligand, [Zr(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$){OC(OR) = CMe$_2$}-(L)]$^+$, which obviously is isoelectronic with our yttrium initiating system. Therefore, the group-transfer mechanism, already well-established for the lanthanocene systems [21], appears to be plausible for the mechanism of the acrylate polymerization by the complexes [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)(THF)-(μ-H)]$_2$ and [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)(CH$_2$Si-Me$_3$)(THF)].

When acrylonitrile is added to a toluene solution of the hydride complex, an intense red solution develops and the precipitation of yellow atactic poly(acrylonitrile) soon follows. This unusual color is ascribed to an intramolecular charge-transfer band of an f^{0}d^0-complex to an electron acceptor. According to GPC results, the poly(acrylonitrile) samples exhibit molecular weights in the range of 10^4, but broad, multimodal molecular weight distributions of $M_w/M_n > 5$ (Table 3), probably due to the formation of precipitates. For the mechanism of the acrylonitrile polymerization, we propose a group-transfer-type polymerization related to that for the *tert*-butyl acrylate polymerization, involving a keteniminato intermediate [21]. However, when the yttrium hydrido complex [Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_3$)(THF)(μ-H)]$_2$ is treated with 1 equiv. of acrylonitrile at −78 °C, a mixture of what appears to be *cis*- and *trans*-isomers of dimeric μ-vinylimido complexes is obtained (Scheme 7). Obviously, the methyl keteniminato complex, the product of 1,4-addition, is not detectable, but
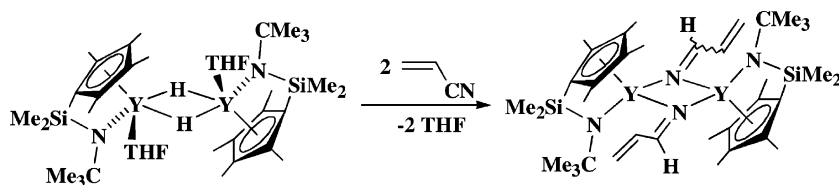
Scheme 7.

its tautomers resulting from 1,2-addition is formed. Nonetheless, this compound is capable of initiating the polymerization of acrylonitrile.

3. Conclusion

In conclusion, we have shown that hydrido and alkyl complexes of yttrium, $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ and $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\text{-}(CH_2SiMe_3)(THF)]$, supported by a linked amido-cyclopentadienyl ligand can be synthesized by the σ-bond metathesis reactions. They constitute isoelectronic analogs of the alkyl cations of group 4 metals $[M(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR')R'']^+$ which are conveniently studied by the introduction of the tridentate ligand system. The reactivity studies of the dimeric yttrium hydride $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ revealed a rich olefin insertion chemistry with structurally well-characterized mono(insertion) products. Efficient and controlled polymerization of styrene could be developed by the use of the monomeric n-alkyl complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{(CH_2CH_2)_nH\}(THF)]$. Similar to the samarocene initiators [21], rare earth metal complexes supported by a linked amido-cyclopentadienyl ligand appear to be promising polymerization initiators for both nonpolar and polar monomers. However, the challenge to develop a truly versatile catalysts/initiators for the copolymerization of nonpolar monomers with polar monomers still remains [22].

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