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Discrete Lanthanide Aryl(alk)oxide Trimethylaluminum Adducts as Isoprene Polymerization Catalysts

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ABSTRACT: The structure−reactivity relationship of the rare-earth metal aryl(alk)oxide-promoted coordination polymerization of isoprene was investigated using *binary* initiating systems $Ln(OR)_3(AlMe_3)_x/Et_2AlCl$ (Ln = La, Nd, Y). Depending on the degree of the rare-earth metal aryl(alk)oxide prealkylation (x = 1, 2, 3), such discrete trimethylaluminum (TMA) adduct complexes of rare-earth metal alkoxide and aryloxide components displayed a distinct initiating capability. The heterobimetallic bis-TMA adducts $Ln(OAr^{iPr})_3(AlMe_3)_2$ and tris-TMA adducts $Ln(OCH_2tBu)_3(AlMe_3)_3$ (Ln = La, Nd) produced highly reactive initiators, whereas the mono-TMA adducts $Ln(OAr^{tBu})_3(AlMe_3)$ were catalytically inactive. The highest reactivities and stereoselectivities (>99% cis) were obtained for a $n_{Ln}:n_{Cl}$ ratio of 1:2. The alkoxide-based tris-TMA adducts gave narrower molecular weight distributions than the aryloxide-based bis-TMA adduct complexes (M_w/M_n = 1.74−2.37 vs 2.03−4.26). A plausible mechanistic activation/deactivation scenario of the formation of the catalytically active/inactive species is presented.

Introduction

Ziegler-type catalysts based on the lanthanide metal neodymium (as well as the transition metals titanium, cobalt, and nickel) are used in the industrial-scale production of butadiene (i.e., *cis*-1,4-polybutadiene, BR) and isoprene rubber (i.e., *cis*-1,4-polyisoprene, IR).[1] Particularly, neodymium catalysts facilitate the formation of high-quality synthetic rubbers with improved thermal and mechanical properties due to high *cis*-1,4-stereospecificities (cis ≥ 97%). The catalytically active species is routinely formed via empirically designed *ternary* mixtures comprising a hydrocarbon-soluble Nd(III) precursor (e.g., carboxylate, phosphate),[2] an aluminum alkyl halide, and aluminum alkyls or aluminum alkyl hydrides.[3−6] For comparison, Nd(III) catalyst mixtures utilizing alkylmagnesium cocatalysts such as $MgBu_2$ in the absence of any chlorinating reagent have been reported to produce predominantly trans polymers.[7,8] It is generally assumed that lanthanide alkyl moieties are generated in situ upon combining the lanthanide precursor with the alkylaluminum cocatalysts, acting as the polymerization initiating species. Recently, the first structurally fully characterized organoaluminum-alkylated rare-earth metal species revealed intrinsic structure−reactivity relationships of the neodymium carboxylate-based diene polymerization catalysts.[9−11]

Previous studies on carboxylate-, alkoxide-, and phosphate-based Nd(III) catalysts also showed that the Nd:cocatalyst(s) ratio(s) governs the catalyst activity and polymer properties, i.e., molecular weight, polydispersity, and microstructure.[12] In the course of our investigations into the structure−reactivity relationships of lanthanide-based diene polymerization catalysts[9,13,14] we have also examined Ln alkoxide and aryloxide derivatives. In contrast to rare-earth metal carboxylate derivatives, Ln aryl(alk)oxide complexes $Ln(OR)_3$ and $Ln(OAr^R)_3$ comprise highly soluble discrete molecules of well-defined nuclearity (mono-, di-, tri-, tetra-, and penta-) depending on the bulkiness of the residue R.[15] The diverse and multifaceted synthetic access combined with the intrinsic thermodynamically stable/kinetically labile bonding feature make lanthanide aryl(alk)oxide complexes ideal components of Ziegler-type catalysts.[16] Herein, we would like to report the use of discrete lanthanide aryl(alk)oxide trimethylaluminum adduct complexes with various $n_{Ln}:n_{Al}$ ratios in the *cis*-1,4-stereospecific polymerization of isoprene.[17,18]

Results and Discussion

Synthesis and Characterization of Lanthanide Aryl(alk)oxide TMA Adducts. Three distinct homoleptic aryl(alk)oxide complexes $\{Ln(OR)_3\}_n$ were envisaged as rare-earth metal components. Complexes $[Ln(OAr^{tBu})_3]$ (Ln = La (**1a**), Nd (**1b**), Y (**1c**)), $[\{Ln(OAr^{iPr})_3\}_2]$ (Ln = La (**2a**), Nd (**2b**), Y (**2c**)), and $[\{Ln(OCH_2tBu)_3\}_4]$ (Ln = La (**3a**), Nd (**3b**), Y (**3c**)) were obtained from $Ln[N(SiMe_3)_2]_3$ and three equivalents of the corresponding phenol or alcohol derivatives (Scheme 1, silylamide route). The purity of the monomeric (n = 1; **1**), dimeric (n = 2; **2**), and tetrameric complexes (n = 4; **3**) was proven by elemental analysis and proton and carbon NMR spectroscopy. The rare-earth metals lanthanum, neodymium, and yttrium were selected according to size/reactivity criteria: while diamagnetic lanthanum(III) and yttrium(III) feature the largest and a relatively small Ln(III) metal center, respectively, neodymium supposedly displays the catalytically most active one. The phenols 2,6-di-*tert*-butyl-4-methylphenol ($HOAr^{tBu}$) and 2,6-diisopropylphenol ($HOAr^{iPr}$), as well as neopentyl alcohol ($HOCH_2tBu$ = HONp), were chosen to investigate the influence of the steric bulk of the aryl(alk)oxide ligands on the formation of the first intermediates upon addition of the cocatalyst(s).

Trimethylaluminum (TMA) was then employed as a methyl group transfer reagent (alkylating component) and added to hexane mixtures of complexes **1**−**3**. Depending on the steric

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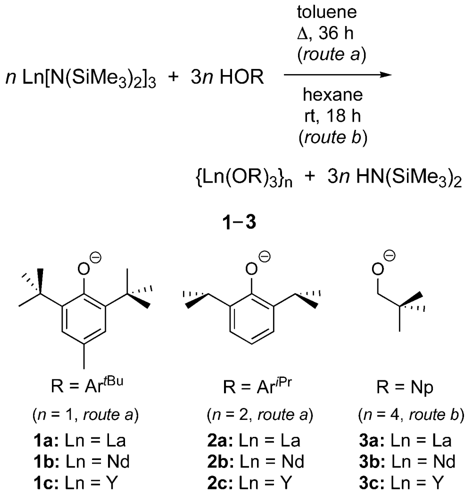
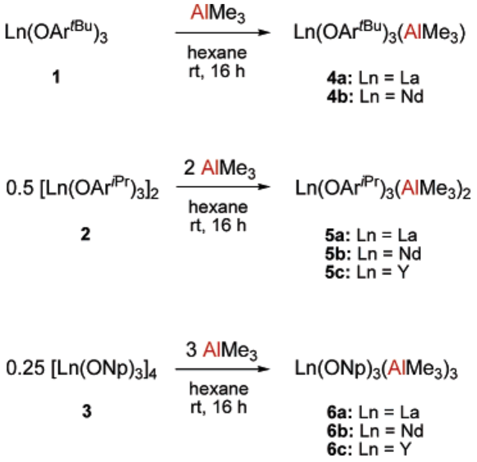
Scheme 1. Synthesis of Homoleptic Lanthanide Aryl(alk)oxides



Scheme 2. Distinct TMA Adduct Formation by Lanthanide Aryl(alk)oxides



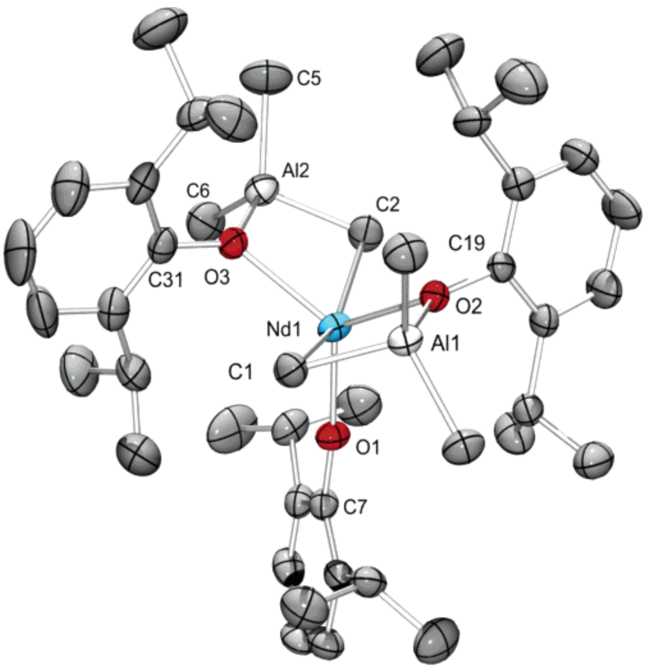


Figure 1. Solid-state structure of complex Nd(OAr^{iPr})[(μ-OAr^{iPr})(μ-Me)AlMe$_2$]$_2$ (**5b**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd−O1 2.090(3), Nd−O2 2.319(2), Nd−O3 2.324(3), Nd−C1 2.694(4), Nd−C2 2.667(6), Al1−O2 1.849(3), Al2−O3 1.866(4), Al1−C1 2.061(5), Al1−C4 1.959(5), Al1−C3 1.962(5), O1−Nd−O2 120.0(1), O1−Nd−O3 117.7(1), O2−Nd−O3 122.1(1), O1−Nd−C1 101.5(1), O1−Nd−C2 101.6(2), O2−Nd−C1 70.8(1), O2−Nd−C2 100.8(1), C1−Nd−C2 156.6(2), Nd−O1−C7 173.9(3), Nd−O2−C19 116.7(2), and Nd−O3−C31 126.2(3).

bulk of the aryl(alk)oxide ligands three different types of TMA adducts were obtained in quantitative yields, as evidenced by mono- (**4**), bis- (**5**), and tris-TMA adducts (**6**) (Scheme 2). Complexes Ln(OAr^{iPr})$_3$(AlMe$_3$)$_2$ (**5**) and Ln(OCH$_2$*t*Bu)$_3$(AlMe$_3$)$_3$ (**6**) form preferentially with stoichiometric amounts of TMA. For the bulkier aryloxide ligand, exclusive mono-TMA adduct formation, Ln(OAr^{tBu})$_3$(AlMe$_3$), was observed for the larger metal centers lanthanum and neodymium, even in the presence of large excess of the alkylation reagent and prolonged reaction time.[19]

Recrystallization of compound **5b** from saturated hexane solutions at −35 °C gave purple single crystals suitable for an X-ray structure analysis.[20] Complex **5b** (Figure 1) is isostructural with the previously reported yttrium, samarium, and lanthanum derivatives.[13,21,22] The rare-earth metal center is five-coordinated in a distorted trigonal-bipyramidal fashion with bridging methyl groups in the apical positions. All of the Nd−O and Nd−C bond lengths are in good agreement with literature data.[23] As expected, the Nd−O(bridging) distances (2.319(2) and 2.324(3) Å) are significantly longer than the Nd−O(terminal) bond length (2.090(3) Å). For comparison, the Nd−O distances (2.349(4)−2.368(4) Å) of the six-coordinate homoleptic neodymium aryloxide [Nd{(μ-OC$_6$H$_4$Me-4)$_2$AlMe$_2$}$_3$] are only slightly longer.[24]

Polymerization of Isoprene. The initiating performance of the alkylated lanthanide precursors **4**−**6** for the stereospecific *cis*-polymerization of isoprene was investigated using diethylaluminum chloride Et$_2$AlCl as second "weakly cationizing" cocatalyst. Note that in the absence of a cationizing source TMA adducts **4**−**6** do not polymerize dienes. Accordingly, the precatalysts were stirred in hexane, activated with 1, 2, or 3 equivalents of the cocatalyst, aged for 30 min at ambient temperature and stirred for 24 h upon addition of the isoprene monomer. The polymerization reactions were terminated by pouring the mixtures into large amounts of acidified 2-propanol. Monomer conversions were determined gravimetrically and polymer properties including molecular weights, polydispersities, and stereospecificities were analyzed by means of size exclusion chromatography and ^{13}C{^{1}H} NMR spectroscopy, respectively. The results are summarized in Table 1.

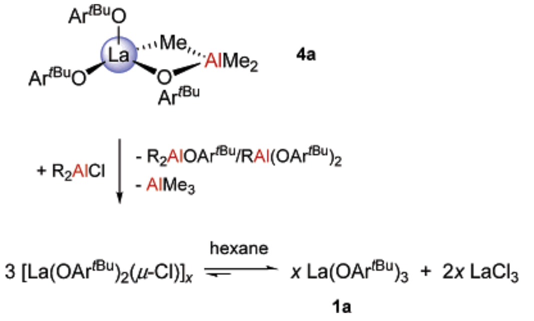
Catalytic Activity. The implications of the Ln metal center as well as the n_{Ln}:n_{Cl} ratio for diene polymerization has been reported previously for carboxylate and halide based *ternary* catalyst mixtures.[25] Accordingly, highest activities were obtained for Nd(III) catalysts (→intrinsic neodymium effect) and 2−3 equiv of the alkylaluminum chloride reagent. The *binary* catalyst mixtures Ln(OR)$_3$(AlMe$_3$)$_x$/Et$_2$AlCl under study fully support these former findings. Under similar polymerization conditions, highest activities were observed for the neodymium-based initiators, whereas all of the yttrium precatalysts did not polymerize isoprene (runs 13−15 and 22−24). Noteworthy, only a few examples of diene polymerization catalysts based on smaller lanthanide metal centers have been reported so far.[14,26−29] Both the bis-TMA adducts **5** and the tris-TMA adducts **6** gave highest activities for n_{Ln}:n_{Cl} ratios of 1:2, with quantitative yields for Nd(OAr^{iPr})$_3$(AlMe$_3$)$_2$ (**5b**, run 11), La(ONp)$_3$(AlMe$_3$)$_3$ (**6a**, run 17), and Nd(ONp)$_3$(AlMe$_3$)$_3$ (**6b**, run 20). Not surprisingly, the catalytic activities decreased drastically in the presence of a third equivalent of the chloride source, most likely due to the formation of a larger amount of catalytically inactive [LnCl$_3$]. Completely inactive mixtures resulted upon addition of three

Table 1. Effect of Rare-Earth Metal Size and Amount of Coordinated Alkylaluminum Reagent (TMA) on the Aryl(alk)oxide-Based Polymerization of Isoprene

run[a]	precatalyst	Et_2AlCl[b] (equiv)	yield (%)	cis[c] (%)	M_n[d] ($\times 10^3$)	M_w[d] ($\times 10^3$)	PDI[d]
	Mono-TMA Adducts						
1	$La(OAr^{tBu})_3(AlMe_3)$ (**4a**)	1	0				
2	$La(OAr^{tBu})_3(AlMe_3)$ (**4a**)	2	0				
3	$La(OAr^{tBu})_3(AlMe_3)$ (**4a**)	3	0				
4	$Nd(OAr^{tBu})_3(AlMe_3)$ (**4b**)	1	0				
5	$Nd(OAr^{tBu})_3(AlMe_3)$ (**4b**)	2	0				
6	$Nd(OAr^{tBu})_3(AlMe_3)$ (**4b**)	3	0				
	Bis-TMA Adducts						
7	$La(OAr^{iPr})_3(AlMe_3)_2$ (**5a**)	1	53	98.0	76	325	4.26
8	$La(OAr^{iPr})_3(AlMe_3)_2$ (**5a**)	2	54	>99	390	870	2.23
9	$La(OAr^{iPr})_3(AlMe_3)_2$ (**5a**)	3	33	>99	76	318	4.17
10	$Nd(OAr^{iPr})_3(AlMe_3)_2$ (**5b**)	1	92	98.9	355	744	2.10
11	$Nd(OAr^{iPr})_3(AlMe_3)_2$ (**5b**)	2	>99	>99	223	453	2.03
12	$Nd(OAr^{iPr})_3(AlMe_3)_2$ (**5b**)	3	38	>99	107	371	3.46
13	$Y(OAr^{iPr})_3(AlMe_3)_2$ (**5c**)	1	0				
14	$Y(OAr^{iPr})_3(AlMe_3)_2$ (**5c**)	2	0				
15	$Y(OAr^{iPr})_3(AlMe_3)_2$ (**5c**)	3	0				
	Tris-TMA Adducts						
16	$La(ONp)_3(AlMe_3)_3$ (**6a**)	1	78	98.9	270	641	2.37
17	$La(ONp)_3(AlMe_3)_3$ (**6a**)	2	>99	>99	517	954	1.85
18	$La(ONp)_3(AlMe_3)_3$ (**6a**)	3	0				
19	$Nd(ONp)_3(AlMe_3)_3$ (**6b**)	1	90	98.6	339	693	2.05
20	$Nd(ONp)_3(AlMe_3)_3$ (**6b**)	2	>99	>99	384	670	1.74
21	$Nd(ONp)_3(AlMe_3)_3$ (**6b**)	3	0				
22	$Y(ONp)_3(AlMe_3)_3$ (**6c**)	1	0				
23	$Y(ONp)_3(AlMe_3)_3$ (**6c**)	2	0				
24	$Y(ONp)_3(AlMe_3)_3$ (**6c**)	3	0				

[a] General polymerization procedure: 0.02 mmol precatalyst, 8 mL of hexane, 0.02−0.06 mmol of Et_2AlCl (1−3 equiv), 20 mmol of isoprene; 24 h, 40 °C. [b] Catalyst preformation 30 min at ambient temperature. [c] Measured by means of ^{13}C NMR spectroscopy in $CDCl_3$. [d] Determined by means of size exclusion chromatography (SEC) against polystyrene standards.

Scheme 3. "Deactivation" of Complex 4a with R_2AlCl (R = Me, Et)



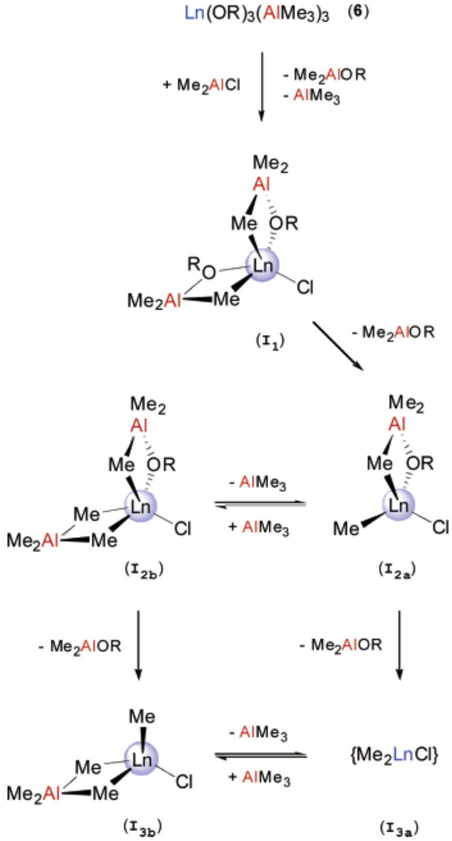
equivalents of Et_2AlCl to the lanthanide alkoxide complexes **6** (runs 18 and 21), while the bis-TMA adducts **5a** and **5b** remained active with isolated polymer yields of 33 (run 9) and 38% (run 12), respectively. This distinct polymerization protocol implies a marked influence of the stereoelectronic features of the aryl(alk)oxide ligand on the aryl(alk)oxide/alkylaluminum ratio. Importantly, none of the mono-TMA adducts **4** was catalytically active (runs 1−6). To better understand the catalytic inactivity of the mixtures **4**/Et_2AlCl, we studied the equimolar reactions of **4a** with dimethyl- and diethylaluminum chloride in more detail. ^1H NMR spectroscopic investigation of the benzene-d_6 soluble parts revealed the formation of the dialkylaluminum aryloxides $R_2AlOAr^{tBu}/RAl(OAr^{tBu})_2$[30] as well as of homoleptic $La(OAr^{tBu})_3$ (**1a**)[13] and several unidentified (minor) products. This finding is in agreement with an initial [AlCl]→[LnCl] chloride transfer, which generates R_2AlOAr^{tBu} and $[La(OAr^{tBu})_2(\mu\text{-Cl})]_x$, thus "deactivating" precatalysts **4** (Scheme 3). The heteroleptic lanthanide intermediate $[La(OAr^{tBu})_2(\mu\text{-Cl})]_x$ most likely forms insoluble and inactive $LaCl_3$ and $La(OAr^{tBu})_3$ due to rapid ligand redistribution.[31,32] In the presence of a second or third equivalent of the Et_2AlCl cocatalyst larger amounts of $LaCl_3$ were generated, with the reaction mixture remaining inactive.

In contrast, the enhanced catalytic activity of prealkylated **5** and **6** upon addition of the Et_2AlCl cocatalyst can be rationalized on the basis of the presence of a second and third equivalent of TMA coordinated to the metal centers, i.e., a second and third reactive Ln−Me moiety. A plausible mechanism of the activation of compounds **6** with Me_2AlCl is proposed in Scheme 4. The addition of the chloride source most likely affords the monochloro bis-TMA species $\mathbf{I_1}$ as a first intermediate, which was not detectable by means of NMR spectroscopy. Upon cleavage of additional kinetically labile Ln−O bonds and formation of a second and/or third equivalent of $[Me_2AlONp]_2$,[33] "LnMe" (intermediates $\mathbf{I_{2a}}$ and $\mathbf{I_{3a}}$) or "$Ln(AlMe_4)$" species (intermediates $\mathbf{I_{2b}}$ and $\mathbf{I_{3b}}$) might be generated, which are potentially active in isoprene polymerization.

A complete series of NMR spectra obtained for the activation sequence of **2b**/**5b**, involving the separation of $[Me_2Al(OC_6H_3iPr_2\text{-}2,6)]_2$,[34] is shown in the Supporting Information.

Stereospecificity. All of the isoprene polymers obtained display high cis-stereoselectivity (≥ 98.0). The presence of a second and third equivalent of the cis-directing halide source further increased the stereospecificities, which is in agreement with previous studies.[9] For the most efficient catalyst mixtures, signals assignable to *trans*- or 1,2-polymers could not be observed by means of carbon NMR spectroscopy (runs 8, 9, 11, 12, 17, 20). For comparison, a metallocene complex bearing an aryloxide ligand, $(C_5H_4Me)_2Sm(OC_6H_2tBu\text{-}2,6\text{-}Me\text{-}4)$, was found to be inactive in butadiene polymerization upon activation with AlR_3 (R = Me, Et, *i*Bu; Al/Ln = 30).[35] However, this complex initiated the polymerization of butadiene in the presence of MAO (Al/Ln > 500, $T = 80$ °C), albeit with poor stereoselectivity ($cis_{max} = 78.4\%$, $M_{n,max} = 18.1 \times 10^{-3}$).

Scheme 4. Proposed Activation Scenario of Lanthanide Alkoxide Complexes 6



Molar Masses and PDI. High molecular weights ($M_{\mathrm{n,max}} = 339 \times 10^{-3}$) with fairly narrow molecular weight distributions were obtained for most of the catalytically active *binary* mixtures, except those used in runs 7, 9, and 12. Interestingly, both for bis-TMA adducts **5** (2.03 and 2.23) and tris-TMA adducts **6** (1.74 and 1.85) the presence of 2 equiv of cocatalyst produced the lowest PDI values. Similar molecular weight distributions have been reported for *ternary* alkoxide-based systems such as Nd(O*i*Pr)$_3$/MAO/*t*BuCl (PDI = 1.57−2.04).[17c] Monomer conversions and polymer molecular weights indicate that less than one polymer chain per rare-earth metal center is formed.

Conclusions

Discrete trimethylaluminum (TMA) adducts of rare-earth metal aryl(alk)oxide complexes, Ln(OR)$_3$(AlMe$_3$)$_x$, have been shown to provide valuable and precise insights into the coordination polymerization of isoprene. Their initiating performance intrinsically depends on the extent of TMA adduct formation (x ≥ 2), which can be seen as a true alkylation of the rare-earth metal center. Consequently, in *binary* initiating systems Ln(OR)$_3$(AlMe$_3$)$_x$/Et$_2$AlCl the polymerization efficiency is governed by the stereoelectronic properties of the ancillary ligand OR, that is, sterically highly demanding aryl(alk)oxide ligands counteract multiple TMA adduct formation, and hence, an efficient polymerization behavior. Furthermore, the superb catalytic performance of such heterobimetallic bis- and tris-TMA adducts Ln(OAr$^{i\mathrm{Pr}}$)$_3$(AlMe$_3$)$_2$ and Ln(ONp)$_3$(AlMe$_3$)$_3$ (Ln = La, Nd), respectively, is in accordance with previous findings for *ternary* Ln alkoxide-based systems. The highest reactivities and highest stereoselectivities (cis >99%) were obtained for the neodymium metal center and for a n_{Ln}:n_{Cl} ratio of 1:2. Certainly, our proposed mechanistic activation/deactivation scenario of the formation of the catalytically active/inactive species is oversimplified. However, all of the reaction sequences depicted can be rationalized on the basis of the reactivity of discrete rare-earth metal aryl(alk)oxide complexes toward organolaluminum reagents[13] as well as related organolanthanide carboxylate chemistry.[9,36]

Experimental Section

General Considerations. All operations were carried out with rigorous exclusion of air and water, using standard Schlenk and glovebox techniques (MBraun MB150B-G-II; <1 ppm of O$_2$, <1 ppm of H$_2$O). Hexane was predried and passed through two columns of activated alumina and supported copper redox catalyst, respectively. Toluene was predried and distilled from Na/K alloy (benzophenone ketyl) under argon. C$_6$D$_6$ (obtained from Merck) was degassed and dried over Na/K alloy. AlMe$_3$, Me$_2$AlCl, and Et$_2$AlCl were purchased from Aldrich and used as received. ***CAUTION!*** Alkylaluminum reagents react violently with moisture. Isoprene was obtained from Aldrich, dried several times over activated molecular sieves (3 Å), and distilled prior to use. Complexes **1**, **2**, **3**, **4a**,**c**, and **5a**,**c** were synthesized according to previously published procedures.[13,37,38]

NMR spectra were recorded either on a JEOL-GX-400 (FT; ^{1}H, 399.78 MHz; ^{13}C, 100.5 MHz), a Bruker-Biospin-AV500 (5 mm BBO; ^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz), a Bruker-Biospin-AV600 (5 mm cryo probe; ^{1}H, 600.13 MHz; ^{13}C, 150.91 MHz), or a JEOL JNM-GX-270 (FT; ^{1}H, 270.16 MHz; ^{13}C, 67.93 MHz; polymers) spectrometer. ^{1}H and ^{13}C shifts are referenced to internal solvent resonances and reported in *parts per million* relative to TMS. NMR data for paramagnetic Nd(III) complexes Nd[N(SiMe$_3$)$_2$]$_3$, **1b**, **2b**, and **3b** are reported in the Supporting Information. IR spectra were recorded on a Perkin-Elmer 1650-FTIR spectrometer as Nujol mulls. Elemental analyses were performed in the microanalytical laboratory of the Technische Universität München.

Nd(OC$_6$H$_2$*t*Bu$_2$-2,6-Me-4)$_3$(AlMe$_3$) (4b). To a suspension of **1b** (0.383 g, 0.48 mmol) in hexane was slowly added a hexane solution of 2.5 equiv of TMA (0.087 g, 1.20 mmol), and the mixture was stirred at ambient temperature overnight. Then, the solvent and the excess TMA were removed in vacuo. The remaining solid was crystallized from a hexane mixture at −45 °C to yield **4b** as a blue to purple solid (0.355 g, 0.41 mmol, 85%). IR: 1419 m, 1262 m, 1236 m, 1212 m, 1117 w, 887 w, 860 w, 834 m, 824 m, 804 w, 776 w, 718 w, 702 w, 532 m cm^{-1}. ^{1}H NMR (500.1 MHz, benzene-*d*$_6$): δ 19.72 (s, 2 H, OAr*H*), 10.39 (s, 3 H, Ar*Me*), −5.72 (br s, 18 H, C*Me*$_3$), −9.67 (s, 3H, Al*Me*$_3$), −17.36 (s, 6H, Al*Me*$_3$). Anal. Calcd for C$_{48}$H$_{78}$AlNdO$_3$: C, 65.94; H, 8.99. Found: C, 66.29; H, 9.25.

Nd(OC$_6$H$_3$*i*Pr$_2$-2,6)$_3$(AlMe$_3$)$_2$ (5b). To a suspension of **2b** (0.352 g, 0.26 mmol) in hexane was slowly added a hexane solution of 2.0 equiv of TMA (0.075 g, 1.04 mmol) and the mixture was stirred at ambient temperature overnight. Then, the solvent was removed in vacuo. The remaining solid was crystallized from hexane at −45 °C to yield **5b** as purple crystals (0.174 g, 0.21 mmol, 81%). IR: 1587 w, 1365 m, 1320 m, 1298 w, 1256 m, 1198 m, 1170 s, 1097 m, 1053 w, 1041 m, 934 w, 887 m, 866 m, 836 m, 798 m, 754 s, 701 s, 603 m, 565 m, 534 w, 477 m cm^{-1}. ^{1}H NMR (600.1 MHz, benzene-*d*$_6$): δ 31.57 (s, 4 H, C*H*Me$_2$), 20.25 (d, 6 Hz, 4 H, OAr *meta*), 14.95 (t, 6 Hz, 2 H, OAr *para*) 2.28 (t, 6 Hz, 2 H, OAr *meta*), −12.81 (br s, 18 H, Al*Me*$_3$), −27.17 (br s, 36 H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (150.9 MHz, benzene-*d*$_6$): δ 201.3 (μ-OAr *ipso*), 201.3 (OAr *ipso*), 144.2, 143.8, 141.2, 140.8, 139.4, 127.6, 125.7, 125.6, 125.4, 122.5, 113.3, 42.4 (Al*Me*$_3$), 26.7 (μ-*C*HMe$_2$), 26.5 (*C*HMe$_2$), 25.6 (μ-CH*Me*$_2$), 25.3 (CH*Me*$_2$). Anal. Calcd for C$_{42}$H$_{69}$Al$_2$NdO$_3$: C, 61.50; H, 8.48. Found: C, 61.45; H, 8.51.

La(OCH$_2$*t*Bu)$_3$(AlMe$_3$)$_3$ (6a). To a solution of **3a** (0.320 g, 0.20 mmol) in hexane was slowly added a hexane solution of 3.0 equiv of TMA (0.173 g, 2.40 mmol) and the mixture was stirred at ambient temperature for 1 h. Then, the solvent was removed in vacuo. The remaining solid was crystallized from hexane at −45 °C to yield **6a** as colorless needles (0.315 g, 0.51 mmol, 64%). IR:

1402 w, 1364 m sh, 1208 w, 1193 m, 1036 m, 1013 m, 702 s, 592 w, 582 w, 572 m, 487 w, 461 m cm^{-1}. ^{1}H NMR (400.1 MHz, benzene-d_6): δ 3.60 (s, 6 H, CH_2), 0.83 (s, 27 H, CMe_3), −0.23 (s, 27 H, AlMe_3). ^{13}C{^{1}H} NMR (100.5 MHz, benzene-d_6): δ 77.0 (CH$_2$), 32.9 (CMe$_3$), 27.1 (CMe_3), −1.6 (AlMe_3). Anal. Calcd for $C_{24}H_{60}Al_3LaO_3$: C, 46.75; H, 9.81. Found: C, 46.28; H, 9.55.

Nd(OCH$_2$*t*Bu)$_3$(AlMe$_3$)$_3$ (6b). Following the procedure described above for **6a**, **3b** (0.325 g, 0.20 mmol) and TMA (0.173 g, 2.40 mmol) yielded **6b** as blue needles (0.404 g, 0.65 mmol, 81%). IR: 1404 w, 1313 w, 1258 w, 1211 w, 1195 m, 1036 m, 1009 s, 936 w, 703 s br, 573 m, 536 w, 482 w, 463 w cm^{-1}. ^{1}H NMR (500.1 MHz, benzene-d_6): δ 5.32 (br s, 6 H, CH_2), 4.32 (br s, 27 H, CMe$_3$), −18.91 (br s, 27H, AlMe_3). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 32.0, no additional signals detected. Anal. Calcd for $C_{24}H_{60}Al_3NdO_3$: C, 46.35; H, 9.72. Found: C, 46.94; H, 10.04.

Y(OCH$_2$*t*Bu)$_3$(AlMe$_3$)$_3$ (6c). Following the procedure described above for **6a**, **3c** (0.280 g, 0.20 mmol) and TMA (0.173 g, 2.40 mmol) yielded **6c** as colorless needles (0.336 g, 0.60 mmol, 74%). IR: 1405 w, 1366 s sh, 1315 w, 1261 w, 1216 m, 1195 m, 1035 m, 1009 s, 936 w, 698 s, 590 m, 577 m, 572 m, 539 w, 478 m cm^{-1}. ^{1}H NMR (400.1 MHz, benzene-d_6): δ 3.74 (s, 6 H, CH_2), 0.88 (s, 27 H, CMe_3), −0.26 (s, 27 H, AlMe_3). ^{13}C{^{1}H} NMR (100.5 MHz, benzene-d_6): δ 77.2 (CH$_2$), 33.1 (CMe$_3$), 26.9 (CMe_3), −2.9 (AlMe_3). Anal. Calcd for $C_{24}H_{60}Al_3O_3Y$: C, 50.88; H, 10.67. Found: C, 50.87; H, 10.70.

Reaction of Compounds 4, 5, and 6 with Dimethyl- and Diethylaluminum Chloride. The reaction procedure is representatively described for **4a**. To a solution of **4a** (87.4 mg, 0.10 mmol) in hexane 0.1 mL of a 1.0 M solution of Me_2AlCl in hexane was added at ambient temperature. The mixture was stirred for 1 h. Then, the volatiles were removed under vacuum and the residue characterized by NMR spectroscopy in benzene-d_6. Al_2Me_6 was detected when the chlorination reaction was performed as an NMR experiment. The NMR data of all $R_2AlOR/RAl(OR)_2$ separation products are listed in the Supporting Information (cf., refs 30, 33, and 34).

Polymerization of Isoprene. All manipulations were performed in a glovebox under an argon atmosphere. A detailed polymerization procedure (run 20, Table 1) is described as a typical example. To a solution of **6b** (12.4 mg, 0.02 mmol) in 8 mL of hexane 2 equiv Et_2AlCl (5 μL, 0.04 mmol) were added and the mixture was "aged" for 30 min. After the addition of isoprene (2.0 mL, 20 mmol), the polymerization was carried out at 40 °C for 24 h. The polymerization was terminated by pouring the mixture into a large quantity of acidified 2-propanol containing 0.1% (w/w) 2,6-di-*tert*-butyl-4-methylphenol as stabilizer. The polymer was washed with 2-propanol and dried under vacuum at ambient temperature to constant weight. The monomer conversion was determined gravimetrically.

Polymer Characterization. The molar masses (M_w, M_n) of the polymers were determined by size exclusion chromatography (SEC) with a SEC apparatus operated with a pump supplied by Waters (type: Waters 510) and Ultrastyragel columns with pore sizes of 500, 1000, 10000, and 100000 Å (eluent, $CHCl_3$; flow rate, 0.5 mL/min). Sample solutions (1.0 mg of polymer per mL of $CHCl_3$) were filtered through a 0.2 μm syringe filter prior to injection. The signals were detected by a differential refractometer (Waters 410) and calibrated against polystyrene standards from Fluka (M_w/M_n < 1.15). The microstructure of the polyisoprene samples was examined by ^{13}C NMR experiments in $CDCl_3$.

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Supporting Information Available: Text and figures showing the NMR data for paramagnetic Nd(III) complexes Nd[N(SiMe$_3$)$_2$]$_3$, **1b**, **2b**, and **3b**, text discussing the activation sequence of **2b**/**5b** and $R_2AlOR/RAl(OR)_2$ separation products, and a crystallographic information file (CIF) for compound **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) For comparison, in the case of the smaller metal center yttrium, the increased steric bulk of the *tert*-butyl-substituted aryloxide OAr^{tBu} led to the formation of the bis(aryloxide)−mono(tetramethylaluminate) complex [Y(OAr^{tBu})$_2$(AlMe$_4$)] via aryloxide → alkyl exchange; see ref 13.

(20) Crystallographic data for compound **5b**: $C_{42}H_{69}Al_2NdO_3$, $M = 820.17$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 11.714$ (1) Å, $b = 18.289$ (1) Å, $c = 20.855$ (1) Å, $V = 4467.9$ (5) Å^3, $Z = 4$, $\rho_{calcd} = 1.219$ gcm^{-3}, $F(000) = 1724$, μ(Ag Kα) = 0.661 mm^{-1}, $\lambda = 0.56087$ Å, and $T = 173$ K. The 33840 reflections measured on a STOE IPDS2 IP area detector yielded 8970 unique data ($\Theta_{max} = 20.5°$, $R_{int} = 0.084$) [7694 observed reflections ($I > 2\sigma(I)$)]. $R1 = 0.0557$, $wR2 = 0.0795$, GooF = 0.977. All hydrogen atoms except those of the bridging methyl

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