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Polymerization

Cationic Rare-Earth-Metal Half-Sandwich Complexes for the Living *trans*-1,4-Isoprene Polymerization**

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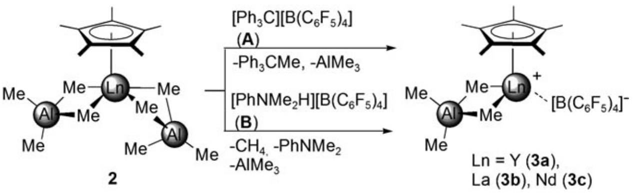
Dedicated to Professor William J. Evans on the occasion of his 60th birthday

Nature provides mankind with highly stereoregular polyterpenes, i.e., polymers of isoprene, featuring distinct properties.[1] Natural rubber (NR, caoutchouc or *cis*-1,4-polyisoprene, cPIP; $>99\%$ *cis* content, $M_n \approx 2\times10^6\,\mathrm{g\,mol^{-1}}$) is the most important polymer produced by plants and is the raw material for numerous rubber applications. Taking into account new developments in synthetic polymer chemistry, a mechanism for living carbocationic polymerization has recently been proposed for NR biosynthesis.[2] Gutta-percha obtained from *Palaquium gutta* and several other evergreen trees of East Asia is an isomer of NR displaying an all-*trans* ($>99\%$) configuration and much lower molecular weight ($M_n = 1.4$–$1.7\times10^5\,\mathrm{g\,mol^{-1}}$).[1] Unlike NR it is a thermoplastic crystalline polymer with a melting point (T_m) of 62 °C. Although for most applications gutta-percha has been superseded by advanced functional polymers, controlled cross-linking of synthetic *trans*-1,4-polyisoprene or its blending (with, for example, natural rubber, styrene–butadiene rubber, and butadiene rubber) and block copolymerization (e.g., with α-olefins) might afford new high-performance materials.[3]

The synthesis of highly stereoregular cPIP with Ziegler-type catalysts is well established.[4,5] In particular, catalyst mixtures with rare-earth-metal components such as neodymium represent a prominent class of high-performance catalysts for the industrial stereospecific polymerization ($>98\%$ *cis*-1,4) of 1,3-dienes, even though the molecular weights and molecular weight distributions remain difficult to control.[6] Molecular systems based on lanthanide metallocene and postmetallocene congeners afford polymers with very narrow molecular weight distributions and very high stereoregularity.[7–10] A combination of $[(C_5Me_5)_2Ln(AlMe_4)]$/$Al(iBu)_3$/$[Ph_3C][B(C_6F_5)_4]$ (Ln = Sm, Gd) gave *cis*-1,4-polybutadiene with excellent stereocontrol (up to 99.9% *cis*) and narrow molecular weight distributions ($M_w/M_n = 1.20$–1.23), while the polymerization of isoprene was not observed to be living.[7] cPIP with comparable characteristics (95–99% *cis*-1,4; $M_w/M_n = 1.3$–1.7) was obtained with neodymium allyl complexes in the presence of aluminum alkyls as activators[8,9] as well as with supported catalysts of the type $Et_2AlCl@Nd(AlMe_4)_3@MCM\text{-}48$.[10] It was only recently that cationic lanthanide alkyl initiators $[\{PNP^{Ph}\}Ln(CH_2SiMe_3)(thf)_2]^+$ ($PNP^{Ph} = (\{2\text{-}(Ph_2P)C_6H_4\}_2N]$, Ln = Sc, Y, Lu) were reported to yield high *cis*-1,4 selectivity in the living polymerization of isoprene and butadiene in the absence of any aluminum additive ($>99\%$ *cis*-1,4; $M_w/M_n = 1.05$).[11] The fabrication of synthetic gutta-percha and gutta-balata has been achieved by utilization of mixed organo-Ln/Mg initiators such as $[(CMe_2C_5H_4)_2Sm(C_3H_5)MgCl_2(OEt_2)_2LiCl(OEt_2)]$ ($>95\%$ *trans*-1,4; $M_w/M_n = 1.32$)[12] and half-sandwich-based $[(C_5Me_4nPr)Nd(BH_4)_2(thf)_2]/Mg(nBu)_2$ (Mg/Nd = 0.9; 98.5% *trans*-1,4, $M_w/M_n = 1.15$).[13–16]

Intrigued by the exceptional catalytic performance of the cationic monocyclopentadienyl complexes $[\{C_5Me_4(SiMe_3)\}Ln(CH_2SiMe_3)(thf)][B(C_6F_5)_4]$ developed by Hou et al.,[17] we examined similar cationization reactions of our half-sandwich bis(tetramethylaluminate) complexes $[(C_5Me_5)Ln(AlMe_4)_2]$. Herein we describe the reactivity of these half-sandwich complexes toward fluorinated borate and borane activators as well as their catalytic performance in the polymerization of isoprene.

Half-sandwich complexes $[(C_5Me_5)Ln(AlMe_4)_2]$ (Ln = Y (**2a**), La (**2b**), Nd (**2c**)) were synthesized according to the alkylaluminate route utilizing $[Ln(AlMe_4)_3]$ (**1**) and $[H\text{-}(C_5Me_5)]$.[6b,18] In small-scale reactions of **2** (in NMR tubes) with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ (**A**) or $[PhNMe_2H][B(C_6F_5)_4]$ (**B**) as solutions in C_6D_6, the NMR signals for **2** disappeared instantly and the quantitative formation of Ph_3CMe and one equivalent $AlMe_3$ and quantitative formation of $PhNMe_2$, one equivalent of $AlMe_3$, and CH_4, respectively, were observed (Scheme 1). New signals for the C_5Me_5 ligand appeared shifted to slightly higher field in accordance with a stronger coordination toward the highly electron-deficient rare-earth-metal cation. High-field shifts were also observed for the signals of the remaining $[AlMe_4]$ ligand. The stability of cationic species **3**, however, signifi-



Scheme 1. Cationization of **2** with borate reagents **A** and **B**.

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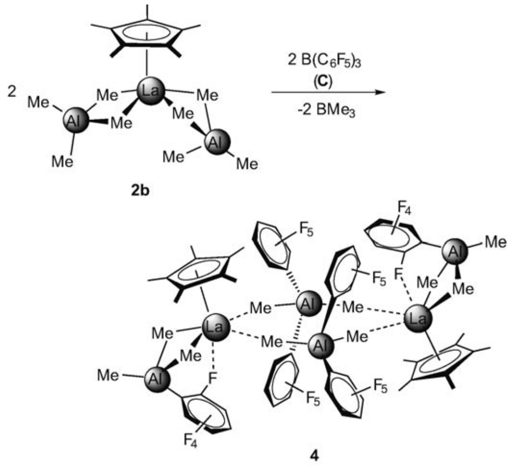
cantly depends on the size of the lanthanide cation (La $\gg$ Nd > Y).

Ion pair $[(C_5Me_5)La(AlMe_4)][B(C_6F_5)_4]$ (**3b**), obtained from **2b** and **A**, dissolves in C_6D_6 or C_6D_5Cl, and such solutions are stable for several days enabling closer more-detailed NMR spectroscopic investigations. The ^{11}B NMR spectrum of **3b** in C_6D_6 revealed a broad resonance at $\delta = -16.2$ ppm, which, combined with a ^{19}F chemical shift difference for the *p*- and *m*-F atoms of $\delta = 4.2$ ppm, suggests the existence of a tight ion pair (C_6D_5Cl).[19] A broad singlet at $\delta = -0.30$ ppm (12H) in the ^{1}H NMR spectrum clearly corresponds to one $[AlMe_4]$ ligand.[20]

On the other hand, treatment of $[(C_5Me_5)La(AlMe_4)_2]$ (**2b**) with one equivalent of Lewis acidic $B(C_6F_5)_3$ (**C**) in C_6H_5Cl at ambient temperature instantly and quantitatively yielded ion pair $[\{[(C_5Me_5)La\{(\mu\text{-}Me)_2AlMe(C_6F_5)\}][Me_2Al(C_6F_5)_2]\}_2]$ (**4**) as the product of very fast sequential CH_3/C_6F_5 exchange processes (Scheme 2). **Caution**: Owing to the formation of thermal and shock-sensitive $[Me_2Al(C_6F_5)_2]^-$, extra caution should be exercised when handling this mixture, especially in higher concentrations).[21,22]



Scheme 2. Synthesis of **4**.

Layering hexane on the reaction mixture of **2b** and **C** afforded light yellow single crystals of **4**.[23] The X-ray diffraction study revealed a dimeric contact ion pair, in which two lanthanum-containing cationic units are bridged by two $[Me_2Al(C_6F_5)_2]$ anions (Figure 1). Comparatively short bonds La···C1 (2.78(1) Å) and La···C2′ (2.79(1) Å) suggest a tight interaction of the electron-deficient lanthanum cation with the counterion.[24,25] (All hydrogen atoms at the sp^3-hybridized C1 and C2 carbon atoms were located and refined isotropically.) The electron deficiency is further substantiated by significantly shortened La–C(C_5Me_5) bonds (av. 2.66 Å versus 2.78 Å in **2b**).

Moreover, a CH_3/C_6F_5 exchange at the former tetramethylaluminate ligand facilitates a close La···F contact (La···F5 2.62(1) Å) in the solid state,[26] which is apparently favored over $\{La(\mu\text{-}Me)_3Al(C_6F_5)\}$ coordination.[27] This La···F interaction results in an almost linear bond angle between the (C_5Me_5) centroid, the lanthanum center, and the adjacent fluorine atom ((C_5Me_5)(centroid)–La···F5 177.2(2)°) and a considerable elongation of the C11–F5 bond to 1.35(1) Å. (The lengths of C–F bonds to noncoordinating fluorine atoms average to 1.30 Å).

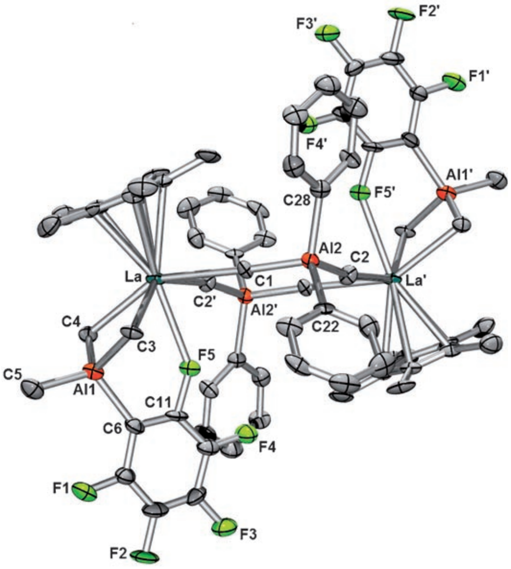


Figure 1. X-ray crystal structure of **4** (atomic displacement parameters set at the 50% level). Hydrogen atoms and fluorine atoms at $Al(C_6F_5)_2$ are omitted for clarity. Selected distances [Å] and angles [°]: La–C(C_5Me_5) 2.63(1)–2.67(1), La···C1 2.78(1), La···C2′ 2.79(1), La–C3 2.62(1), La–C4 2.65(1), La···Al1 3.16(1), Al1–C3 1.99(1), Al1–C4 1.98(1), Al1–C5 1.88(1), Al1–C6 1.95(1), Al2–C1 1.96(1), Al2–C2 1.95(1), Al2–C22 1.95(1), Al2–C28 1.96(1), La···F5 2.62(1); C1···La···C2′ 82.2(3), C3-La-C4 76.8(4), La-C3-Al1 85.1(4),La-C4-Al1 84.5(4), C3-Al1-C5 111.7(6), C3-Al1-C6 101.2(5), La-C1-Al2 169.3(6), La-C2′-Al2′ 176.8(5), La···F5-C11 139.8(7), C3-Al1-C4 111.0(5), C1-Al2-C22 108.9(5), C1-Al2-C28 112.1(5), C2-Al2-C22 109.6(5), C2-Al2-C28 110.2(5), (C_5Me_5)(centroid)-La···F5 177.2(2) [symmetry code: $1-x$, $1-y$, $1-z$].

The ^{1}H, ^{19}F, and ^{27}Al NMR spectra of **4** indicate a solution structure consistent with that observed in the solid state. Two sets of C_6F_5 resonances with $\Delta\delta_{m,p} = 5.5$ and 4.1 ppm appear in the ^{19}F NMR spectrum at 25 °C which are assigned to the $\{Me_2Al(C_6F_5)_2\}$ and $\{AlMe_3(C_6F_5)\}$ unit, respectively. However, the La···F5 interaction appears to be less pronounced in solution, based on the absence of any upfield ^{19}F signals.[28] Further evidence of two aluminium-containing moieties is provided by the ^{27}Al NMR spectrum, which exhibits two distinct signals at $\delta = 142$ and 157 ppm (**2b**: $\delta = 166$ ppm).[29] Facile alkyl/C_6F_5 exchange is a favorable reaction observed in several catalytic systems based on methylaluminoxane (MAO)/AlR_3 and $M(C_6F_5)_3$ (M = Al, B) activators and is commonly discussed as an undesirable catalyst-deactivation pathway.[21,22,30]

In contrast, the cationic species generated in situ upon treatment of **2** with one equivalent of **A**, **B**, or **C** showed good to excellent activities for the polymerization of isoprene (Table 1).[31] The stereoregularity of the produced polyisoprene corresponds very well to the stability of the cationic species (see above) and depends on the size of the rare-earth-metal cation and the boron activator involved. While high *cis*-

Table 1: Effect of Ln size and the cocatalyst on the polymerization of isoprene.

Entry[a]	Precat.	Cocat.[b]	*t* [h]	Yield [%]	Structure[c]			M_n (×10^5)[d]	M_w/M_n	Eff.[e]
					trans-1,4-	*cis*-1,4-	3,4-			
1	**2a** (Y)	**A**	24	>99	20.6	60.5	18.9	0.2	8.95	3.98
2	**2a** (Y)	**B**	24	>99	28.7	43.5	27.8	0.6	1.59	1.06
3	**2a** (Y)	**C**	24	>99	93.6	1.9	4.5	0.9	1.78	0.82
4	**2c** (Nd)	**A**	24	>99	69.7	14.0	16.3	0.3	2.87	2.11
5	**2c** (Nd)	**B**	24	>99	79.9	6.9	13.2	0.4	1.16	1.73
6	**2c** (Nd)	**C**	24	>99	92.4	3.8	3.8	1.3	1.35	0.52
7	**2b** (La)	**A**	24	>99	87.0	3.5	9.5	0.7	1.28	1.98
8	**2b** (La)	**B**	24	>99	79.5	3.4	17.1	0.6	1.22	1.08
9	**2b** (La)	**C**	24	>99	99.5	–	0.5	2.4	1.18	0.28
10	**2b** (La)	**A**	1	>99	89.4	1.2	9.4	0.7	1.28	1.04
11	**2b** (La)	**B**	1	>99	87.5	2.9	9.6	0.7	1.23	1.04
12	**2b** (La)	**C**	18	>99	99.5	–	0.5	2.4	1.18	0.28
13[f]	**2b** (La)	**A**	2	>99	92.5	0.7	6.8	1.3	1.22	1.03
14[f]	**2b** (La)	**B**	2	>99	89.7	1.5	8.8	1.2	1.23	1.17
15[g]	**2b** (La)	**C**	24	>99	99.4	–	0.6	4.4	1.19	0.31
16	**4**	–	24	>99	99.0	0.2	0.8	2.3	1.19	0.30
17[h]	**2b** (La)	**C**	24	>99	98.7	–	1.3	n.d.[i]	n.d.[i]	–

[a] Conditions: 0.02 mmol precatalyst, [Ln]/[cocat.] = 1:1, 8 mL toluene, 20 mmol isoprene, 24 h, 40 °C. [b] Catalyst formed within 20 min at 40 °C. [c] Determined by ^{1}H and ^{13}C NMR spectroscopy in $CDCl_3$. [d] Determined by means of size-exclusion chromatography (SEC) against polystyrene standards. [e] Initiation efficiency = M_n(calcd)/M_n(found). [f] 12 mL toluene; after polymerization of 20 mmol of isoprene for 1 h, another 20 mmol of isoprene were added and the reaction mixture was stirred for another hour. [g] 12 mL toluene; after polymerization of 20 mmol of isoprene for 18 h, another 20 mmol of isoprene were added and the reaction mixture was stirred for another 6 h. [h] 8 mL hexane. [i] Not determined.

1,4 selectivity was a striking feature of tetramethylaluminate-containing catalyst mixtures reported so far (e.g., [Ln($AlMe_4$)$_3$] (**1**)/Et_2AlCl and [(C_5Me_5)$_2$Sm($AlMe_4$)]/Al(*i*Bu)$_3$/[Ph_3C][B(C_6F_5)$_4$]),[6,7,10] the catalyst systems reported herein afford highly regular *trans*-1,4 PIP.[12–14] The *trans*-1,4 selectivity increases significantly with increasing size of the rare-earth-metal cation and when B(C_6F_5)$_3$ is used as the activator (Table 1, entries 1–9). Polyisoprene with very high *trans*-1,4 content (99.5 %) and very narrow molecular weight distributions (M_w/M_n = 1.18) could be obtained from a [(C_5Me_5)La($AlMe_4$)$_2$]/B(C_6F_5)$_3$ catalyst mixture (Table 1, entry 9); this polymeric product has the highest *trans*-1,4 content so far reported for those generated with a homogeneous single-site catalyst.[12–14] Signals assignable to *cis*-1,4-PIP units were not observed in the ^{13}C NMR spectrum. Employing the isolated cationic complex **4** as catalyst under the same reaction conditions afforded *trans*-1,4-PIP with almost the same polymer properties (Table 1, entry 16); this supports the assumption that well-defined **4** serves as the catalytically active species in the catalyst mixture prepared in situ.

In accordance with a different activation mechanism, the use of **A** and **B** as activators for [(C_5Me_5)Ln($AlMe_4$)$_2$] led to extremely high activity for the polymerization reactions, however, with lower *trans*-1,4 selectivity than that observed with **C** as the activator (up to 89.4 %, Table 1, entry 10). The highest number of *trans*-1,4 connectivities and very narrow molecular weight distributions were again observed for cationized derivatives of lanthanum precursor **2b** (Table 1, entries 7 and 8).

Catalyst precursor **2b** was therefore examined in more detail. Mixtures **2b**/**A** and **2b**/**B** afforded polyisoprene quantitatively in 1 h (Table 1, entries 10 and 11). In both cases the activities of 68 kg mol^{-1} h^{-1} are a factor of 2 higher than those mentioned in literature for similar *trans*-specific polymerizations.[12–14] Activities obtained for **2b**/**C** are comparatively low (Table 1, entry 12) because of a long induction period; however, the polymerization rates increase slowly with time (see the Supporting Information). The first insertion of an isoprene monomer into the La–Me bond of the very stable cation **4** appears to be kinetically disfavored and furthermore explains the low initiation efficiency (28 %). Theoretical studies on permethylated lanthanidocene catalysts point to a dependency of the monomer coordination on the steric hindrance around the metal center. Accordingly, the sterically crowded complex **4** is proposed to favor a single η^2 coordination of the diene over an η^4 coordination, leading to *trans* polymerization.[32] In any case, the molecular weight of the resulting polymers increased linearly with increasing isoprene conversion. Addition of another 1000 equivalents of monomer to a completed polymerization run yielded PIP with almost double the molecular weight, sustained high *trans*-1,4 selectivity, and narrow molecular weight distributions (M_w/M_n = 1.19–1.23, Table 1, entries 13–15).

In conclusion, cationization of donor-solvent-free half-sandwich complexes [(C_5Me_5)Ln($AlMe_4$)$_2$] with fluorinated borate/borane reagents gave access to new initiators for controlled isoprene polymerization. The systematic investigation of the affect of the size of the metal ion and interactions with the cocatalyst (borate vs. borane) resulted in highly active, *trans*-1,4-selective (99.5 %) catalysts for the living polymerization. Successful isolation and structural characterization of the cationic complex **4** give unprecedented insights into the activation mechanism and provide a "single-component" catalyst for the production of polyisoprene with high *trans*-1,4 selectivity. Our findings point to a stabilizing effect of organoaluminum reagents for cationic rare-earth-metal half-sandwich complexes involving the formation of polymerization-active (fluorinated) tetraalkylaluminate ligands.

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[20] a) The ion pair obtained from **2b** and **B** shows slightly different ^1H NMR chemical shifts for the $[AlMe_4]$ moiety and $AlMe_3$, probably owing to interaction with $[PhNMe_2]$; b) The ^1H NMR spectrum of the $[(C_5Me_5)Y(AlMe_4)][B(C_6F_5)_4]$ (**3a**) shows almost identical signals and chemical shifts. The lifetime of the cationic complex in C_6D_6 at 25 °C, however, is limited and hampers further spectroscopic investigations.

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[23] Compound **4** ($C_{66}H_{60}Al_4F_{30}La_2$, $M_r = 1808.88$) crystallizes from a hexane/chlorobenzene mixture in the triclinic space group $P\bar{1}$ with $a = 12.0679(11)$, $b = 13.0408(12)$, $c = 13.2763(12)$ Å, $\alpha = 61.189(1)$, $\beta = 66.538(1)$, $\gamma = 89.390(2)°$, $V = 1636.1(3)$ Å^3, and $d_{calcd} = 1.836\ \mathrm{g\,cm^{-3}}$ for $Z = 1$. Data were collected at 103 K on a BRUKER-AXS 2K CCD system. The structure was solved by direct methods, and least-square refinement of the model based on 5750 (all data) and 4388 reflections ($I > 2.0\sigma(I)$) converged to a final $wR2 = 0.1924$ and $R1 = 0.0903$, respectively. CCDC 653206 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[24] For other examples of similar contact ion pairs, see: a) $[(C_5H_4SiMe_3)_2Y\{(\mu\text{-}FC_6F_4)(\mu\text{-}CH_3)(B(C_6F_5)_2\}]$: X. Song, M. Thornton-Pett, M. Bochmann, *Organometallics* **1998**, *17*, 1004; b) $[\{(nacnac)Sc(CH_3)\}\{H_3CB(C_6F_5)_3\}]$ (nacnac = β-diketiminato):, P. G. Hayes, W. E. Piers, R. McDonald, *J. Am. Chem. Soc.* **2002**, *124*, 2132.

[25] $[(C_5Me_5)La(AlMe_4)_2]$ (**2b**): La–CH_3 av. 2.749 Å; $[(C_5Me_5)_2La(AlMe_4)]_2$: La–$CH_3$ av. 2.828 Å, H. M. Dietrich, E. Herdtweck, K. W. Törnroos, R. Anwander, unpublished results.

[26] For an example of secondary La···F interactions in organometallic compounds, see: $[(dme)_3Ln(SC_6F_5)_2]_2[Hg_2(SC_6F_5)_4(\mu_2\text{-}SC_6F_5)_2]$ (dme = 1,2-dimethoxyethane): 2.797(2) Å; S. Banerjee, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **2004**, *43*, 6307.

[27] M. Zimmermann, N. Å. Frøystein, A. Fischbach, P. Sirsch, H. M. Dietrich, K. W. Törnroos, E. Herdtweck, R. Anwander, *Chem. Eur. J.* **2007**, *13*, 8784.

[28] B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, *Angew. Chem.* **1995**, *107*, 1867; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1755.

[29] Formation of BMe_3 could be proven by ^1H and ^{11}B NMR spectroscopy in C_6D_5Cl at 25 °C in an NMR tube equipped with a Young valve; signals at $\delta = 0.88$ and 86.3 ppm, respectively, were observed.

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[31] Compounds **2** did not show activity for the polymerization of isoprene without borate cocatalyst or with 1 equiv and 2 equiv of Me_2AlCl.

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