Polymerization Catalysts

Stereospecific Polymerization of Isoprene with Molecular and MCM-48-Grafted Lanthanide(III) Tetraalkylaluminates**

*Andreas Fischbach, Michael G. Klimpel, Markus Widenmeyer, Eberhardt Herdtweck, Wolfgang Scherer, and Reiner Anwander**

Organolanthanide compounds are not only unique model systems for studying the elementary processes of α-olefin polymerization but they can also act as competitive precatalyst systems,[1] however, to date their implementation in this area has been very limited. In contrast, the interaction of low-agglomerated rare-earth metal ("neodymium") complexes, such as alkoxide or carboxylate derivatives, with various organoaluminum reagents is successfully exploited to generate high-performance catalysts for industrial 1,3-diene polymerization.[2] Solubility in aliphatic solvents, low Al:lanthanide(Ln) ratios, *cis*-stereospecificity, and medium polydispersity are the criteria to be met by such ternary "Ziegler Mischkatalysatoren" (Mischkatalysatoren = mixed catalysts), the mechanisms of which are still not completely understood.[3] Although the homoleptic tetraalkylaluminate complexes $Ln(AlR_4)_3$ have a unique preorganized set of bridged, heterobimetallic moieties, their application in olefin transformations has not been reported so far.[4] Moreover, the compounds $Ln(AlR_4)_3$ are exceptional for they are obtained as alkyl-only ligated monomeric systems, without the formation of ate complexes for the entire lanthanide series. Herein we describe the use of a $Ln(AlR_4)_3/Et_2AlCl$ binary precatalyst system in highly (*cis*)stereoregular isoprene polymerization. Additionally, the use of grafted variants as storable single-component heterogeneous catalysts is investigated by employing periodic mesoporous silica MCM-48 as a structured support material.

Homoleptic tetramethylaluminate complexes of the trivalent lanthanide metals $[Ln\{(\mu\text{-}Me)_2AlMe_2\}_3]$ (**1**) are readily available by the reaction of $LnCl_3(thf)_x$ with three equivalents of $LiNMe_2$ and a subsequent $AlMe_3$-mediated $[NMe_2]\rightarrow[AlMe_4]$ transformation. Following this synthetic strategy Y

[*] A. Fischbach, Dr. M. G. Klimpel, Dr. M. Widenmeyer, Dr. E. Herdtweck, Dr. R. Anwander
Anorganisch-chemisches Institut
Technische Universität München
Lichtenbergstrasse 4, 85747 Garching (Germany)
Fax: (+49) 89-289-13473
E-mail: reiner.anwander@ch.tum.de
Prof. W. Scherer
Institut für Physik
Universität Augsburg, 86159 Augsburg (Germany)

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(**1a**), Nd (**1c**), and Sm (**1d**) derivatives have been obtained previously and fully characterized.[4] To address any stereoelectronic factors, for the present study we also prepared the La (**1b**) and Gd (**1e**) derivatives and the corresponding tetraethylaluminate complexes $[Ln(AlEt_4)_3]$ (**2**). Complexes **1b** and **1e** were isolated as thin colorless needles from saturated hexane solutions at −45 °C in good yields and their composition confirmed by elemental analysis and spectroscopic data. Although a $[NR_2]\rightarrow[AlEt_4]$ transformation was clearly indicated by ^{1}H NMR spectroscopy, the isolation of complexes $[Ln(AlEt_4)_3]$ was tricky owing to the difficult separation of the highly soluble complexes from residual $AlEt_3$ and the alkylated by-product $[\{Et_2Al(\mu\text{-}NMe_2)\}_2]$. Only the reaction of $[La\{N(SiHMe_2)_2\}_3(thf)_2]$ (**3b**) with $AlEt_3$ produced separable single crystals, these took several weeks to form (Scheme 1).

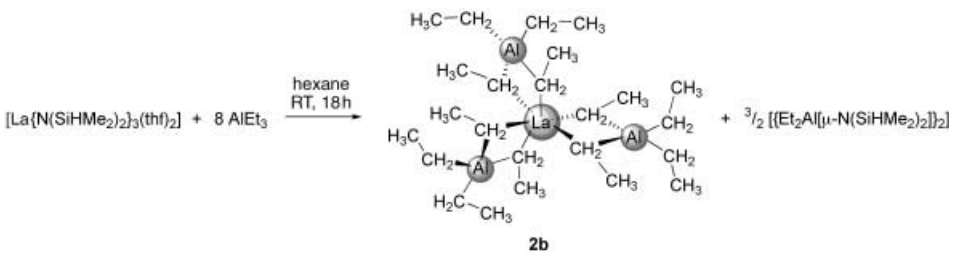
Compound **2b** was fully characterized by elemental analysis and IR and NMR spectroscopy. The protons of the ethyl ligands appear as one set of signals, that is, as a triplet at $\delta = 2.78$ ppm and a quartet at $\delta = 0.18$ ppm in the ^{1}H NMR spectrum. According to a variable temperature NMR study decoalescense of the signals indicating the presence of two bridging and two terminal ethyl groups did not occur even at −90 °C. This fluxional behavior clearly documents a less distinct bonding of the sterically more encumbered tetraethylaluminate units to the large La(III) center compared to the tetramethylaluminate bonding in complexes **1a** and **1d**. Scheme 1 also shows the molecular connectivity of complex **2b** to be $[La\{(\mu\text{-}Et)_2AlEt_2\}_3]$ as derived from an X-ray crystallographic study.[5] Three tetraethylaluminate ligands coordinate in a η^2-fashion implying a distorted trigonal-antiprismatic coordination geometry at the lanthanum center.

Upon activation with 1–3 equivalents of Et_2AlCl, complexes $[Nd(AlMe_4)_3]$ (**1c**, Table 1, entries 7–9) and $[Gd(AlMe_4)_3]$ (**1e**, Table 1, entries 12–14) initiated the stereospecific polymerization of isoprene in quite an efficient manner. Quantitative yields of highly stereospecific *cis*-polymers were obtained within 24 h. Signals assignable to *trans*-1,4-polyisoprene units were not observed in the ^{13}C NMR spectra. Molecular weights and polydispersities follow a similar pattern in the Nd- and Gd-based experiments, seemingly adjustable by the ratio of lanthanide to Et_2AlCl (the n_{Cl}:n_{Ln} ratio). A n_{Cl}:n_{Ln} ratio of 1:1 afforded approximately double the molecular weight than ratios of 2:1 or 3:1. Assuming a living polymerization, this would imply two polymer chains per metal center for the higher n_{Cl}:n_{Ln} ratios. With the smallest and largest metal centers, Y (**1a**) and La (**1b**), respectively, quantitative or almost quantitative yields were obtained only with two equivalents of the chloride source (Table 1, entries 2 and 5);[6] addition of a third equivalent deactivated the catalyst system (Table 1, entries 3 and 6). Whereas **1b** produced *cis*-polymers exclusively, the number of *cis*-connectivities in the yttrium-catalyzed systems increased with the n_{Cl}:n_Y ratio from 67 to 97 %. This is in agreement with other Ln-based catalysts for the polymerization of butadiene and isoprene.[7] Interaction of the cocatalyst with $[Sm(AlMe_4)_3]$ (**1d**) produced low-valent Sm species as shown by the formation of a black solid after 1–2 h, which afforded only 1–7 % of highly stereospecific *cis*-1,4-polyisoprene after one day (Table 1, entries 10 and 11).

The polymerization experiments were repeated with two equivalents of the cocatalyst and stopped after 15 min by pouring the mixtures onto isopropanol. Gravimetrically determined polymer yields increased in the order Y(1) < La(4 %) < Gd(60 %) < Nd(99 %), once more corroborating the intrinsic "neodymium effect" (Table 2, entries 1–4).[8]

To develop a more convenient catalytic system, in situ formation of $[Nd(AlMe_4)_3]$ (**1c**) from $[Nd\{N(SiHMe_2)_2\}_3(thf)_2]$ (**3c**) was examined. Accordingly, silylamide **3c** was treated with 8 equivalents of trimethyl- or triethylaluminum for 15 min and then further activated with 1–3 equivalents of Et_2AlCl. We found that the yields and *cis* stereospecificities from the 24-h reactions were similar to those obtained with pre-isolated **1c** (Table 1, entries 7–9 vs. 15–17). However, molecular weight, polydispersity index (Table 1, entries 15–17), and polymerization rate (Table 2, entries 5 and 6) seemed to be markedly affected by the presence of the by-products $[AlMe_3(thf)]$ and $[\{Me_2Al[\mu\text{-}N(SiHMe_2)_2]\}_2]$. Also, commercially available $[Nd\{N(SiMe_3)_2\}_3]$ (**4**) could be activated with excess trimethylaluminum in the presence of Et_2AlCl to quantitatively polymerize isoprene after 24 h (not listed).[9] In situ activation of **4** in the presence of $AlEt_3$ instead of $AlMe_3$ markedly increased the catalytic activity (Table 2, entries 7 and 8).

The development of more efficient large-scale industrial processes often requires immobilized catalyst species.[10] Such gas-phase and slurry polymerizations favor the control of polymer morphology as well as low cocatalyst(Al):catalyst ratios. Periodic mesoporous silica (PMS) of the M41S and SBA families were recently discussed as versatile supports for organometallic species.[11,12] Notably, extrusion polymerization of α-olefins from group 4-grafted PMSs was proposed to be crucial for morphology control (e.g., "polyethylene nanofibers").[13] In a preliminary study, cubic MCM-48 featuring a three-dimensional mesopore system[14] was applied to make the binary $[Nd(AlMe_4)_3]$(**1c**)/Et_2AlCl precatalyst system



Scheme 1. Synthesis of $[La\{(\mu\text{-}Et)_2AlEt_2\}_3]$ (**2b**).

Table 1: Effect of Ln size, in situ preparation, and immobilization on the [Ln(AlMe$_4$)$_3$]-based polymerization of isoprene after 24 h.

Entry[a]	Precatalyst	Et_2AlCl[b] [equiv]	Yield [%]	*cis*[c] [%]	M_n[d] [$\times 10^{-3}$]	M_w[d] [$\times 10^{-3}$]	PDI[d]
Homogeneous tetramethylaluminate complexes:							
1	[Y{(μ-Me)$_2$AlMe$_2$}$_3$] (**1a**)	1	65	67.1	54	226	4.21
2	[Y{(μ-Me)$_2$AlMe$_2$}$_3$] (**1a**)	2	97	75.9	101	400	3.95
3	[Y{(μ-Me)$_2$AlMe$_2$}$_3$](**1a**)	3	2	97.3	n.d.[e]	n.d.	n.d.
4	[La{(μ-Me)$_2$AlMe$_2$}$_3$](**1b**)	1	92	>99	128	546	4.25
5	[La{(μ-Me)$_2$AlMe$_2$}$_3$](**1b**)	2	99	>99	184	600	3.26
6	[La{(μ-Me)$_2$AlMe$_2$}$_3$](**1b**)	3	<1	>99	n.d.	n.d.	n.d.
7	[Nd{(μ-Me)$_2$AlMe$_2$}$_3$](**1c**)	1	>99	>99	228	788	3.45
8	[Nd{(μ-Me)$_2$AlMe$_2$}$_3$](**1c**)	2	>99	>99	117	326	2.78
9	[Nd{(μ-Me)$_2$AlMe$_2$}$_3$](**1c**)	3	>99	>99	113	329	2.92
10	[Sm{(μ-Me)$_2$AlMe$_2$}$_3$](**1d**)	1	<1	>99	n.d.	n.d.	n.d.
11	[Sm{(μ-Me)$_2$AlMe$_2$}$_3$](**1d**)	2	7	>99	n.d.	n.d.	n.d.
12	[Gd{(μ-Me)$_2$AlMe$_2$}$_3$](**1e**)	1	>99	>99	278	937	3.33
13	[Gd{(μ-Me)$_2$AlMe$_2$}$_3$](**1e**)	2	>99	>99	146	377	2.58
14	[Gd{(μ-Me)$_2$AlMe$_2$}$_3$](**1e**)	3	>99	>99	195	486	2.49
In situ preparation of the active catalyst:							
15	[Nd{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] + 8 AlMe$_3$	1	>99	98.7	121	539	4.47
16	[Nd{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] + 8 AlMe$_3$	2	>99	>99	223	611	2.74
17	[Nd{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] + 8 AlMe$_3$	3	94	>99	50	236	4.77
Immobilized tetramethylaluminate complexes:							
18	[Nd(AlMe$_4$)$_3$]@Et_2AlCl@MCM48 (**8b**)	0	32	>99	357	670	1.88
19[f]	[Nd(AlMe$_4$)$_3$]@Et_2AlCl@MCM48 (**8b**)	0	>99	>99	641	1026	1.60
20	Et_2AlCl@[Nd(AlMe$_4$)$_3$]@MCM48 (**6b**)	0	38	>99	771	1029	1.33
21	[Nd(AlMe$_4$)$_3$]@Et_2AlCl@AS200 (**7b**)	0	>99	>99	324	897	2.45
Siloxide-based model complexes:							
22	[Nd{OSi(O*t*Bu)$_3$}(AlMe$_4$)$_2$(AlMe$_3$)] (**9b**)	1	51	98.0	52	115	2.24
23	[Nd{OSi(O*t*Bu)$_3$}(AlMe$_4$)$_2$(AlMe$_3$)] (**9b**)	2	>99	>99	116	233	2.00
24	[Nd{OSi(O*t*Bu)$_3$}(AlMe$_4$)$_2$(AlMe$_3$)] (**9b**)	3	16	>99	113	269	2.38

[a] Polymerization procedure: 0.02 mmol precatalyst, 8 mL hexane, 0.02–0.06 mmol Et_2AlCl (1–3 equiv), 20 mmol isoprene; 24 h, 40 °C. [b] Catalyst preformation 15 min at RT. [c] Measured by ^{13}C NMR spectroscopy in $CDCl_3$. [d] Determined by means of size exclusion chromatography (SEC) against polystyrene standards. [e] n.d. = Not determined. [f] 0.053 mmol precatalyst.

Table 2: Results of the isoprene polymerization after 15 min.

Entry[a]	Precatalyst	Yield [%]
1	[Y{(μ-Me)$_2$AlMe$_2$}$_3$] (**1a**)	1
2	[La{(μ-Me)$_2$AlMe$_2$}$_3$] (**1b**)	4
3	[Nd{(μ-Me)$_2$AlMe$_2$}$_3$] (**1c**)	>99
4	[Gd{(μ-Me)$_2$AlMe$_2$}$_3$] (**1e**)	60
5	[Nd{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (**3c**) + 8 AlMe$_3$	19
6	[Nd{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (**3c**) + 8 AlEt$_3$	17
7	[Nd{N(SiMe$_3$)$_2$}$_3$] (**4**) + 6 AlMe$_3$	9
8	[Nd{N(SiMe$_3$)$_2$}$_3$] (**4**) + 6 AlEt$_3$	18

[a] Polymerization procedure: 0.02 mmol precatalyst, 8 mL hexane, 0.04 mmol Et_2AlCl (2 equiv), 20 mmol isoprene; 15 min, 40 °C; catalyst preformation 15 min at RT.

heterogeneous. All of the organometallic–inorganic hybrid materials were characterized by FTIR spectroscopy, elemental analysis, and nitrogen physisorption (Table 3). Initially, a dehydrated sample of pore-enlarged MCM-48 (**5**) was treated with excess of [Nd(AlMe$_4$)$_3$] (**1c**) to give a blue reaction mixture, from which after several hexane washings blue-green material **6a** was isolated (Scheme 2).

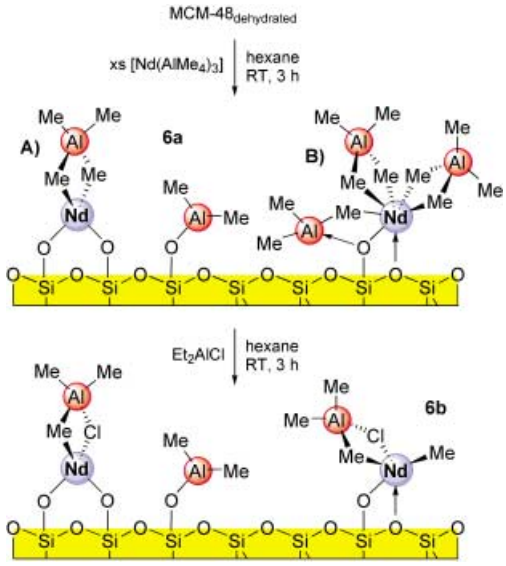
Subsequent reaction of hybrid material **6a** with one equivalent of Et_2AlCl for 3 h gave light blue-green material **6b**. Approximately 0.85 mmol of complex **1c** could be grafted per gram of MCM-48 corresponding to a surface coverage of 0.56 Nd^{III} nm^{-2}. The nitrogen adsorption/desorption isotherms of materials **5**, **6a**, and **6b** (Figure 1) clearly indicated the filling of the mesopores upon consecutive grafting with **1c** and Et_2AlCl, while mesoporosity of the hybrid materials was retained. Consequently, analysis of the Barret–Joyner–Halenda (BJH)[15] pore size distributions shows reduced pore diameters after each step.

Nd-grafted **6b** performed as an efficient single-component catalyst in a slurry polymerization of isoprene (Table 1, entry 20). Polymer analysis revealed a high *cis* stereospecificity of the grafted Nd centers. In comparison to the homogeneous system, the immobilized variant produced higher molecular weights and smaller PDIs. The order of the grafting sequence seems to have minor implications for the catalyst performance (Table 3; hybrid materials **8a** and **8b**; Table 1, entry 18). Two control experiments employing a threefold increased precatalyst concentration (Table 1, entry 19) and identically Al- and Nd-grafted nonporous Aerosil-200 (AS200) materials **7a** and **7b**, respectively (0.50 mmol of complex **1c** per gram of AS200, 1.51 Nd^{III} nm^2; Table 1, entry 21) showed that the lower conversions are due to the inaccessibility of Nd surface sites in the pores (pore

Table 3: Analytical data, pore volume, surface area, and effective mean pore diameter of supported catalysts.

Material[a]	wt% C	a_s [$m^2 g^{-1}$][b]	V_p [$cm^3 g^{-1}$][c]	d_p [nm][d]
MCM-48 (**5**)[e]	–	950	1.02	3.5
[Nd{(μ-Me)$_2$AlMe$_2$}$_3$]@MCM-48 (**6a**)	11.2	520	0.44	2.5
Et$_2$AlCl@AS200 (**7a**)	2.87	–	–	–
Et$_2$AlCl@MCM-48 (**8a**)	8.9	530	0.46	2.7
Et$_2$AlCl@[Nd{(μ-Me)$_2$AlMe$_2$}$_3$]@MCM-48 (**6b**)	11.0	480	0.39	2.4
[Nd{(μ-Me)$_2$AlMe$_2$}$_3$]@Et$_2$AlCl@AS200 (**7b**)	4.24	–	–	–
[Nd{(μ-Me)$_2$AlMe$_2$}$_3$]@Et$_2$AlCl@MCM-48 (**8b**)	11.3	450	0.32	2.5

[a] Pretreatment temperature: 280 °C, 4 h, 10^{-3} torr for **5**; 25 °C, 5 h, 10^{-3} torr for **6**–**8**. [b] Specific BET surface area. [c] BJH desorption cumulative pore volume of pores between 1.5 and 6.5 nm diameter. [d] Pore diameter according to the maximum of the BJH pore size distribution. [e] A pore-expanded sample of **5** was synthesized by using $[CH_3(CH_2)_{21}N(CH_3)_2(CH_2)_{12}N(CH_3)_2(CH_2)_{21}CH_3]^{2+}2\,Br^-$ ($\hat{=}C_{22\text{-}12\text{-}22}$) *gemini* surfactants as structure directing agents and hydrothermal restructuring.[14]



Scheme 2. Proposed surface species of hybrid materials **6a** and **6b** after the immobilization of **1c** and Et$_2$AlCl on MCM-48 (**5**). **A** = catalytically inactive [(≡SiO)$_2$NdR] surface sites, **B** = covalently bonded alkylated surface species (compare with complexes **9**, Scheme 3).

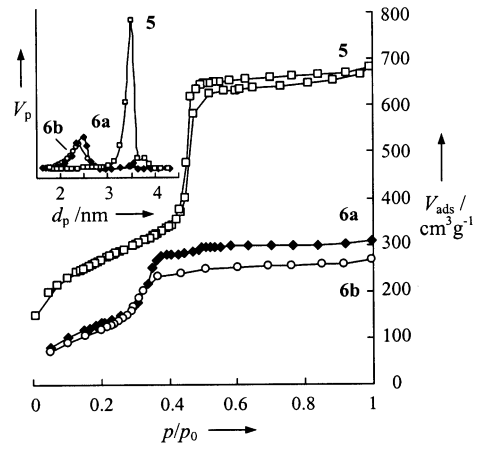
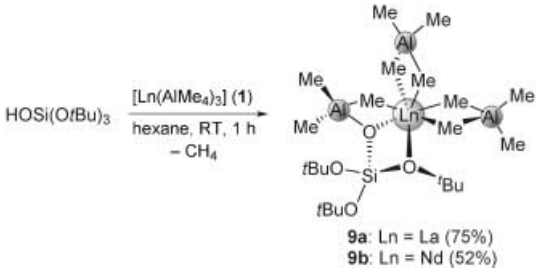


Figure 1. Nitrogen adsorption/desorption isotherms at 77.4 K and the corresponding BJH pore size distributions (*dp*, inset) of the parent and modified MCM-48 materials **5** (□), **6a** (◆), and **6b** (○; see Table 3).

blockage) and/or the formation of catalytically inactive [(≡SiO)$_2$NdR] surface sites (Type **A**, Scheme 2). The narrow molecular-weight distributions produced by the heterogeneous single-component catalyst can be attributed to the absence of any organoaluminum cocatalyst dissociation/reassociation processes at the active Nd center.

To get a deeper insight into the reactivity of compounds [Ln(AlMe$_4$)$_3$] (**1**) towards silanol functionalities we treated the homoleptic tetramethylaluminate complexes **1b** and **1c** with equimolar amounts of tris(*tert*-butoxy)silanol HOSi(O*t*Bu)$_3$ (Scheme 3). The resulting heteroleptic complexes **9** represent the first structurally characterized alkylated rare-earth-metal siloxide derivatives and can be regarded as molecular models



Scheme 3. Synthesis of [Ln{OSi(O*t*Bu)$_3$}(AlMe$_4$)$_2$(AlMe$_3$)] (**9**).

of the covalently bonded alkylated surface species **B** proposed for hybrid material **6a** in Scheme 2. An X-ray structure analysis of the lanthanum derivative **9a** revealed a 7-coordinate rare-earth metal center (Figure 2): two asymmetrically η^2-coordinating tetramethylaluminate ligands, an asymmetrically η^2-coordinating siloxide ligand and one methyl group of a trimethylaluminum donor give a distorted pentagonal bipyramidal geometry.[16,17] After activation with Et$_2$AlCl alkylated siloxide **9b** produced *cis*-1,4-polyisoprene within 24 h in yields of 16 to >99% (Table 1, entries 22–24).

In conclusion, we have shown that homoleptic complexes [Ln{(μ-Me)$_2$AlMe$_2$}$_3$] can be efficiently used to design binary and single-component precatalysts for 1,3-diene polymerization. Their favorable polymerization behavior not only provides strong evidence that heterobimetallic {Ln(μ-R)$_2$Al} moieties act as important reaction intermediates but also establishes compounds [LnAl$_3$R$_{12}$] as unique catalyst precursors for mechanistic investigations of rare-earth-based Ziegler Mischkatalysatoren.

Experimental Section

Representative synthesis of **2b**: A 12-fold excess of AlEt$_3$ (1.0 M in hexane, 6.00 mL, 6.00 mmol) was added to a solution of [La{N(SiH-

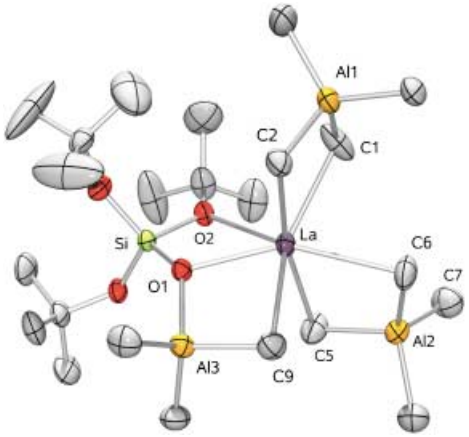


Figure 2. PLATON drawing of complex [La{OSi(O*t*Bu)$_3$}(AlMe$_4$)$_2$-(AlMe$_3$)] (**9a**). Hydrogen atoms are omitted for clarity. Selected bond lenghts [Å] and angles [°]: La-C1 2.668(5), La-C2 2.714(3), La-C5 2.680(4), La-C6 2.800(4), La-C9 2.798(3), La-O1 2.409(2), La-O2 2.727(2), O1-La-O2 56.83(5), O1-La-C1 131.2(1), O1-La-C2 89.50(8), O1-La-C5 99.56(9), O1-La-C6 146.8(1), O1-La-C9 69.56(8), O2-La-C1 83.5(1), O2-La-C2 109.63(8), O2-La-C5 84.9(1), O2-La-C6 152.16(8), O2-La-C9 123.50(8), C1-La-C2 77.5(1), C1-La-C5 104.2(1), C1-La-C6 80.6(1), C1-La-C9 151.8(1), C2-La-C5 165.5(1), C2-La-C6 89.0(1), C2-La-C9 84.8(1), C5-La-C6 77.2(1), C5-La-C9 87.7(1), C6-La-C9 77.3(1).

Me$_2$)$_2$}$_3$(thf)$_2$] (0.340 g, 0.50 mmol) in hexane at ambient temperature in an argon-filled glovebox. After the reaction mixture was stirred overnight, it was filtered through a Celite pad and crystallized at −45 °C. After several weeks 0.236 g (0.24 mmol, 48 %) of **2b** were isolated as colorless crystals. IR (nujol): $\tilde{\nu}$ = 1408 m, 1189 m, 1096 m, 978 s, 945 s, 722 s, 651 s, 589 s, 550 m, 501 m, 467 cm^{-1} w. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 2.78 (t, $^3J_{HH}$ = 7.8 Hz, 12 H, CH_3), 0.18 ppm (q, $^3J_{HH}$ = 7.8 Hz, 8 H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 11.0 (CH_3), 6.7 ppm (CH_2). Elemental analysis calcd. for $C_{24}H_{60}Al_3La$: C 50.70, H 10.64; found: C 51.29, H 10.85.

Representative synthesis of **8a** and **8b**: Dehydrated MCM-48 (**5**, 500 mg) was suspended in hexane and a solution of Et$_2$AlCl (360 mg, 2.99 mmol) in hexane was added. The mixture was stirred for 3 h at ambient temperature, then centrifuged, the separated white solid **8a** washed several times with hexane, and dried until constant weight. Yield: 625 mg. Elemental analysis found (%): C 8.85, H 1.77, Cl 8.33, Al 6.9. Et$_2$AlCl@MCM-48 (**8a**, 200 mg) was suspended in hexane and a solution of **1c** (162 mg, 0.40 mmol) in hexane was added. The blue mixture was stirred for 3 h at ambient temperature. After centrifugation and several hexane washings separated light blue-green material **8b** was dried until constant weight. Yield: 230 mg. Elemental analysis found (%): C 11.28, H 2.45, Cl 5.92, Al 6.6. The amount of recovered **1c** was determined as 82 mg (0.20 mmol, 51 %).

9a: [La(AlMe$_4$)$_3$] **1b** (124 mg, 0.31 mmol) was dissolved in hexane and a solution of HOSi(O*t*Bu)$_3$ (82 mg, 0.31 mmol) was added. After stirring the solution for 1 h at ambient temperature, the solvent was removed in vacuo. The remaining solid was recrystallized from hexane at −45 °C to give **9a** (151 mg, 0.23 mmol, 75 %) as colorless crystals. IR: 1305 w, 1246 m, 1188 s, 1089 s, 1062 s, 1027 m, 941 m (sh), 923 m, 897 s, 832 w, 820 m, 802 w, 695 s (br), 573 m, 532 m, 492 cm^{-1} m. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.24 (s, 27 H, CMe_3), 0.06 (s, 24 H, $AlMe_4$), −0.14 ppm (s, 9 H, $AlMe_3$). ^{13}C{^{1}H} (100 MHz, C_6D_6, 25 °C) NMR: δ = 78.0 (*C*Me$_3$), 31.6 (C*Me*$_3$), 6.0 ($AlMe_4$), 0.2 ppm ($AlMe_3$). Elemental analysis calcd (%) for $C_{23}H_{60}Al_3LaO_4Si$: C 42.59, H 9.32; found: C 42.85, H 9.32.

Representative polymerization procedure (Table 1, entry 8): To a solution of **1c** (8.1 mg, 0.02 mmol) in hexane (8 mL) 2 equiv of Et$_2$AlCl (5.0 μL, 0.04 mmol) were added and the mixture aged at RT for 15 min. After the addition of isoprene (2.0 mL, 20 mmol) the polymerization was carried out at 40 °C for 24 h. The polymerization mixture was poured onto a large quantity of acidified isopropanol containing 0.1 % (w/w) 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer. The polymer was washed with isopropanol and dried under vacuum at ambient temperature to constant weight. The polymer yield was determined gravimetrically.

Full experimental and physicochemical details for complexes **1**, **2b**, and **9** as well as for hybrid materials **6–8** are available in the Supporting Information.

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[6] Treatment of [Y(AlMe$_4$)$_3$] with 1 equivalent of Et$_2$AlCl produced a fine precipitate and approximately 2 equivalents of AlMe$_3$, formally giving a "Me$_2$YCl" species, however ^{1}H NMR spectroscopy showed that signals assignable to a "YEt" species were also present.

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[16] Compound **9a** ($C_{23}H_{60}Al_3LaO_4Si$, $M_r = 648.65$) crystallizes from hexane in the monoclinic space group $P2_1/c$ with $a = 10.3104(1)$, $b = 17.3973(1)$, $c = 19.9956(2)$ Å, $\beta = 104.7345(3)°$, $V = 3468.72(5)$ Å^3, and $\rho_{calcd} = 1.242\ g\,cm^{-3}$ for $Z = 4$. Data were collected at 123 K on a Nonius Kappa-CCD system. The structure was solved by Patterson methods, and least-square refinement of the model based on 6359 (all data) and 5491 reflections ($I > 2.0\sigma(I)$) converged to a final $wR2 = 0.0654$ and $R1 = 0.0263$, respectively. All hydrogen atoms of the methyl groups bonded to aluminum were found in the difference Fourier maps and allowed to refine freely. All of the other hydrogen atoms were placed in calculated positions (riding model). CCDC-226742 (**9a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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