Polymerization Catalysts

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Rare-Earth Metal Mixed Chloro/Methyl Compounds: Heterogeneous–Homogeneous Borderline Catalysts in 1,3-Diene Polymerization**

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The nature of the active rare-earth-metal species of Ziegler mixed catalysts has been a matter of dispute since the early discoveries of their superior performance in the stereospecific polymerization of 1,3-dienes.[1,2] A prominent example for a ternary catalyst system is the industrially applied carboxylate-based mixture [Nd(O_2CR)$_3$]/$Et_3Al_2Cl_3$/$i$$Bu_2AlH$ (1:1:8).[2] It is commonly accepted that the active rare-earth metal center is obtained in a two-step activation sequence involving the formation of a reactive Ln−alkyl or Ln−hydride bond and Al→Ln chloride transfer ("cationization"). Using an alkylation–chlorination sequence, we found that preformed Ln/Al heterobimetallic complexes such as [$LnAl_3Me_8(O_2CC_6H_2iPr_3$-2,4,6)$_4$], [Ln(OR)$_3$($AlMe_3$)$_n$] (R = neopentyl, 2,6-$R^*{}_2C_6H_3$ (R^* = tBu, iPr)), and [Ln($AlMe_4$)$_3$] can be considered as alkylated intermediates which, upon further activation with Et_2AlCl, give highly efficient initiators for isoprene polymerization.[3–5] We proposed [Me_2LnCl]$_n$ and [$MeLnCl_2$]$_n$ as the actual initiating species,[3,6] which is in line with the scenarios discussed by Taube and Okuda and their co-workers involving cationic initiators of the type $[Nd(C_3H_5)(C_4H_6)_n]^{2+}([MAO\text{-}R']^-)_2$ (MAO = methylalumoxane, R = allyl or chloride)[7] or $[YMe_2(solv)_5]^+[BR_4]^-$ and $[YMe(solv)_6]^{2+}([BR_4]^-)_2$ as true active species.[8] We also suggested 1) an exclusive better-to-handle and solubility-imparting action of *O*-coordinating carboxylate or aryl(alk)oxide ligands, 2) cluster formation during the initiating step, and 3) that the various organoaluminum compounds present in the catalyst mixtures act as chain-transfer reagents.[3–5] Herein, we describe the synthesis and isolation of the putative active species [Me_2LnCl]$_n$ and [$MeLnCl_2$]$_n$ utilizing lanthanide precursors with preformed Ln−Cl moieties (i.e. a chlorination–alkylation sequence) as well as their successful application in highly *cis*-stereoregular isoprene polymerization. In addition, the implications of rare-earth metal cation size, in situ preparation, solvent, and chlorine versus borate activation are addressed. Given the ease of organoaluminum-mediated Ln−NR_2→Ln−alkyl transformations,[1b] we selected heteroleptic amido/chloride complexes of the rare-earth metals as target molecules. Keeping the routinely encountered dilemma of hard-to-control Ln−Cl/NR_2 salt metathesis ligand exchange reactions (i.e. ease of ate complexation and ligand redistribution) in mind, we chose $[N(SiHMe_2)_2]^-$ as the amido component because of its relatively low basicity and favorable exchangeability (extended silylamide route).[9] Heteroleptic derivatives featuring the sterically larger bis(trimethylsilyl)amido ligand have been described, including X-ray structures of [{Ln{N($SiMe_3$)$_2$}$_2$(μ-Cl)(thf)}$_2$] (Ln = Ce, Nd, Eu, Gd, Yb),[10–12] [{Yb{N($SiMe_3$)$_2$}$_2$(μ-Cl)}$_2$],[12] and [Sc{N($SiMe_3$)$_2$}Cl_2(thf)$_2$].[13] On the other hand, complexes [Ln{N($SiHMe_2$)$_2$}$_3$(thf)$_n$] (**1**) are obtained ate-complex-free from the reaction of [$LnCl_3$(thf)$_n$] with three equivalents of LiN($SiHMe_2$)$_2$.[9] For the smaller rare-earth metal centers, the two-equivalent reaction afforded a mixture of **1** and the envisaged dimeric species [{Ln{N($SiHMe_2$)$_2$}$_2$(μ-Cl)(thf)}$_2$] (**2a**: Ln = Sc, **2b**: Ln = Y; Scheme 1).

^{1}H NMR spectroscopy revealed the formation of complexes **2** in 50 to 70% yields with proton resonances shifted slightly downfield compared to **1**. The monoamido derivatives [Ln{N($SiHMe_2$)$_2$}Cl_2(thf)$_n$] (**3**) were initially detected only in traces, whereas after several weeks in hexane solution, extensive ligand scrambling in **2** occurred, with formation of **1** and **3** as the main components.[10–12] Because of their similar solubility in both polar and apolar solvents, complete separation of **1**, **2**, and **3** was unsuccessful. However, single-crystalline **2a** (Sc) and **2b** (Y) could be obtained by fractional crystallization. As found for [{Ln{N($SiMe_3$)$_2$}$_2$(thf)(μ-Cl)}$_2$] (Ln = Ce, Nd, Eu, Gd, Yb),[10–12] X-ray structural analyses of **2a** and **2b** revealed dimeric complexes with penta-coordinate metal centers (Figure 1A, for **2a** see the Supporting Information).[14]

The Ln−N bond distances (**2a** Sc−N(av) 2.049 Å; **2b** Y−N(av) 2.231 Å) differ marginally from those observed in four-coordinate [Sc{N($SiHMe_2$)$_2$}$_3$(thf)] (**1a**; 2.069 Å (av)) and five-coordinate [Y{N($SiHMe_2$)$_2$}$_3$(thf)$_2$] (**1b**; 2.260 Å (av)).[9,15] Significant Ln···(Si−H) β-agostic interactions, as often found for {LnN($SiHMe_2$)$_2$} moieties, are detected, one for each Sc center in **2a** and two for each Y center in **2b,** as indicated by acute angles to the amido ligands $\sphericalangle$(Ln-N-Si) (e.g. $\sphericalangle$(Y-N2-Si4) = 99.28(7)) and by distinct $\tilde{\nu}_{SiH}$ stretching vibrations (e.g. 1942 cm^{-1} for **2b**).[16] For paramagnetic neodymium(III), the analogous reaction gave compound **4d**, which, according to identical ^{1}H NMR spectra of the crude and crystallized product, did not contain [Nd{N($SiHMe_2$)$_2$}$_3$(thf)$_2$] (**1d**; see the Supporting Information).

Compound **4d** was obtained reproducibly when 1.9–2.1 equivalents of LiN($SiHMe_2$)$_2$ were used. An X-ray crystallo-

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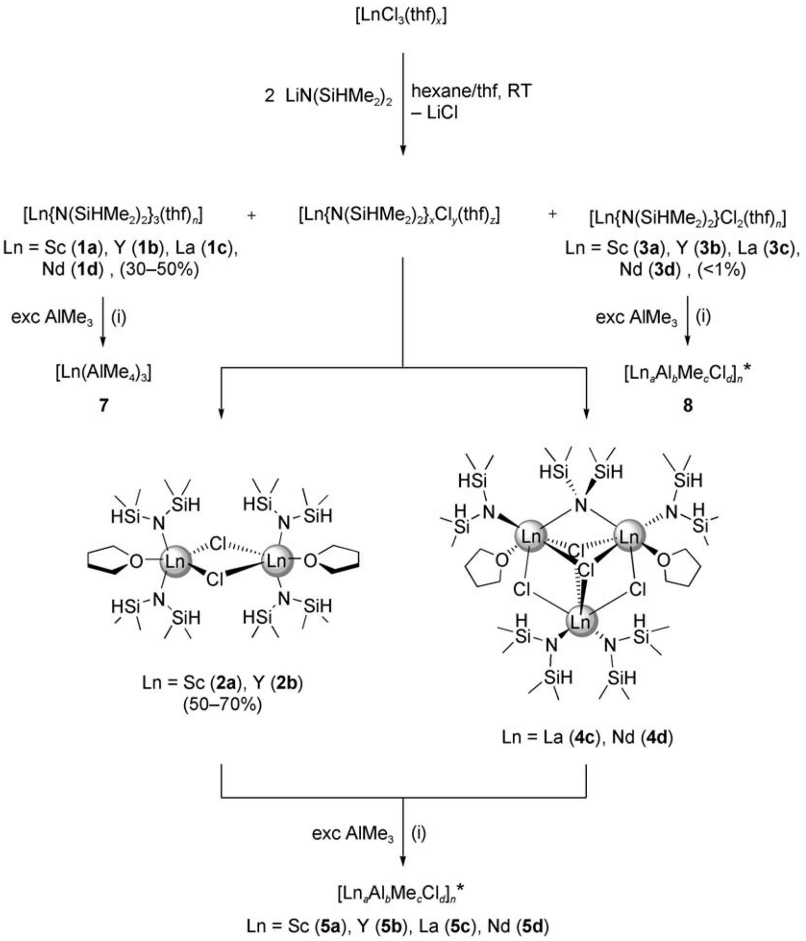


Scheme 1. Salt-metathesis synthesis of mixed amide/chloride lanthanide complexes **2**–**4** and subsequent $AlMe_3$-mediated alkylation to yield mixed methyl/chloride species **5**; (*) $a+b=1$, $a>b$; $c+d=3$, $d>c$ (**5**), $d \gg c$ (**8**); i) hexane, RT, $-[(Me_2Al\{\mu\text{-}N(SiHMe_2)_2\})_2]$, $-[AlMe_3(thf)]$.

graphic investigation of **4d** revealed the formation of a mixed neodymium amide/chloride cluster of molecular composition $[\{Nd\{N(SiHMe_2)_2\}(thf)\}_2(Nd\{N(SiHMe_2)_2\}_2)(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_2\text{-}\{\mu\text{-}N(SiHMe_2)_2\}]$ (Figure 1B).[14] The size criterion suggests a similar trimetallic cluster for the lanthanum derivative **4c**. Compound **4d** features six-coordinate neodymium centers with distorted octahedral coordination (unlike $[Yb_3X_4O\{N(SiMe_3)_2\}_3(thf)_3]$ (X = Cl, Br)),[12,15] with two distinct metal coordination environments. Two neodymium atoms (Nd2 and Nd3) are each surrounded by one terminal and one μ_2-amido ligand as well as one μ_2- and two μ_3-chlorine atoms. Nd1, on the other hand, is surrounded by two terminal amido ligands as well as two μ_3- and two μ_2-chlorine atoms. The terminal Nd–N bond lengths (av 2.296 Å) are significantly shorter than those in five-coordinate **1d** (av 2.344 Å).[16] The Nd–μ_3-Cl separations (av 2.8868 Å) are longer than the Nd–μ_2-Cl ones (av 2.8009 Å) and fall in the range of those observed for $[Nd_5Cp^*_5\{(\mu\text{-}Me)_3AlMe\}(\mu_4\text{-}Cl)(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_6]$ (2.731(4)–3.000(4) Å; $Cp^* = C_5Me_5$).[17] In the solid state, all silylamido ligands are agostically distorted, each forming one acute angle ∢(Nd-N-Si) (e.g. ∢(Nd2-N1-Si) = 94.1(2); Nd2···Si1 3.227(1) Å).

When the initially formed and isolated **1** + **2**/**4** product mixtures were treated with an excess of $AlMe_3$ in hexane, instantaneous precipitation of amorphous solids $[Ln_aAl_bMe_cCl_d]_n$ (**5a** Ln = Sc, **5b** Ln = Y, **5c** Ln = La, **5d** Ln = Nd; $a+b=1$, $a>b$; $c+d=3$, $d>c$) occurred, as indicated by elemental analysis and magic-angle-spinning (MAS) NMR spectroscopy (Scheme 1).[18] According to the literature, $[Ln\{N(SiHMe_2)_2\}_3(thf)_n]$ **1** reacts with $AlMe_3$ to form hexane-soluble $[Ln(AlMe_4)_3]$ (**7**), which can be separated together with the hexane-soluble coproducts $[(AlMe_2\{\mu\text{-}N(SiHMe_2)_2\})_2]$ and $[AlMe_3(thf)]$.[5,9] The monoamido derivatives **3** might form mixed chloro/methyl compounds **8** with lower methyl content than **5** (i.e. $d \gg c$). The ^1H MAS NMR spectrum of **5b** shows a broad resonance centered at 4.1 ppm that exhibits one well-resolved shoulder at approximately $\delta = 8.9$ ppm (Figure 2A; compare to $[YMe_3]_n$: $\delta = 1.0$ (sh), 0.1 (sh), −0.3 ppm).[19] In the ^{13}C MAS NMR spectrum, the resonance of the methyl carbon atoms of **5b** appears at about $\delta = 12$ ppm (Figure 2B) and, hence, is shifted considerably upfield compared to that of $[YMe_3]_n$ ($\delta = 28.3$ ppm). The low-temperature solution ^{13}C NMR spectrum of $[Y(AlMe_4)_3]$ in $[D_5]$toluene ($\delta = 13.7$ ppm $Y(\mu\text{-}CH_3)Al$; $\delta = -8.5$ ppm $AlCH_3$) suggests bridging methyl groups as the predominant carbon species, while terminal methyl groups seem to be absent (compare to $\delta = -6.4$ ppm $Al(CH_3)_2Cl$; $\delta = -7.2$ ppm $Al(CH_3)_3$).[20]

The white **5a**, **5b**, and **5c** and bluish **5d** materials are completely insoluble in hexane, toluene, or benzene, which eases further purification by washing with these solvents (Caution! Compounds **5**, **5′**, and **6** (see below) ignite spontaneously when exposed to air). The alkylated products **5** dissolve in Et_2O and thf, and it is tempting to speculate about the initial formation of cationic species such as $[LnMe_2(thf)_5]^+Cl^-$ and $[LnMe(thf)_6]^{2+}(Cl^-)_2$, consistent with Okuda and co-workers' $[LnMe_2(thf)_5]^+[BPh_4]^-$ and $[LnMe(thf)_6]^{2+}([BPh_4]^-)_2$.[8,21] However, a solution of $[Y_aAl_bMe_cCl_d]_n$ (**5b**) in thf was shown to form a white precipitate immediately. After several days, crystals could be harvested, which were identified as $[YCl_2(thf)_5]^+[YCl_4(thf)_2]^-$ by X-ray structural analysis.[22]

The mixed Me/Cl compounds **5** exhibit a reactivity which is fundamentally different from that found for the homoleptic species $[YMe_3]_n$.[19,23] For example, neither protonolysis reactions with *t*Bu-substituted phenols or HCp* nor alkylation of 9-fluorenone were observed.[23] Instead, a remarkable performance of the neodymium derivative **5d** in 1,3-diene polymerization was found, which is indicative of a "single-component" initiator. Solid $[Nd_aAl_bMe_cCl_d]_n$ (**5d**) polymerized isoprene with greater than 99 % *cis* stereospecificity and in quantitative yield (run 4, Table 1; monomer conversion

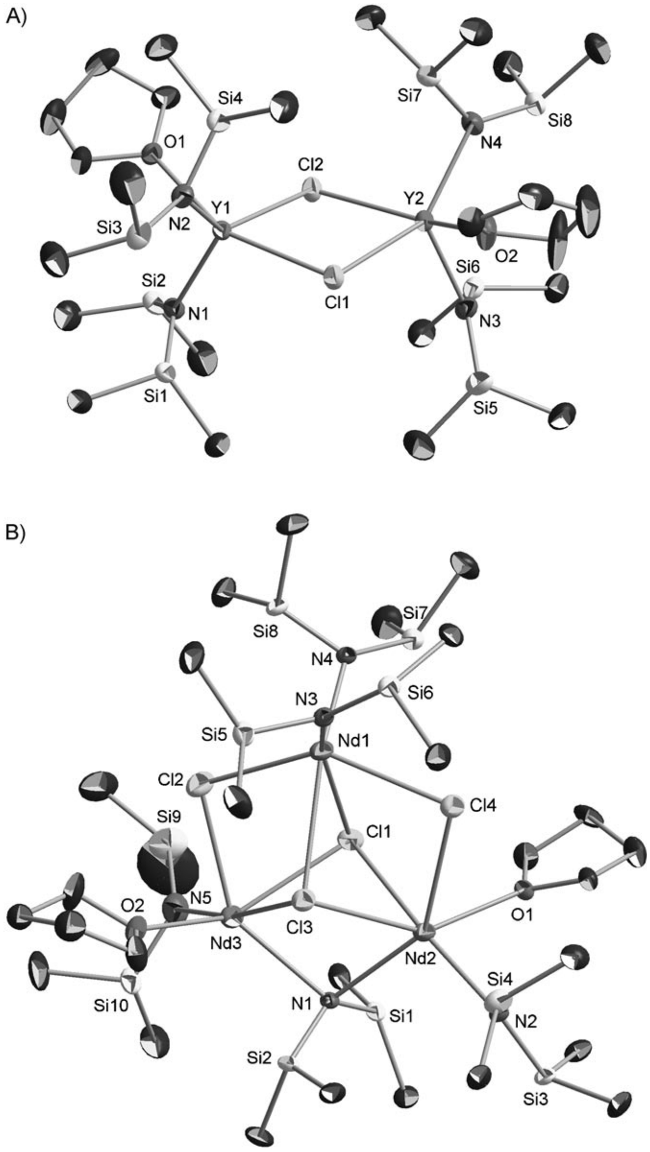


Figure 1. Molecular structures of A) **2b** with thermal ellipsoids set at the 50% probability level and B) **4d** with thermal ellipsoids of the $\{Nd_3Cl_4\}$ core set at the 50% probability level and all others set at the 30% probability level. For clarity, all hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: **2b** Y1–N1 2.2207(14), Y1–N2 2.2449(15), Y1–O1 2.3372(12), Y1–Cl1 2.6852(4), Y1–Cl2 2.7100(4); Y1-N1-Si1 105.06(7), Y1-N1-Si2 125.17(8), Y1-N2-Si3 133.06(8), Y1-N2-Si4 99.27(7), Y2-N3 2.2111(15), Y2-N4 2.2488(15), Y2-O2 2.3323(13), Y2-Cl1 2.7001(5), Y2-Cl2 2.7140(4), Y2-N3-Si5 126.95(7), Y2-N3-Si6 105.18(7), Y2-N4-Si7 100.72(7), Y2-N4-Si8 129.26(9). **4d** Nd1–N3 2.304(3), Nd1–N4 2.301(3), Nd1–Cl1 3.1256(10), Nd1–Cl2 2.8316(10), Nd1–Cl3 3.0290(9), Nd1–Cl4 2.8097(10), Nd2–N1 2.610(3), Nd2–N2 2.301(3), Nd2–Cl1 2.8802(9), Nd2–Cl3 2.8675(9), Nd2–Cl4 2.8020(9), Nd2–O1 2.458(3), Nd3–N1 2.564(3), Nd3–N5 2.278(3), Nd3–Cl1 2.8858(10), Nd3–Cl2 2.7607(10), Nd3–Cl3 2.9136(9), Nd3–O2 2.478(3); Nd1-N3-Si5 104.9(2), Nd1-N3-Si6 131.5(2), Nd1-N4-Si7 130.2(2), Nd1-N4-Si8 102.3(2), Nd2-N1-Si1 94.1(2), Nd2-N1-Si2 119.2(2), Nd2-N2-Si3 135.3(2), Nd2-N2-Si4 101.7(2), Nd3-N1-Si1 123.1(2), Nd3-N1-Si2 94.7(2), Nd3-N5-Si9 129.5(2), Nd3-N5-Si10 103.7(2).

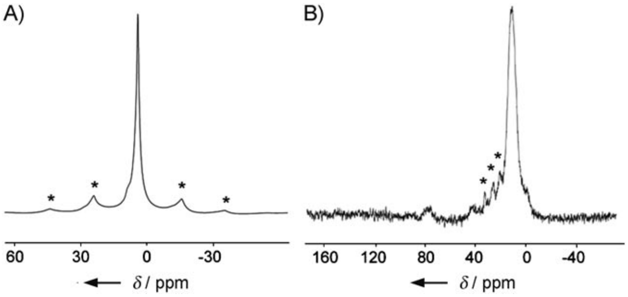


Figure 2. A) ^1H and B) ^{13}C magic angle spinning (MAS) NMR spectra of neat $[Y_aAl_bMe_cCl_d]_n$ (**5b**). Rotational side bands (A) and solvent (B, hexane) are indicated by asterisks.

seems to be complete after 15 min as indicated by a wedged stirring bar).

The overall low efficiency (16%) originates from an initially heterogeneous catalysis ("borderline") and hence non-availability of a major portion of the Nd centers in **5d**. The efficiency could be improved to 64% by using toluene instead of hexane as the solvent (run 5, Table 1). Solid $[Nd_aAl_bEt_cCl_d]_n$ (**6**), obtained by alkylation of cluster **4d** with $AlEt_3$, gave a lower monomer conversion but with the same high *cis* stereoregularity (run 6, Table 1). These findings are highly supportive of the sequential alkylation–chlorination scenario that was recently suggested for the binary system $[Ln(AlMe_4)_3]/R_2AlCl$ (Scheme 2).[3,5] Accordingly, the $n_{Cl}:n_{Ln}$ ratio (1 versus 2) directs the formation of transient $[Me_2LnCl]_n$ and $[MeLnCl_2]_n$ as active species in isoprene polymerization.

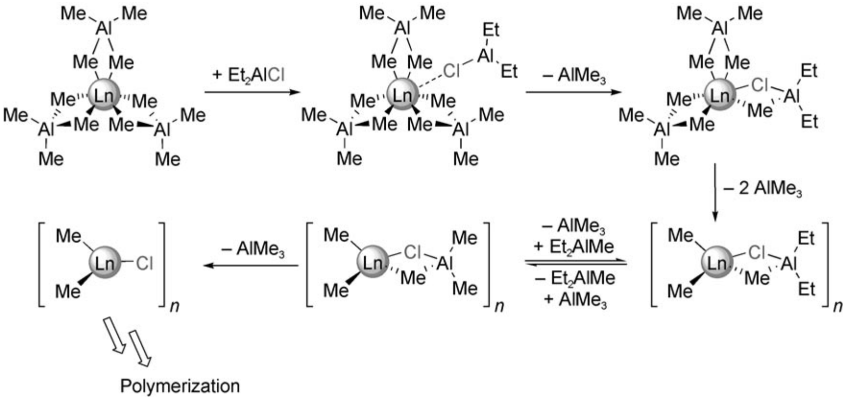
For comparison, the donor-free mono- and dichloro oligobutadienyl Nd-based initiators $[Nd(\eta^3\text{-}C_3H_4R)_2Cl]$ and $[Nd(\eta^3\text{-}C_3H_4R)Cl_2]$ (obtained in situ by pretreatment of solvent-free $[Nd(\eta^3\text{-}C_3H_5)_3]$ with a small amount of butadiene and addition of one or two equivalents of Ph_3CCl) afforded lower yields, similarly low efficiency, and less than 90% *cis* content.[24] Importantly, the efficiency of the latter in situ generated catalyst system $[Nd(\eta^3\text{-}C_3H_4R)Cl_2]$ could be markedly increased by addition of five equivalents $AlMe_3$ or $AlEt_3$, the former organoaluminum "auxiliary" (M_n/M_w 2.7; 88% *cis*) being more favorable than the latter (M_n/M_w 7.5–17.6; ca. 60% *cis*).[25] The scandium (**5a**, run 1, Table 1), yttrium (**5b**, run 2, Table 1), and lanthanum (**5c**, run 3, Table 1) compounds either did not polymerize isoprene or did so poorly, which is in accordance with the intrinsic neodymium effect previously found in binary and ternary catalyst mixtures.[1–5]

To better compare the chlorination–alkylation and alkylation–chlorination sequences, we had another look at the binary system $[Nd(AlMe_4)_3]$/co-catalyst.[5] The efficiency of the 1,4-*cis*-polymerization of isoprene was enhanced by selecting toluene as a solvent, albeit to some extent at the expense of polymer yields (runs 7–10, Table 1). It has been suggested that π coordination of toluene molecules at the Nd^{III} centers partly blocks the isoprene coordination and hence leads to slightly lower yields and changed molecular weights.[1,2,26] We also examined a larger-scale reaction of $[Nd(AlMe_4)_3]$ (**7d**) with two equivalents of Me_2AlCl, the mixture of which represents the most active catalyst. The

Table 1: Effect of Ln size, in situ preparation, type of solvent, and electron-withdrawing anions on the polymerization of isoprene.

Run[a]	Catalyst	Co-catalyst[e]	Yield [%]	Selectivity [%][f]	M_n [$\times 10^3$][g]	M_w [$\times 10^3$][g]	M_n/M_w[g]	Eff. [%][h]
Chlorination–alkylation sequence:								
1	$[Sc_aAl_bMe_cCl_d]_n$ (**5a**)	–	ca. 2	> 99:0:0	119	266	2.23	< 1
2	$[Y_aAl_bMe_cCl_d]_n$ (**5b**)	–	ca. 1	> 99:0:0	n.d.[j]	n.d.[j]	n.d.[j]	n.d.[j]
3	$[La_aAl_bMe_cCl_d]_n$ (**5c**)	–	30	> 99:0:0	135	288	2.13	15
4	$[Nd_aAl_bMe_cCl_d]_n$ (**5d**)	–	> 99	> 99:0:0	430	908	2.11	16
5[b]	$[Nd_aAl_bMe_cCl_d]_n$ (**5d**)	–	> 99	> 99:0:0	106	223	2.10	64
6	$[Nd_aAl_bEt_cCl_d]_n$ (**6d**)	–	52	> 99:0:0	90	421	4.67	39
Alkylation–chlorination sequence (in situ cationization):								
7	$[Nd(AlMe_4)_3]$ (**7d**)	$n_{Et_2AlCl}:n_{Nd} = 1:1$	> 99	> 99:0:0	181 (228)[i]	530 (788)[i]	2.92 (3.45)[i]	38
8[b]	$[Nd(AlMe_4)_3]$ (**7d**)	$n_{Et_2AlCl}:n_{Nd} = 1:1$	82	> 99:0:0	56	207	3.53	100
9	$[Nd(AlMe_4)_3]$ (**7d**)	$n_{Et_2AlCl}:n_{Nd} = 2:1$	> 99	> 99:0:0	198 (117)[i]	440 (326)[i]	2.23 (2.78)[i]	34
10[b]	$[Nd(AlMe_4)_3]$ (**7d**)	$n_{Et_2AlCl}:n_{Nd} = 2:1$	> 99	> 99:0:0	46	219	4.75	148
11	$[Nd_aAl_bMe_cCl_d]_n$ (**5d′**)	–	> 99	> 99:0:0	285	501	1.76	24
12	$[Nd_aAl_bMe_cCl_d]_n$ (**5d′**)[c]	–	> 99	n.d.[j]	135	237	1.75	50
13	$[Nd(AlMe_4)_3]$ (**7d**)	$n_{[PhNHMe_2][B(C_6F_5)_4]}:n_{Nd} = 1:1$	89	57:39:4	94	304	3.24	64
14[b]	$[Nd(AlMe_4)_3]$ (**7d**)	$n_{[PhNHMe_2][B(C_6F_5)_4]}:n_{Nd} = 1:1$	> 99	48:48:4	93	184	1.98	73
15	$[Nd(AlMe_4)_3]$ (**7d**)	$n_{[PhNHMe_2][B(C_6F_5)_4]}:n_{Nd} = 2:1$	44	63:33:4	72	272	3.79	42
16[b]	$[Nd(AlMe_4)_3]$ (**7d**)	$n_{[PhNHMe_2][B(C_6F_5)_4]}:n_{Nd} = 2:1$	77	53:42:5	98	218	2.23	53
17	$[Nd(carboxylate)_3]$[d]	$n_{Et_2AlCl}:n_{HAliBu_2}:n_{Nd} = 1:8:1$	> 99	n.d.[j]	27	111	4.11	252
18	$[PhNHMe_2][B(C_6F_5)_4]$	–	0	n.d.[j]	n.d.[j]	n.d.[j]	n.d.[j]	n.d.[j]

[a] Polymerization procedure: 0.02 mmol catalyst, 8 mL hexane, 20 mmol isoprene, 24 h, 40 °C. [b] Polymerization procedure: 0.02 mmol catalyst, 8 mL toluene, 20 mmol isoprene, 24 h, 40 °C. [c] + 50 equivalents $AlMe_3$. [d] carboxylate = 2,2-dimethylbutyrate. [e] Preformation time before addition of isoprene 15 min. [f] Measured by ^{13}C NMR spectroscopy in $CDCl_3$; ratio: *cis*/*trans*/3,4. [g] Determined by means of size exclusion chromatography (SEC) against polystyrene standards. M_n = number-average molecular weight; M_w = weight-average molecular weight. [h] Efficiency: M_n(calculated)/M_n(measured); $[isoprene]_0/[cat] = 1000:1$. [i] Literature value in parentheses.[5] [j] n.d. = not determined.



Scheme 2. A mechanistic scenario for the formation of the active species $[Me_2LnCl]_n$ from $[Ln(AlMe_4)_3]$ and Et_2AlCl. Ligand scrambling has not been taken into account.

bluish precipitate, which could be isolated from hexane, was identified as $[Nd_aAl_bMe_cCl_d]_n$ (**5d′**) (for ^1H and ^{13}C CPMAS NMR spectra (CP = cross polarization) of **5d′** and the yttrium congener **5b′**, see the Supporting Information).[27] This result is in accordance with the scenario shown in Scheme 2 considering the action of a second equivalent of co-catalyst Et_2AlCl. Like **5d**, compound **5d′** could be employed as a single-component catalyst (i.e. it needs no soluble organoaluminum compounds), affording markedly lower M_n/M_w (1.76, run 11, Table 1) compared to the corresponding in situ generated $[Nd(AlMe_4)_3]/Et_2AlCl$ ($n_{Ln}:n_{Cl} = 1:2$) catalyst mixture (run 9, Table 1) and to the commercialized carboxylate ternary initiator (run 17, Table 1).[28]

The crucial *cis*-directing role of the chloride co-ligand could be further corroborated by examining the binary system $[Nd(AlMe_4)_3]/[PhNHMe_2][B(C_6F_5)_4]$ featuring $[B(C_6F_5)_4]^-$ instead of Cl^- as the electron-withdrawing cationizing anion (runs 13–16, Table 1). Use of a $n_{Ln}:n_{[PhNHMe_2][B(C_6F_5)_4]}$ ratio of 1:1 and toluene as a solvent gave a reasonably active initiator system.[29] However, the *cis* selectivity was very low (63 %), which is in agreement with the polymerization performance of in situ generated catalyst systems $[Y(AlMe_4)_3]/[PhNHMe_2][B(C_6F_5)_4]$[8] and $[Nd\{N(SiMe_3)_2\}_3]/[PhNHMe_2][B(C_6F_5)_4]/AliBu_3$.[30]

In conclusion, we could show that the active species of neodymium-based Ziegler mixed catalysts can be isolated and fully characterized. Two convergent strategies, a chlorination–alkylation and an alkylation–chlorination sequence, give access to polymeric species, which we denote $[Nd_aAl_bMe_cCl_d]_n$ and which are highly active catalysts for 1,3-diene polymerization. We also emphasize that the ratio c:d, which markedly affects the polymer characteristics (M_n and M_n/M_w), is difficult to control owing to complex disproportion reactions. This lack of control is certainly a pivotal dilemma in the development of such Ziegler mixed catalysts. Our ongoing investigations address the effect of alternative weakly coordinating anions and the applicability of solids $[Ln_aAl_bMe_cCl_d]_n$ for olefin transformations in general.

Experimental Section

Representative syntheses of **2b** and **5b**: In a glovebox, $LiN(SiHMe_2)_2$ (1.95 equiv, 0.295 g, 2.12 mmol) was added to a suspension of $[YCl_3(thf)_{3.5}]$ (1 equiv, 0.485 g, 1.08 mmol) in hexane (15 mL). After stirring for 24 h, the reaction mixture was centrifuged, filtered, and the solvent was removed in vacuum. The remaining solid was recrystallized from hexane at −35 °C to give $[\{Y\{N(SiHMe_2)_2\}_2(thf)(\mu\text{-}Cl)\}_2]$ (**2b**) and $[Y\{N(SiHMe_2)_2\}_3(thf)_2]$ (**1b**) in a ratio of 1:0.27 as colorless crystals. The overall amount of **2b** in the crude mixture was determined by ^{1}H NMR spectroscopy to be 73 % (0.365 g, 0.40 mmol). Excess $AlMe_3$ (0.270 g, 3.75 mmol) was added to a mixture of **2b** (0.208 g, 0.23 mmol) and **1b** in hexane (15 mL). The white slurry was stirred for 5 h and the supernatant removed by decantation to give a white powder. After several hexane washings, the material was dried until constant weight to give **5b** (0.047 g, 0.30 mmol, 67 %). Elemental analysis (%) calcd for C_2H_6ClY (154.43 g mol^{-1}): C 15.56, H 3.92; found: C 14.78, H 3.67. For this batch, the Al content was not determined.

Full experimental and physicochemical details for complexes **1–7** are available in the Supporting Information.

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[28] Similar molecular weight distributions have been reported for the binary systems [Nd(OC$_6$H$_3$*i*Pr-2,6)$_3$(AlMe$_3$)$_2$]/Et$_2$AlCl ($M_n/M_w = 2.03$)[4] and [Nd(neopentanolate)$_3$(AlMe$_3$)$_3$]/Et$_2$AlCl ($M_n/M_w = 1.74$)[4] as well as [Nd(AlMe$_4$)$_3$]/Et$_2$AlCl immobilized on MCM-48 ($M_n/M_w = 1.33$–1.88).[5]

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