Rare earth alkoxides as inorganic precursors for olefin polymerization: an alternative to traditional lanthanocene chemistry

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The combination of the neodymium *tert*-butoxide [Nd$_3$(μ_3-OBu^t)$_2$(μ-OBu^t)$_3$(OBu^t)$_4$(THF)$_2$] 1 with 1 equivalent of a dialkylmagnesium reagent affords an efficient catalyst for the pseudo-living polymerization of ethylene.

Trivalent rare earth metal hydrides and alkyl complexes stabilized by two cyclopentadienyl-type ligands, Cp$_2$LnR have attracted much attention because of their high efficiency in polymerizing ethylene.[1] Currently, there is considerable interest in developing related organolanthanide complexes involving ancillary ligands other than the commonly used Cp-type ligands. In this respect, hard, electronegative ligands such as alkoxides are particularly attractive because they offer strong metal–oxygen bonds that are expected to stabilize complexes.[2] Although the mixed Cp*–aryloxide system [Y(C$_5$Me$_5$)(OC$_6$H$_3$-Bu$^t_2$-2,6)(η-H)]$_2$ has been shown to be active for the polymerization of α-olefins,[3] no equivalent Cp-free alkoxy catalyst system had been developed to date.[4] We report here that some lanthanide *tert*-alkoxides are efficient inorganic precatalysts, when combined with dialkylmagnesium compounds, for the pseudo-living polymerization of ethylene and ethylene–MMA block copolymerization.

The reaction of NdCl$_3$ with 3 equiv. of NaOBu^t in THF at 25 °C for 3 days gives a single primary product 1, that can be isolated in 80–90% yield as a very air-sensitive compound. An X-ray crystallographic study revealed that 1 is a trimetallic compound with the formula [Nd$_3$(μ_3-OBu^t)$_2$(μ-OBu^t)$_3$(OBu^t)$_4$(THF)$_2$] (Fig. 1).[5] Some lanthanum analogues isostructural to 1 have been reported: La$_3$(OBu^t)$_9$(THF)$_2$ 2, prepared by ionic metathesis,[6] and [La$_3$(μ_3-OBu^t)$_2$(μ-OBu^t)$_3$(OBu^t)$_4$(HOBu^t)$_2$] 3, obtained by alcoholysis of La{N(SiMe$_3$)$_2$}$_3$.[7] Com-plexes 2 and 3 are, however, respectively, much less efficient than 1 and totally inefficient for the polymerization catalysis described hereafter.

The addition of 1 equivalent of di(*n*-hexyl)magnesium to 1 in toluene solution at 0 °C offers an active catalyst for ethylene polymerization. The typical ethylene flow rate for a batch experiment conducted under 1.1 atm is shown in Fig. 2. The maximum consumption of ethylene, reached after a few minutes, corresponds to the appearance of insoluble polymer. The typical average catalytic activity calculated over 1 h on the basis of the amount of Nd initially introduced is *ca.* 10 g mmol^{-1} h^{-1} atm^{-1} at 0 °C. This places this new catalyst system on a moderate rate of effectiveness on Gibson's scale,[1d] and compares well to traditional alkyl–lanthanocenes under similar conditions. The Mg(*n*-hex)$_2$–1 system gives linear high density and highly crystalline (>80%) polyethylene (T_m = 139–141 °C) with M_n = (3–4) × 10^5 and M_w/M_n = 2.3–2.5. GPC analysis of aliquots revealed that the molecular weight and the polydispersity do not increase significantly during the reaction course. These results are tentatively ascribed to slow *in situ* catalyst generation, rapid propagation relative to the rate of initiation and/or concomitant heterogenezation due to precipitation of long-chain metal–alkyl species from solution. The monomodality of the GPC curves is, however, consistent with the generation of one type of active species. Progressive deactivation of the catalyst system was observed above 20 °C, resulting in lower productivities and formation of low molecular weight PE (*e.g.* at 80 °C: [a]$_{1h}$ = 0.6 g mmol^{-1} h^{-1} atm^{-1}, M_n = 1720, M_w/M_n = 1.55, 29% vinyl terminations).

When the polymerization was carried out at 0 °C in the presence of PhSiH$_3$ as a transfer agent[8] (10 equiv. *vs.* Nd), the activity profile and the productivity over 1 h were the same as those observed in the absence of this reagent. The polymer recovered after MeOH quenching and work-up was shown by ^{1}H and ^{13}C NMR to be end-capped PhSiH$_2$–polyethylene, with M_n = 14 300 and broad polydispersity (M_w/M_n = 25). Using 2% of H$_2$ in ethylene as an alternative transfer agent[9] resulted in
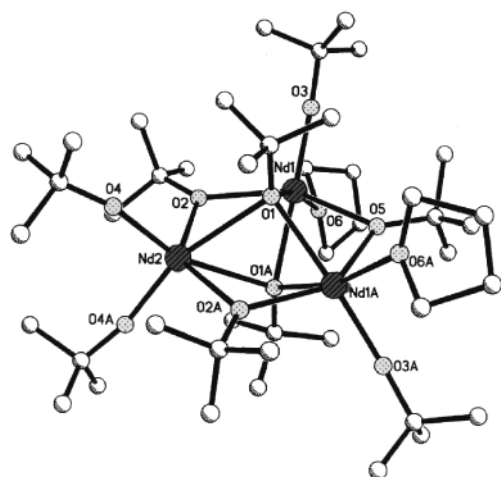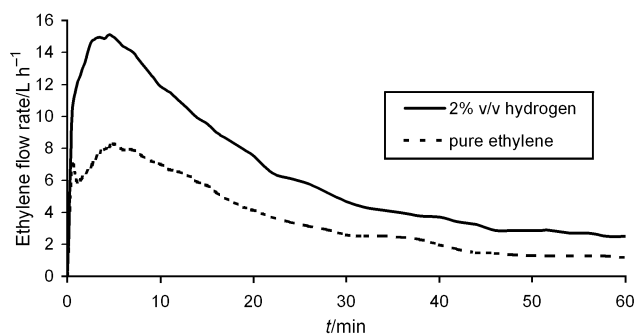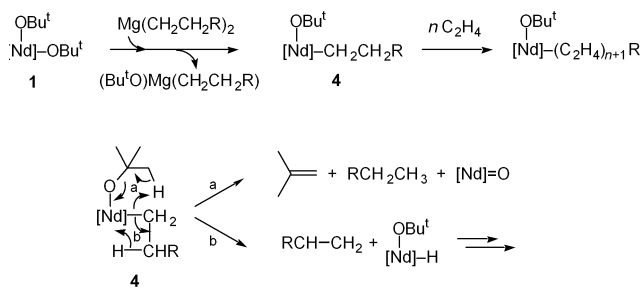

Fig. 1 Molecular structure of 1 in the crystal. Selected bond lengths (Å): Nd1–O3 2.147(4), Nd1–O2 2.333(3), Nd1–O5 2.399(3), Nd1–O1 2.409(3), Nd1–O1A 2.520(3), Nd1–O6 2.661(4), Nd1–Nd1A 3.6318(6), Nd1–Nd2 3.7161(4), Nd2–O4 2.163(3), Nd2–O2 2.458(3), Nd2–O1 2.624(3).

Fig. 2 Typical ethylene consumption plots observed with the 1–Mg(*n*-hex)$_2$ system with pure C$_2$H$_4$ and a 98∶2 v/v C$_2$H$_4$–H$_2$ mixture (0.33 mmol 1, 1.0 mmol Mg, 100 mL toluene, 0 °C, 1.1 atm ethylene kept constant).

$$\underset{\mathbf{1}}{[Nd]-OBu^t\ (OBu^t)} \xrightarrow[\text{(Bu}^t\text{O)Mg(CH}_2\text{CH}_2\text{R)}]{\text{Mg(CH}_2\text{CH}_2\text{R)}_2} \underset{\mathbf{4}}{[Nd]-CH_2CH_2R\ (OBu^t)} \xrightarrow{n\,C_2H_4} [Nd]-(C_2H_4)_{n+1}R\ (OBu^t)$$

$$\mathbf{4}\quad \begin{array}{l} \xrightarrow{a}\ \searrow\!\!=\!\!+ RCH_2CH_3 + [Nd]{=}O \\[4pt] \xrightarrow{b}\ RCH{-}CH_2 + [Nd]-H\ (OBu^t) \longrightarrow \end{array}$$

Scheme 1 Schematic presentation of proposed activation (up) and deactivation (down) pathways.

a *ca.* 25% increase in the catalyst productivity (Fig. 2) and formation of polyethylene with $M_n = 17\,000$ (constant value $\pm$ 500 for five samples collected every 10 min) and broad polydispersity ($M_w/M_n = 5.8$). In both cases, no end-group associable with conventional (*e.g.* β-H elimination) chain transfer processes was detected by NMR in the polymers. Further evidence for the pseudo-living character of the Mg(*n*-hex)₂–**1** catalyst system at 0 °C is provided by the possibility of achieving ethylene–MMA block copolymerization through initial homopolymerization of ethylene and sequential addition of MMA.[10]

All of these results support a polymerization mechanism for the present system similar to that established for traditional lanthanocenes. We assume that alkylation of **1** by the di-alkylmagnesium[11] *in situ* generates an active alkyl–Nd species **4** (Scheme 1). Preliminary NMR investigations of Mg(CH₂CH₂R)₂–**1** systems (R = H, Et, Bu) show the formation, at as low as −60 °C, of the corresponding alk-1-ene, RCH=CH₂, in 15–40% yield *vs.* Nd. This is consistent with the formation of an alkyl–Nd species **4** which further evolves, *e.g.* *via* β-H elimination (a). Also, the slow formation of isobutene in 2–40% yield *vs.* Nd with concomitant release of the alkane [clearly evidenced with SiMe₄ upon using Mg(CH₂SiMe₃)₂] supports the generation of **4** and indicates that *tert*-butoxy ligands are likely involved in the degradation of the active species (b).[12]

Among the large variety of alkylating reagents so far investigated in combination with **1**, only dialkylmagnesium derivatives, in particular those bearing long alkyl chains, led to appreciable ethylene polymerization activity. Best activities are obtained with 1.0 equiv. of MgR₂ *vs.* Nd, as deviation from this stoichiometry resulted in a rapid drop in catalytic activity. Other tris(alkoxy)lanthanide complexes have been investigated as precatalysts, among which some show similar properties but contrasting performances; *e.g.* the Sm^{III} *tert*-butoxide–Mg(*n*-hex)₂ system gives low molecular weight PE ($[a]_{1h} = ca.$ 2 g mmol^{-1} h^{-1} atm^{-1}, $M_n = 2500$, $M_w/M_n = 6.1$). On the other hand, alkoxylanthanide precursors such as **3** or its Nd equivalent, both prepared by alcoholysis of amide precursors, are totally inactive. In fact, alkoxy ligands having no hydrogen in the β-position, the absence of coordinated protic solvent and of chloro ligands, as well as structural constraints in the

nuclearity of the complex appear to be prerequisites for the successful development of these new-generation lanthanide catalysts.

Notes and references

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4 To our knowledge, only the dialkyl(aryloxy)yttrium complex (Me₃-SiCH₂)₂Y(OC₆H₃Bu$^t_2$-2,6)(THF)₂ shows (very low) ethylene polymerization activity [9 × 10^{-3} g mmol^{-1} h^{-1} atm^{-1} at room temp. (RT)]: W. J. Evans, R. N. R. Broomhall-Dillard and J. W. Ziller, *J. Organomet. Chem.*, 1998, **569**, 89; Sc complexes containing amide-diphosphane and triaza ligands, as well as benzamidinate yttrium complexes have been recently shown to polymerize ethylene with very low activity; see ref. 1(*d*).

5 *Crystal data*: C₄₄H₉₇O₁₁Nd₃, $M = 1234.92$, orthorhombic, space group *Pbcn*, $a = 17.0538(10)$, $b = 20.0343(12)$, $c = 17.7400(11)$ Å, $V = 6061.1(6)$ Å^3, $T = 158$ K, $Z = 4$, μ(Mo-Kα) = 2.581 mm^{-1}. 38059 reflections collected, 7315 unique. Hydrogen atoms were included using a riding model. The *tert*-butoxide ligand located on the two-fold axis and the THF ligand were disordered. The carbon atoms associated with these ligands were included using multiple components with partial site occupancy factors. There was also one disordered THF solvent molecule present per formula unit. Hydrogen atoms associated with the disordered *tert*-butoxide ligand and with the solvent molecule not included in the refinement. Final R values [$F > 2\sigma(F)$]: $R1 = 0.0410$, $wR2 = 0.1044$. CCDC 182/1798. See http://www.rsc.org/suppdata/cc/b0/b006941h/ for crystalographic files in .cif format.

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