

Binary Neodymium Alkoxide/Dialkylmagnesium Polymerization Systems: Studies on the Nature of the Reaction Intermediates and Active Species

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Attempts to identify the intermediates and/or active species generated from binary combinations of a lanthanide alk(aryl)-oxide with a dialkylmagnesium reagent, which behave as efficient olefin polymerization systems, are reported. The well-defined trinuclear complex $[\text{Nd}_3(\mu_3\text{-OtBu})_2(\mu_2\text{-OtBu})_3(\mu\text{-OtBu})_4(\text{THF})_2]$ (**1**) and the monomeric precursor $[\text{Nd}(\text{OC}_6\text{H}_2\text{tBu}_2\text{-2,6-Me-4})_3(\text{THF})]$ (**2**) were used in association with $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{Et}_2\text{O})]$ (**3**). The new heterodimetallic complex $[(\text{THF})\text{Nd}(\mu_3\text{-OtBu})_2(\mu_2\text{-OtBu})_2(\text{OtBu})\text{Mg}_2(\text{CH}_2\text{TMS})_2]$ (**4**) and the alkylanthanide complex

$[\text{Nd}(\text{OC}_6\text{H}_2\text{tBu}_2\text{-2,6-Me-4})_2(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ (**5**) have been isolated and characterized in the solid state and in solution. Complex **4** is proposed to be a reaction intermediate in the active species formation, while complex **5** is the first alkylanthanide species isolated from an "Ln(OR)₃₂ mixture, consistent with the observed behavior of these combinations in olefin polymerization.

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Introduction

We have recently described new versatile polymerization systems based on combinations of a neodymium alk(aryl)-oxide and a dialkylmagnesium reagent that enable the synthesis of original materials such as high molecular weight poly(ethylene-*b*-methyl methacrylate)^[1] and poly(butadiene-*b*-glycidyl methacrylate)^[2] diblock copolymers. For this purpose, the well-defined trinuclear complex $[\text{Nd}_3(\mu_3\text{-OtBu})_2(\mu_2\text{-OtBu})_3(\mu\text{-OtBu})_4(\text{THF})_2]$ (**1**) and the monomeric precursor $[\text{Nd}(\text{OC}_6\text{H}_2\text{tBu}_2\text{-2,6-Me-4})_3(\text{THF})]$ (**2**) were employed.

The active species formed in situ from these combinations act either as initiators with lanthanidocene-like properties, for example for ethylene^[1] and methyl methacrylate (MMA)^[3] controlled homopolymerizations, or as catalysts for 1,3-diene polymerization^[2] along with a fast, reversible transfer reaction to the magnesium centers. From this polymerization behavior, we anticipated that the active

species is likely to be a homonuclear alkylanthanide, or a related mixed alkyl-bridged lanthanide-magnesium species.^[1b,1c] Variable-temperature ¹H NMR monitoring experiments of mixtures of a dialkylmagnesium, for example $\text{Mg}(n\text{-Hex})_2$ or $n\text{BuMgEt}$, with **1** or **2** showed that fast reactions take place in the absence of monomer.^[1b] Complete conversion of the initial alk(aryl)oxides to unidentified species was observed at -70°C , followed upon raising of the temperature by the appearance of the corresponding 1-alkene (1-hexene, 1-butene; ethylene was immediately polymerized in situ), presumably arising from β -hydride elimination of a putative alkylneodymium species. The release of 1-alkene was observed at temperatures as low as -60°C with the *tert*-butoxide precursor **1** while a higher temperature, typically $0\text{--}20^\circ\text{C}$, was required for the aryloxide precursor **2**. As a consequence of this ready decomposition, a reaction product could only be isolated and fully characterized in the case of the $2/\text{Mg}(n\text{-Hex})_2$ combination — the alkylmagnesium aryloxide compound $[(n\text{-Hex})\text{Mg}(\text{OC}_6\text{H}_2\text{tBu}_2\text{-2,6-Me-4})_2]$, consistent with the envisioned transmetallation process.^[1b] Herein we report further studies of these binary polymerization systems, using $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{Et}_2\text{O})]$ (**3**) as a co-reagent, and the isolation and structural characterization of two intermediate alkylanthanide alk(aryl)oxide complexes.

Results and Discussion

To obtain a better understanding of these binary catalyst systems, we decided to concentrate our efforts on the iso-

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lation of the reaction intermediates and active species. For this purpose, the typical co-reagent $\text{Mg}(n\text{-Hex})_2$ used for polymerization and initial mechanistic studies was replaced by $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{Et}_2\text{O})]$ (**3**). The latter reagent, in combination with **1** or **2**, has been shown to also generate active polymerization systems towards ethylene, MMA and 1,3-dienes, with properties similar to those of combinations based on $\text{Mg}(n\text{-Hex})_2$, although somewhat less active.^[1b,2] The dialkylmagnesium **3** was selected to stabilize the corresponding alkylaluminum species, in particular by avoiding $\beta\text{-H}$ elimination reactions.^[4] Another potential advantage of **3** over $\text{Mg}(n\text{-Hex})_2$ and higher long-chain dialkylmagnesium reagents is the better propensity of the CH_2SiMe_3 moiety for crystallization.

Combinations of $[\text{Nd}_3(\text{OtBu})_9(\text{THF})_2]$ and $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{Et}_2\text{O})]$

Toluene solutions of **1** and **3** in various ratios were prepared and stored at low temperature (-30°C). When the reaction was performed in a 1:3 molar ratio (i.e. $\text{Nd}/\text{Mg} = 1$), as optimized for polymerization purposes, in the absence of additive, it was not possible to isolate any species from the resulting dark-brown solution. On the other hand, in the presence of THF (10 equiv. vs. Nd), the solution remained clear and blue. The ^1H NMR spectrum of the blue crystals grown from this solution is identical to the starting trinuclear alkoxide **1**, indicating that an excess of THF prevents the alkylation reaction from taking place. This fact is in direct line with the observed inactivity of the $1/\text{Mg}(n\text{-Hex})_2$ system in the presence of minute amounts of THF for ethylene polymerization.^[1b] Evans et al. have observed a similar phenomenon with their $[\text{Y}(\text{OtBu})_7\text{Cl}_2]/\text{AlMe}_3$ systems and assigned this lack of reactivity to the formation of the unreactive $[\text{AlMe}_3(\text{THF})]$.^[5]

Given the successful isolation by Yasuda et al. of an intermediate in lanthanidocene-based MMA polymerization^[6] and the efficient controlled syndiotactic polymerization of this monomer achieved with $1/\text{Mg}(n\text{-Hex})_2$,^[3] MMA (0.03 equiv. vs. Nd) was added to some crystallization experiments. Under those conditions, colorless crystals of $[(\text{Me}_3\text{SiCH}_2)\text{Mg}(\text{OtBu})(\text{THF})]$ (**5**) formed rapidly (15–20% isolated yield vs. Mg) in a reproducible manner, followed after a few weeks by pale-blue crystals of a neodymium complex (**4**; 30–40% yield vs. **1**) [Equation (1)]. As established by NMR spectroscopy and an X-ray diffraction analysis (Figure 1, Table 1), the product **4** corresponds to the new heterodimetallic complex $[(\text{THF})\text{Nd}(\mu_3\text{-OtBu})_2(\mu_2\text{-OtBu})_2(\text{OtBu})\text{Mg}_2(\text{CH}_2\text{SiMe}_3)_2]$, which obviously, however, does not contain any MMA. The neodymium center in **4** is hexacoordinate, as are most *tert*-butoxyneodymium derivatives,^[7] with six oxygen atoms in its environment, one terminal *tert*-butoxy ligand and a THF molecule. Doubly and triply bridging *t*BuO groups link the neodymium atom to the two tetracoordinate magnesium atoms, each of which bears an alkyl chain. Such segregation of the alkoxide and alkyl ligands in complex **4** can be correlated with the higher oxophilicity of Nd vs. Mg (bond disruption energies: $\text{Nd}-\text{O}$, $703 \pm 13 \text{ kJ}\cdot\text{mol}^{-1}$; $\text{Mg}-\text{O}$, $363 \pm 13 \text{ kJ}\cdot\text{mol}^{-1}$).^[8]

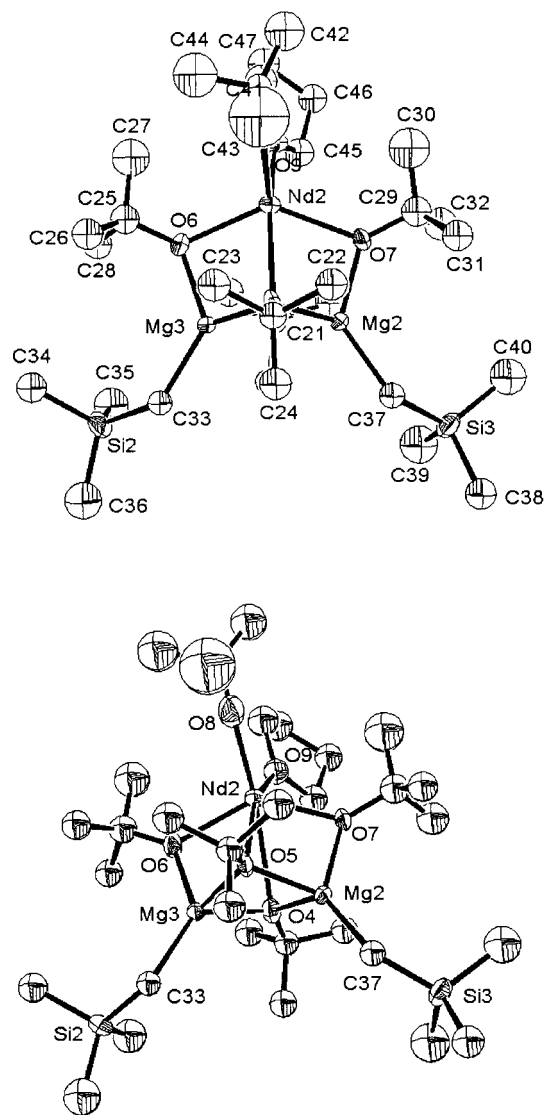
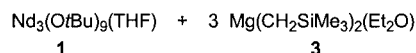


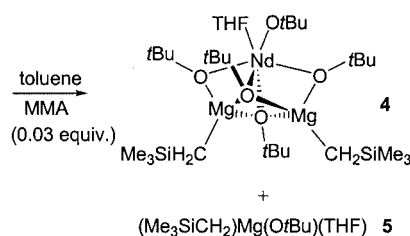
Figure 1. Two views of the molecular structure of $[\text{Nd}(\text{THF})(\mu_3\text{-OtBu})_2(\mu_2\text{-OtBu})_2(\text{OtBu})\text{Mg}_2(\text{CH}_2\text{SiMe}_3)_2]$ (**4**); ellipsoids are drawn at the 40% probability level and hydrogen atoms omitted for clarity

Several well-characterized aluminium-lanthanide alkyl-alk(aryl)oxide complexes have been described previously, most of which were prepared from the interaction of lanthanide alk(aryl)oxides with AlR_3 .^[9] Examples of heterodimetallic organometallic Ln-Mg complexes are much rarer and none of them contain alk(aryl)oxide ligands as in **4**.^[10]



1

3



(1)

Table 1. Selected bond lengths [Å] and angles [°] for **4**

Nd(2)–O(8)	2.241(6)	O(8)–Nd(2)–O(7)	109.5(2)
Nd(2)–O(7)	2.304(3)	O(8)–Nd(2)–O(6)	105.2(2)
Nd(2)–O(6)	2.307(4)	O(7)–Nd(2)–O(6)	135.0(1)
Nd(2)–O(9)	2.350(5)	O(8)–Nd(2)–O(9)	93.3(2)
Nd(2)–O(5)	2.600(4)	O(7)–Nd(2)–O(9)	99.6(1)
Nd(2)–O(4)	2.762(4)	O(8)–Nd(2)–O(5)	107.3(2)
Nd(2)–Mg(2)	3.178(2)	O(7)–Nd(2)–O(5)	71.4(1)
Nd(2)–Mg(3)	3.178(2)	O(8)–Nd(2)–O(4)	162.4(1)
Mg(2)–O(7)	1.984(4)	O(5)–Nd(2)–O(4)	55.3(1)
Mg(2)–O(4)	2.017(4)	O(7)–Mg(2)–O(4)	93.2(2)
Mg(2)–O(5)	2.046(4)	O(4)–Mg(2)–O(5)	75.6(2)
Mg(2)–Mg(3)	3.118(2)	O(6)–Mg(3)–C(33)	130.9(2)
Mg(3)–O(6)	1.974(4)	O(4)–Mg(3)–C(33)	127.9(2)
Mg(3)–O(4)	2.033(4)	O(5)–Mg(3)–C(33)	121.9(2)
Mg(3)–O(5)	2.040(4)	Mg(2)–O(4)–Mg(3)	100.7(2)
Mg(2)–C(37)	2.118(5)	Mg(2)–O(4)–Nd(2)	81.8(1)
Mg(3)–C(33)	2.117(5)	Mg(2)–O(5)–Mg(3)	99.5(2)
O(7)–Mg(2)–C(37)	129.5(2)	Mg(2)–O(5)–Nd(2)	85.4(1)
O(4)–Mg(2)–C(37)	129.8(2)	Mg(3)–O(5)–Nd(2)	85.6(2)
O(5)–Mg(2)–C(37)	121.1(2)	Mg(2)–O(7)–Nd(2)	95.4(1)

In the solid state, complex **4** has basically the same structural framework as the starting trinuclear alkoxide **1**, except that the [Nd(*Or*Bu)(THF)] and [Nd(*Or*Bu)₂] moieties have been replaced by two [Mg(*Or*Bu)(CH₂SiMe₃)] units. It is therefore interesting to compare the geometric features of both structures. The Nd–O distance of the terminal *tert*-butoxide ligand in **4** [Nd(2)–O(8): 2.241(6) Å] is somewhat longer than those found in **1** [2.147(4)–2.163(3) Å],^[1b] while the Nd–O(THF) distance is significantly shorter [2.350(5) Å vs. 2.661(4) Å]. It is worthwhile mentioning that these THF and terminal *Or*Bu ligands are statistically disordered (see Exp. Sect.), which may lead to averaged values. The doubly bridging Nd–O distances are, as expected, longer than those for the terminal alkoxide ligand [Nd(2)–O(7): 2.304(3); Nd(2)–O(6): 2.307(4) Å], and slightly shorter than those measured in **1** [2.333(3)–2.458(3) Å]. Also, the nonequivalent triply bridging Nd–O bonds [Nd(2)–O(4): 2.762(4); Nd(2)–O(5): 2.600(4) Å] are the longest ones observed in the structure and longer than the corresponding values in **1** [2.624(3) and 2.409(3) Å],^[1b] showing that the Nd atom is highly distorted from an ideal octahedral geometry. The angles around the neodymium center are similar to those observed in **1** except for the O(μ₃)–Nd–O(μ₃) angle, which is smaller in the heterodimetallic complex [55.3(1)° in **4** vs. 66.0(1)° in **1**]. This difference may be ascribed to the asymmetry in the complex caused by the shorter Mg–O bonds compared to the Nd–O ones. The equivalent magnesium atoms are four-coordinate, showing a distorted tetrahedral geometry. This geometry has been observed previously in some mixed alkoxy-amido complexes such as [(CMeNC₆H₃iPr₂-2,6)Mg(μ₂-*Or*Bu)(THF)] and [(CMeNC₆H₃iPr₂-2,6)Mg(μ₂-OC₆H₉)].^[11] The doubly bridging Mg–O distances [Mg(2)–O(7): 1.984(4); Mg(3)–O(6): 1.974(4) Å] and Mg–O–Nd angles [Mg(2)–O(7)–Nd(2): 95.4(1);

Mg(3)–O(6)–Nd(2): 95.6(1)°] compare well with the corresponding values observed in [(CMeNC₆H₃iPr₂-2,6)Mg(μ₂-*Or*Bu)(THF)] [Mg–O: 1.997(2) and 1.994(2) Å; Mg–O–Mg: 98.56(6)°].^[11]

The solution structure of complex **4** was briefly studied by ¹H NMR spectroscopy in [D₈]toluene. As shown in Figure 2, interpretation of the variable-temperature NMR spectra is complicated by the high fluxionality of the molecule and, above all, the paramagnetic Nd center, which broadens signals and affects intensity measurements. Thus, the correlation between chemical shift and coordination mode of the alkoxide groups previously noted in diamagnetic yttrium and lanthanum complexes of this type — increased bridging is associated with lower-field shifts^[12] — cannot be applied to determine the geometry of **4** in solution unambiguously. Minimal overlapping of the resonances is observed in the NMR spectrum at –80 °C (Figure 2), which features eight major singlet-like resonances **A–H** with relative integrations 9:9:18:2:18:4:9:4 (from high field to low field). This pattern is consistent with the structure observed in the solid state, considering that both 18 H singlets **C** and **D** correspond to the μ₃-*Or*Bu and μ₂-*Or*Bu groups, which are magnetically equivalent on the NMR timescale at this low temperature,^[12] and that the CH₂SiMe₃ groups are nonequivalent, one of the methylene resonance being obscured by residual solvent resonances (e.g. **I**) or a stronger intensity signal.

Complex **4** was exposed to ethylene (1 bar) in toluene solution. At room temperature, even after a long time period (48 h), the formation of polyethylene was not observed. This was not unexpected considering that **4** does not contain any Nd–C bond susceptible to insert ethylene. Addition of a slight excess of **3** to **4** under ethylene led to an effective polymerization. We can therefore hypothesize that **4** is an intermediate in the formation of the real active species in 1/MgR₂ systems for ethylene polymerization. On the other hand, the 1:1 Nd/Mg stoichiometry imposed for the reaction between **1** and **3** was not recovered in the final complex **4**, and we cannot discard the potential catalytic activity of other products remaining in the mother solution and so far unidentified, such as species of the type [(*t*BuO)₂Nd–R]_n.

Combinations of [Nd(OC₆H₂tBu₂-2,6-Me-4)₃(THF)] and [Mg(CH₂SiMe₃)₂(Et₂O)]

We focused next on [Nd(OC₆H₂tBu₂-2,6-Me-4)₃(THF)] (**2**). This precursor, thanks to its bulky and readily replaceable ligand commonly used in the chemistry of group 1–4 metals, might lead to more stable and/or more easily crystallizable complexes, as evidenced by the isolation of [Mg(OC₆H₂tBu₂-2,6-Me-4)(*n*-Hex)]₂ from a 2/Mg(*n*-Hex)₂ (1:1) mixture in toluene.^[1b] The quantitative formation of the latter compound is in agreement with the assumed *in situ* formation of a bis(aryloxy)alkylneodymium complex. However, the latter could not be isolated either from Mg(*n*-Hex)₂ or upon using the dialkylmagnesium compound **3** in pure toluene, despite repeated efforts. On the other hand,

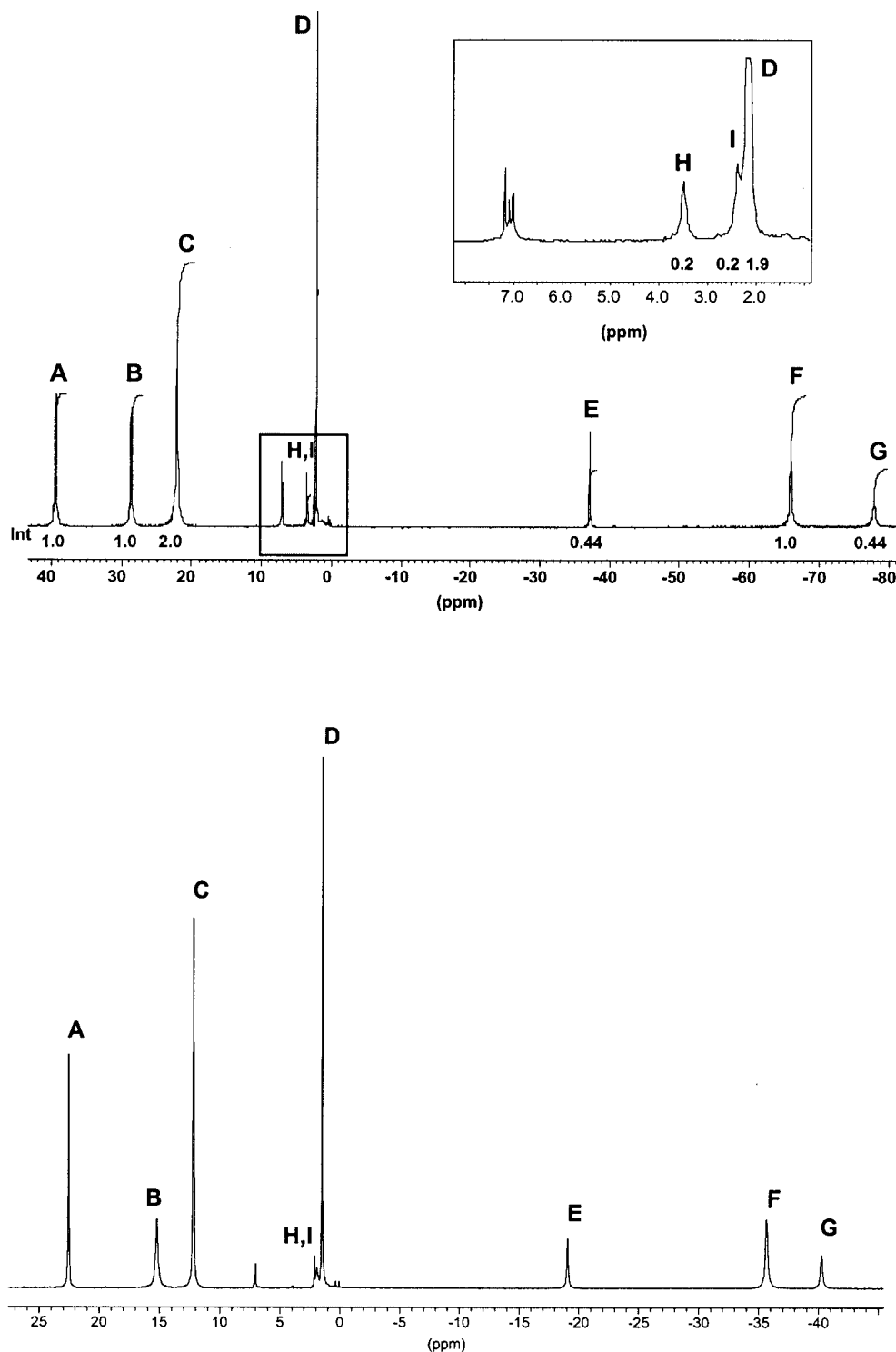
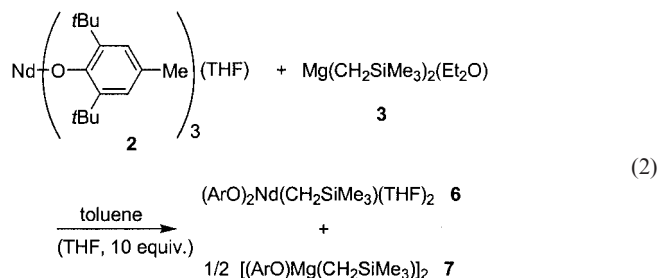


Figure 2. Representative variable-temperature ^1H NMR spectra of $[\text{Nd}(\mu_3\text{-OtBu})_2(\mu_2\text{-OtBu})_2(\text{OtBu})\text{Mg}_2(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ (**4**) in $[\text{D}_8]$ -toluene; top: $-80\text{ }^\circ\text{C}$; bottom: $0\text{ }^\circ\text{C}$ (I denotes residual toluene resonance and/or a signal from **4**)

the addition of THF (10 equiv. vs. Nd) to a mixture of **2** and **3** (1:1) enabled the ready crystallization of the pentacoordinate complex $[(4\text{-Me-2,6-}i\text{Bu}_2\text{C}_6\text{H}_2\text{O})_2\text{Nd}(\text{CH}_2\text{SiMe}_3)-$

$(\text{THF})_2]$ (**6**) along with $[(4\text{-Me-2,6-}i\text{Bu}_2\text{C}_6\text{H}_2\text{O})\text{Mg}(\text{CH}_2\text{-SiMe}_3)]_2$ (**7**), isolated in 34% and 39% yields, respectively [Equation (2)].



The solid-state structure of **6** features the metal center coordinated in a slightly distorted trigonal-bipyramidal mode by one equatorial methyltrimethylsilyl and two aryloxy groups (sum of the angles around Nd = 359.49°), and two axial THF ligands (Figure 3, Table 2). A plane of symmetry (noncrystallographic) embraces the Nd, both O(THF) and the C(CH₂SiMe₃) atoms. Similar trigonal-bipyramidal coordination has been observed previously in Ln(OR)₃L₂ complexes such as [Nd(OC*t*Bu)₃(CH₃CN)₂],^[13] as well as in mixed halogen-aryloxide complexes, such as [SmI(OAr)₂(THF)₂] and [(4-Me-2,6-*t*Bu₂C₆H₂-O)₂LnCl(THF)₂] (Ln = Er, Yb),^[14] and in the mixed aryl-halogen complex [(2,6-dimesitylphenyl)YbCl₂(THF)₂],^[15] in which the chlorine atoms occupy the axial positions. The O(1A)–Nd(1)–O(1B) angle [146.2(1)°] in **6** is much larger than 120°, reflecting the larger steric requirement of the aryloxide ligands compared to the CH₂TMS group. The bulkiness of the equatorial ligands affects the geometry of the axial ligands, with a lower (THF)O–Nd–O(THF) angle [165.46(9)°] than the theoretical value (180°). The increase in coordination number from the four-coordinate, distorted tetrahedral tris(aryloxide) precursor **2** to pentacoordinate complex **6** also likely stems from the decreasing steric requirement of CH₂SiMe₃ compared to the very bulky aryloxide. We assume that this may be the reason why it was not possible to isolate a putative alkyl complex, such as [(ArO)₂Nd(CH₂SiMe₃)], in the absence of THF. The necessary addition of a Lewis base for crystallization has

also been claimed in the case of [Nd(μ₂-OAr)(OAr)₂(py)₂]₂.^[9h]

Table 2. Selected bond lengths [Å] and angles [°] for **6**

Nd(1)–O(1A)	2.235(3)	O(1A)–Nd(1)–O(1B)	146.21(10)
Nd(1)–O(1B)	2.227(3)	O(1A)–Nd(1)–O(3B)	83.70(10)
Nd(1)–O(3A)	2.500(3)	O(1B)–Nd(1)–O(3B)	91.69(10)
Nd(1)–O(3B)	2.487(3)	O(1A)–Nd(1)–C(16)	113.02(12)
Nd(1)–C(16)	2.482(4)	O(1B)–Nd(1)–C(16)	100.26(12)
O(1A)–C(1A)	1.352(5)	O(3B)–Nd(1)–C(16)	88.54(12)
O(1B)–C(1B)	1.355(5)	O(1A)–Nd(1)–O(3A)	84.40(9)
C(16)–Si	1.843(4)	O(1B)–Nd(1)–O(3A)	93.56(10)
C(16)–Nd(1)–O(3A)	103.82(12)	O(3B)–Nd(1)–O(3A)	165.46(9)

The Nd–O(Ar) distances are nearly identical for both ligand units [2.227(3), 2.235(3) Å] and are somewhat longer than those in **2**, but similar to those observed in related complexes.^[16] Also, the Nd–O(THF) distances [2.487(3), 2.500(3) Å] are within the range of values reported for Nd–THF complexes.^[17] The Nd–C distance of 2.482(4) Å can be compared to the terminal Sm–C distance of 2.45(1) Å in [Sm(OAr)₃(CH₂SiMe₃)₂][Li(THF)₂] (Ar = 2,6-*i*Pr₂C₆H₃), reflecting the minimal 2.6% difference in the ionic radii.^[18] It is, however, much lower than that of 2.68(1) Å in [1,1'-(3,5-*t*Bu₂-2-C₆H₂O)₂]La{CH(SiMe₃)₂}(THF)₃] due to the larger ionic radius of lanthanum,^[18] its hexacoordination and the bulkiness of both aryloxide and alkyl groups.^[19]

The characterization of **6** in solution by ¹H NMR spectroscopy was unambiguous and indicated a symmetric structure on the NMR time scale, as observed in the solid state. Complex **6** exhibits the same pattern as **2** for the equivalent aryloxide ligands — narrow signals for the aromatic and Me protons and a broad singlet for the *tert*-butyl groups at higher field. The signals assigned to the alkyl group appear at δ = –1.25 and –7.15 ppm for the methylene and trimethylsilyl groups, respectively, while the two equivalent coordinated THF molecules give broad resonances at δ = –6.90 and –9.66 ppm.

As expected, despite the presence of an Nd–C bond, complex **6** does not initiate ethylene polymerization under the conditions used for catalytic combinations of **2** and **3** (1 atm, 0–80 °C). This is, of course, due to the presence of the two coordinated THF molecules that “block” the active site for the weaker Lewis base ethylene.

In conclusion, some reaction products of the combinations of neodymium alk(aryl)oxides **1** and **2** with [Mg(CH₂SiMe₃)₂(Et₂O)] (**3**) have been isolated and fully characterized. The new heterodimetallic complex **4**, obtained from the association of **1** with **3**, appears to be a plausible intermediate towards the species active in ethylene and methyl methacrylate (co)polymerizations. Indeed, although inert towards ethylene, complex **4** can be further activated upon MgR₂ addition, eventually yielding species that are active in polymerization. The alkylneodymium complex **5** is also inert towards olefins despite its reactive Nd–C bond. The isolation of this complex is, however,

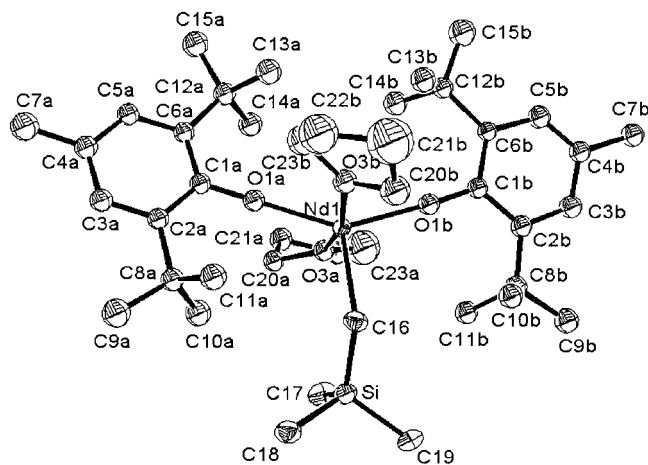


Figure 3. Molecular structure of [(4-Me-2,6-*t*Bu₂C₆H₂O)₃Nd(CH₂SiMe₃)(THF)₂] (**6**); ellipsoids are drawn at the 50% probability level and hydrogen atoms omitted for clarity

noteworthy in this area since it is the first example of an alkyl complex prepared from a neodymium alk(aryl)oxide/dialkylmagnesium mixture. Formation of **5** is the strongest evidence to date corroborating that an alkylanthanide could be the active species in olefin polymerizations initiated by these new binary catalytic systems.

Experimental Section

General: All operations were performed in a glove box under nitrogen. Solvents and deuterated solvents were freshly distilled from sodium-potassium amalgam under argon and degassed prior to use. NMR spectra were recorded in Teflon-valved NMR tubes with a Bruker AC-200 spectrometer. ^1H (200 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (50 MHz) chemical shifts are expressed in ppm vs. SiMe_4 and are referenced to the residual solvent peaks. The complexes $[\text{Nd}_3(\text{OrBu})_9(\text{THF})_2]$,^[1b] $[\text{Nd}(\text{OC}_6\text{H}_2t\text{Bu}_2-2,6\text{-Me-4})_3(\text{THF})]$,^[20] and $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{OEt}_2)]$ ^[21] were prepared according to the reported procedures. Methyl methacrylate (99%, Aldrich) was vacuum-distilled from CaH_2 and stored at -20°C under argon.

Reaction of $[\text{Nd}_3(\mu_3\text{-OrBu})_2(\mu_2\text{-OrBu})_3(\mu\text{-OrBu})_4(\text{THF})_2]$ (1**) with $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{Et}_2\text{O})]$ (**3**). Synthesis of $[\text{Nd}(\mu_3\text{-OrBu})_2(\mu_2\text{-OrBu})_2(\mu\text{-OrBu})\text{Mg}_2(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ (**4**) and $[(\text{Me}_3\text{SiCH}_2)\text{Mg}(\text{OrBu})(\text{THF})]$ (**5**):** $[\text{Nd}_3(\text{OrBu})_9(\text{THF})_2]$ (**1**; 0.124 g, 0.10 mmol) was dissolved in a minimal amount of toluene (ca. 0.25 ml). Methyl methacrylate (10 μL , 0.010 mmol) and $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{OEt}_2)]$ (**3**; 0.084 g, 0.33 mmol) were then added at room temperature to the resulting deep-blue solution. The solution turned green after addition of the magnesium reagent and was immediately cooled to -30°C . After 2 d, colorless crystals of $[(\text{Me}_3\text{SiCH}_2)\text{Mg}(\text{OrBu})(\text{THF})]$ (**5**) were removed from the solution (0.015 g, 17%) and after typically about 10 d, pale-blue crystals of **4** had grown from the dark-green solution (0.027 g, 37%), which proved suitable for X-ray diffraction.

4: ^1H NMR (200 MHz, $[\text{D}_8]\text{toluene}$, 23°C): δ = 19.56 (s, 1 H), 12.82 (br. s, 0.6 H), 10.40 (s, 2 H), 1.37 (s, 2 H), -15.87 (s, 0.4 H), -30.11 (br. s, 0.7 H), -33.43 (br. s, 0.4 H) ppm. ^1H NMR (200 MHz, $[\text{D}_8]\text{toluene}$, -35°C): δ = 27.54 (s, 1 H), 19.09 (s, 1 H), 15.16 (s, 2 H), 2.25 (s, 0.2 H), 2.10 (s, 0.1 H), 1.69 (s, 1.5 H), -24.53 (s, 0.4 H), -44.86 (s, 1 H), -51.62 (s, 0.4 H) ppm. ^1H NMR (200 MHz, $[\text{D}_8]\text{toluene}$, -80°C): δ = 39.38 (s, 9 H), 28.60 (s, 9 H), 22.06 (s, 18 H), 3.48 (s, 2 H), 2.37 (s, 2 H), 2.15 (s, 18 H), -37.21 (s, 4 H), -66.03 (s, 9 H), -78.01 (s, 4 H) ppm. $\text{C}_{32}\text{H}_{75}\text{Mg}_2\text{NdO}_6\text{Si}_2$ (804.96): calcd. C 47.75, H 9.39; found C 47.1, H 9.11.

5: ^1H NMR (200 MHz, $[\text{D}_6]\text{benzene}$, 23°C): δ = 3.68 (m, 4 H, THF), 1.29 (s, 9 H, *t*Bu), 1.24 (m, 4 H, THF), 0.41 (s, 9 H, SiMe_3), -1.33 (s, 2 H, CH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, $[\text{D}_6]\text{benzene}$, 23°C): δ = 69.7 (CH_2O , THF), 67.8 (C_q , *t*Bu), 35.3 (CH_3 , *t*Bu), 25.5 (CH_2 , THF), 5.6 [$\text{Si}(\text{CH}_3)_3$], -6.0 (CH_2Mg) ppm. $\text{C}_{12}\text{H}_{28}\text{MgO}_2\text{Si}$ (256.74): calcd. C 56.14, H 10.99; found C 55.86, H 10.53.

Reaction of $[\text{Nd}(\text{OC}_6\text{H}_2t\text{Bu}_2-2,6\text{-Me-4})_3(\text{THF})]$ (2**) with $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{Et}_2\text{O})]$ (**3**). Synthesis of $[\text{Nd}(\text{OC}_6\text{H}_2t\text{Bu}_2-2,6\text{-Me-4})_2(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ (**6**) and $[(4\text{-Me-2,6-}t\text{Bu}_2\text{C}_6\text{H}_2\text{O})\text{Mg}(\text{CH}_2\text{SiMe}_3)_2]$ (**7**):** $[\text{Nd}(\text{OC}_6\text{H}_2t\text{Bu}_2-2,6\text{-Me-4})_3(\text{THF})]$ (**2**) (0.087 g, 0.10 mmol) was dissolved in a mixture of toluene (0.140 g, 0.16 mL) and THF (0.050 g, 0.70 mmol) THF was weighted to introduce an exact amount. $[\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{Et}_2\text{O})]$ (**3**) (0.027 g;

0.10 mmol) was added at room temperature to the resulting purple solution, and the mixture was immediately cooled to -30°C . After a few days, colorless crystals of $[(4\text{-Me-2,6-}t\text{Bu}_2\text{C}_6\text{H}_2\text{O})\text{Mg}(\text{CH}_2\text{SiMe}_3)_2]$ (**7**) were removed from the solution (0.013 g, 39%) and blue crystals of **6** suitable for X-ray analysis were obtained from the blue solution after a month (0.025 g, 34%).

6: ^1H NMR (200 MHz, $[\text{D}_6]\text{benzene}$, 23°C): δ = 21.36 (s, 2 H, Ar), 10.47 (s, 3 H, Me), 7.99 (br. s, 18 H, *t*Bu), -1.25 (s, 2 H, CH_2), -6.90 (br. s, THF), -7.15 (s, SiMe_3), -9.66 (br. s, THF) ppm. $\text{C}_{42}\text{H}_{73}\text{NdO}_4\text{Si}$ (814.35): calcd. C 61.94, H 9.04; found C 60.45, H 8.96.

7: ^1H NMR (200 MHz, $[\text{D}_6]\text{benzene}$, 23°C): δ = 7.19 (s, 2 H, Ar), 2.29 (s, 3 H, Me), 1.59 (s, 18 H, *t*Bu), 0.06 (s, 9 H, SiMe_3), -1.16 (s, 2 H, CH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6 , 23°C): δ = 159.4 (C_{Ar}), 139.8 (C_{Ar}), 128.9 (C_{Ar}), 127.6 (C_{Ar}), 35.7 (C_q , *t*Bu), 33.9 (CH_3 , *t*Bu), 21.9 (CH_3), 4.1 [$\text{Si}(\text{CH}_3)_3$], -6.2 ($\text{CH}_2\text{-Mg}$) ppm. $\text{C}_{19}\text{H}_{34}\text{MgOSi}$ (330.86): calcd. C 68.97, H 10.36; found C 68.4, H 9.82.

X-ray Crystal-Structure Determination of 4: A pale-blue crystal of approximate dimensions $0.30 \times 0.25 \times 0.10$ mm was mounted on a glass fiber. X-ray data were collected with a Bruker SMART CCD area-detector diffractometer with $\text{Mo-}K_\alpha$ radiation (λ = 0.71073 Å) at T = 100 K. Crystal data: monoclinic, Cc ; a = 26.312(5), b = 11.595(2), c = 22.888(5) Å; β = 109.127(3)°; V = 6597(2) Å³; formula unit: $\text{C}_{32}\text{H}_{75}\text{O}_6\text{Mg}_2\text{NdSi}_2$ with Z = 6; molecular weight: 804.96; calculated density = 1.216 g·cm⁻³; $F(000)$ = 2562; $\mu(\text{Mo-}K_\alpha)$ = 1.297 mm⁻¹. 22487 reflections collected ($2.27^\circ > \theta > 25.00^\circ$). The structure was solved by direct methods.^[22] Of the six neodymium atoms in the cell, two are on the twofold axis and the four others are in general positions. The resolution was complicated by the disorder between the monodentate *Or*Bu ions and THF molecules, which had to be refined as independent parts. Hydrogen-atom positions were calculated on a geometrical basis. Full-matrix least-squares refinement on F^2 based on 11197 independent reflections converged with 620 variable parameters and three restraints. $R1$ = 0.0360 [for 10265 data with $I > 2\sigma(I)$]; $wR2$ = 0.0864; GoF (F^2) = 1.057. $\Delta\rho_{\text{max}}$ = 1.776 and -0.851 e·Å⁻³.

X-ray Crystal Structure Determination of 6: A pale-blue crystal of approximate dimensions $0.45 \times 0.25 \times 0.12$ mm was mounted on a glass fiber. X-ray data were collected with a Bruker SMART CCD area-detector diffractometer with $\text{Mo-}K_\alpha$ radiation (λ = 0.71073 Å) at T = 100 K. Crystal data: orthorhombic, $Pca2_1$; a = 23.732(5), b = 9.799(2), c = 18.902(4) Å; V = 4395.7(16) Å³; formula unit: $\text{C}_{42}\text{H}_{73}\text{O}_4\text{SiNd}$ with Z = 4; molecular weight: 814.33; calculated density = 1.119 g·cm⁻³; $F(000)$ = 1724; $\mu(\text{Mo-}K_\alpha)$ = 1.244 mm⁻¹. 30722 reflections collected ($2.15^\circ > \theta > 28.04^\circ$). The structure was solved by direct methods.^[22] Hydrogen-atom coordinates were generated by geometrical calculations. Full-matrix least-squares refinement on F^2 based on 9437 independent reflections converged with 450 variable parameters and one restraint. $R1$ = 0.0339 [for 7321 data with $I > 2\sigma(I)$]; $wR2$ = 0.0637; GoF (F^2) = 1.010. $\Delta\rho_{\text{max}}$ = 2.015 and -0.808 e·Å⁻³. The largest residuals are close to one of the THF molecule and are probably due to some orientational disorder.

CCDC-228005 (**4**) and -228006 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: (internat.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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