Generation of cationic indenyl silylamide gadolinium and scandium complexes $[(\mathrm{Ind})\mathrm{Ln}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}]^+[\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]^-$ and their reactivity for 1,3-butadiene polymerization†

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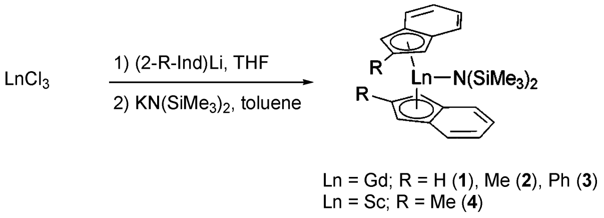
Highly efficient *cis*-polymerization of butadiene was achieved by using new bis(indenyl) silylamide rare earth complexes with the cooperation of both a borate salt and i-Bu$_3$Al; treatment of these complexes with organoboron compounds unexpectedly yielded new cationic mono(indenyl) amido species relevant to polymerization.

Selective 1,4-*cis* polymerization of 1,3-butadiene is of increasing importance, since high 1,4-*cis* content in the polybutadiene chain brings excellent elastomeric properties to the resulting rubbers, which is very useful in tyre manufacturing.[1] Industrially, high *cis*-polybutadiene is produced with Ziegler–Natta Ti-, Co-, Ni- and Nd-based catalysts.[2,3a] In particular, neodymium-based catalysts provide the highest *cis*-1,4-content in polybutadiene.[3] In 1999, samarocene $(\mathrm{C}_5\mathrm{Me}_5)_2\mathrm{Sm(thf)}_2$ was shown to polymerize butadiene in the presence of aluminoxane (MMAO).[4] Since then, the high potential of lanthanocenes such as $[(\mathrm{C}_5\mathrm{Me}_5)_2\mathrm{Ln}(\mathrm{AlMe}_4)]_2$ and related cationic lanthanocene $[(\mathrm{C}_5\mathrm{Me}_5)_2\mathrm{Ln}]^+[\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]^-$ complexes as precatalysts for well controlled 1,4-*cis* butadiene polymerization, upon activation with $[\mathrm{Ph}_3\mathrm{C}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$/i-Bu$_3$Al and i-Bu$_3$Al, respectively, has been demonstrated.[5] With these systems, gadolinium-based catalysts showed very high activity together with the highest *cis*-selectivity. However, polybutadiene with *cis*-content greater than 99% was only obtained under extreme conditions ($T_\mathrm{p} < -20$ °C), resulting in reduced activity and limited molecular weight control.

We report herein that high *cis*-polybutadiene (> 99%) and high activity can be obtained under less severe conditions by using new bis(indenyl) hexamethyldisilylamide rare earth complexes by cooperative action of both a cationizing reagent and i-Bu$_3$Al. We also describe the unexpected displacement of one indenyl ligand in the reaction of these silylamide complexes with cocatalysts such as ammonium borate and trityl borate salts.

The new bis(indenyl) silylamide complexes $(2\text{-R-Ind})_2\mathrm{Ln}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}$(Ln = Gd, R = H (**1**), Me (**2**), Ph (**3**); Ln = Sc, R = Me (**4**)) were prepared following a two step one-pot procedure, by reaction of (2-R-Indenyl)Li (R = H, Me, Ph) with LnCl$_3$ (Ln = Gd, Sc) in THF overnight, and treatment of the resulting chloride derivatives with K{N(SiMe$_3$)$_2$} in toluene for 16 h, after removal of THF in vacuum (Scheme 1). For the preparation of $(2\text{-Ph-Ind})_2\mathrm{Gd}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}$ (**3**), GdCl$_3$ and (2-Ph-Ind)Li(THF) were reacted for 7 d at room temperature. These complexes were characterized by elemental analysis, IR and NMR (for the scandium diamagnetic derivatives **4**) spectroscopy, and X-ray diffraction analysis for **2–4**.



Scheme 1 Preparation of bis(indenyl) silylamide rare earth complexes **1–4**.

The polymerization of 1,3-butadiene was performed in toluene at 20 °C. As a single component, the neutral bis(indenyl) silylamide complexes **1–4** do not polymerize butadiene, neither do the two-component catalytic systems formed from mixtures of **1–4**/$[\mathrm{PhNMe}_2\mathrm{H}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$, **1–4**/$[\mathrm{Ph}_3\mathrm{C}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$ and **1–4**/i–Bu$_3$Al, under these conditions. The addition of one equivalent of triisobutyl aluminium (i-Bu$_3$Al) to **1**/$[\mathrm{PhNMe}_2\mathrm{H}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$ did also not produce an active system for polymerization (Table 1, run 1). However, when $[\mathrm{Ph}_3\mathrm{C}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$ was used in place of $[\mathrm{PhNMe}_2\mathrm{H}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$, **1**/$[\mathrm{Ph}_3\mathrm{C}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$/i-Bu$_3$Al (1 equiv.) induced the polymerization of butadiene with the conversion of 333 equiv. of monomers reaching 64%, in 15 min (run 2). Higher conversion and better molecular weight control was reached with 4 equiv. of i-Bu$_3$Al (run 4). Under these conditions, the ternary systems composed of **1–4**, a borate salt, and i-Bu$_3$Al, successfully promoted the polymerization of butadiene, reaching nearly full monomer conversion within 15 min (runs 4–10). The MWD of the polymers are unimodal and narrow ($M_\mathrm{w}/M_\mathrm{n}$ = 1.10–1.47), consistent with single site behavior of these catalytic systems. Remarkably, polybutadienes produced by the gadolinium based catalysts (**1–3**), possess a very high 1,4-*cis* microstructure, and negligible or nil 1,2-*vinyl* content. In contrast, the scandium complex **4** afforded polybutadiene with a *cis*-content of 87.6% (run 10), showing that stereoregularity is strongly dependent on the metal center.[5d] The three-component catalytic systems composed of **3**/$[\mathrm{PhNMe}_2\mathrm{H}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$/i-Bu$_3$Al, or **3**/$[\mathrm{Ph}_3\mathrm{C}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$/i-Bu$_3$Al were the most active, and the most *cis*-1,4-stereospecific, yielding polybutadienes with very narrow

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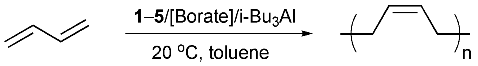
† Electronic supplementary information (ESI) available: Detailed experimental procedures, NMR spectra of the *in situ* generation of **6**-[d$_8$], ^{1}H NMR spectra of the neutral gadolinium complexes **1–3**, ^{13}C NMR spectrum, GPC and IR charts of representative polymer products. CCDC reference numbers 670476 and 670547–670551. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b801707g

Table 1 1,3-Butadiene polymerization using **1–4**/$[B]_N$/i-Bu_3Al, **1–4**/$[B]_C$/i-Bu_3Al, and **5**/i-Bu_3Al[a]



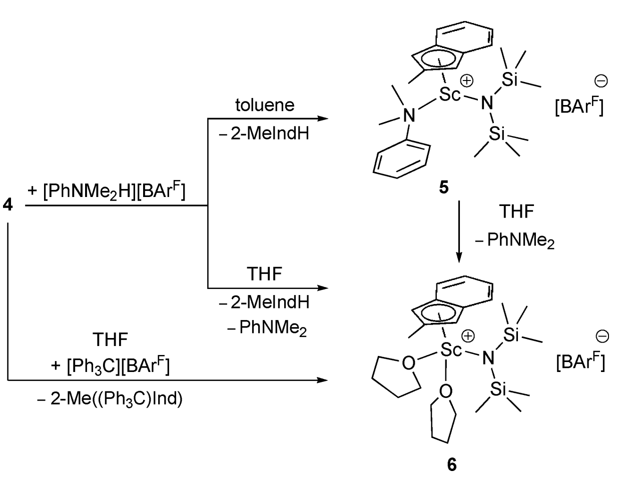
				Microstructure (%)[c]			
Run	$[Ln]_0$	[Borate][b]	Yield (%)	1,4-*cis*	1,2	M_n[d] ($\times 10^{-4}$)	M_w/M_n[d]
1[e]	**1**	$[B]_N$	0	—	—	—	—
2[e]	**1**	$[B]_C$	64	>99	0	39.7	1.41
3[f]	**1**	$[B]_C$	93	98.9	0	23.8	1.22
4	**1**	$[B]_C$	93	98.6	<0.1	10.8	1.15
5	**1**	$[B]_N$	84	>99	0	10.8	1.47
6	**2**	$[B]_C$	95	98.7	<0.2	10.2	1.17
7	**2**	$[B]_N$	90	99	<0.2	12.4	1.24
8	**3**	$[B]_C$	100	>99	0	13.3	1.10
9	**3**	$[B]_N$	100	>99	0	12.0	1.13
10	**4**	$[B]_C$	100	87.6	12.1	18.3	1.15
11	**5**	—	100	88.2	11.8	35.3	1.22

[a] Performed in toluene (total volume = 20 mL); $T_p = 20$ °C; polymerization time = 15 min; $[Ln]_0 = 3 \times 10^{-5}$ mol, $[\text{butadiene}]_0/[Ln]_0 = 333$; $[\text{i-}Bu_3Al]_0/[Ln]_0 = 4$. [b] [Borate]: $[B]_N = [PhNMe_2H][B(C_6F_5)_4]$, $[B]_C = [Ph_3C][B(C_6F_5)_4]$, $[B]_N/[Ln]_0 = [B]_C/[Ln]_0 = 1$. [c] Determined by IR spectroscopy in CS_2. [d] Determined by gel permeation chromatography *vs.* polystyrene standards. [e] $[\text{i-}Bu_3Al]_0/[Ln]_0 = 1$. [f] $[\text{i-}Bu_3Al]_0/[Ln]_0 = 2$.

MWDs (runs 8, 9). For comparison, polybutadiene obtained by using the aluminate gadolinium complex $[(C_5Me_5)_2Gd(AlMe_4)]_2$ under the same conditions as those described in runs 4–10, possesses a significantly lower 1,4-*cis* content (96.4%).[6]

The protonolysis of amido complexes using ammonium borate is well established in organolanthanide chemistry,[7,8] and cationization by abstraction of the amido ligand using trityl borate has also been mentioned in the research literature.[7c,9] Therefore it was postulated that the complexes **1–4** would react with $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ to yield the corresponding cationic species "$[(Ind)_2Ln]^+[B(C_6F_5)_4]^-$". However, the reactions turned out to be very different from our initial expectations.

The addition of $[PhNMe_2H][B(C_6F_5)_4]$ to a toluene solution of **4** gave the mono(indenyl) silylamide cation $[(2\text{-Me-Ind})Sc\{N(SiMe_3)_2\}(PhNMe_2)]^+[B(C_6F_5)_4]^-$, **5** (Scheme 2). The amine complex **5** separates as an oil from the solution mixture, but can be isolated as a powder in good yield after washing the oil with hexane. Layering hexane above the oily residue prior to washing gave single crystals of **5**. An X-ray diffraction study,‡ unambiguously, revealed the displacement of one indenyl ligand, and showed that **5** exists as separated $[(2\text{-Me-Ind})Sc\{N(SiMe_3)_2\}(PhNMe_2)]^+$ cations and $[B(C_6F_5)_4]^-$ anions (Fig. 1).



Scheme 2 Reactions of bis(indenyl) silylamide scandium complex **4** with anilinium borate and trityl borate ($[BAr^F] = [B(C_6F_5)_4]$).

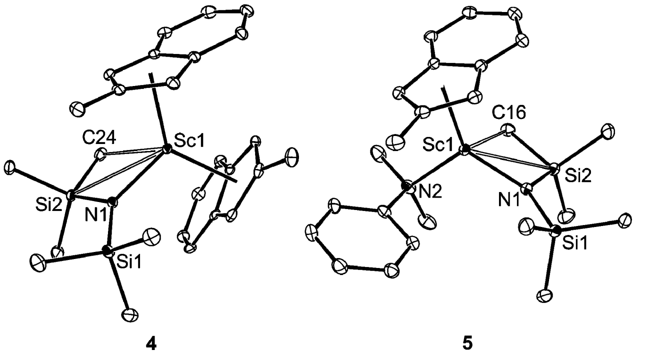


Fig. 1 ORTEP drawings of **4** and **5** with 30% thermal ellipsoids. The hydrogen atoms and the $B(C_6F_5)_4^-$ anion are omitted for clarity. Selected bond lengths (Å) and angles (°): **4**: Sc(1)–Ind(av.) 2.530(2) and 2.550(2), Sc(1)–N(1) 2.071(2), Sc(1)···C(24) 2.850(2), Sc(1)···Si(2) 3.005(1), Sc(1)–N(1)–Si(2) 104.97(7), Sc(1)–N(1)–Si(1) 131.37(8); for **5**: Sc(1)–Ind(av.) 2.466(2), Sc(1)–N(1) 2.005(2), Sc(1)–N(2) 2.317(2), Sc(1)···C(16) 2.614(2), Sc(1)···Si(2) 2.893(1), Sc(1)–N(1)–Si(2) 101.29(7), Sc(1)–N(1)–Si(1) 135.33(9).

As expected, the Sc–Ind (av. 2.466(2) Å) and Sc–amido (2.005(2) Å) bond distances in **5** are significantly shorter than those in the neutral complex **4** (av. 2.550(2), 2.530(2) Å and 2.071(2) Å, respectively). The Sc–aniline (2.317(2) Å) bond distance is comparable to the Sc–amino bond distance of 2.300(3) Å in the cation $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)(\kappa^2 F\text{-}C_6F_5)B(C_6F_5)_3$.[10] As in **4**, the silylamide ligand is asymmetrically bound to the Sc metal center, but the distortion appears accentuated in the cation (Sc–N–Si: **4**: 104.97(7) and 131.37(8)°); **5**: 101.29(7) and 135.33(9)°), so that one SiMe group in **5** appears in close proximity to the Sc metal center. For example, the C(16) and Si(2) in **5** are now, 2.614(2) Å and 2.893(1) Å[11] away from the Sc metal, respectively, as opposed to 2.850(2) Å and 3.005(1) Å in **4**, suggesting that electron deficiency at the Sc^{3+} center is further relieved by a stronger Sc···SiMe intramolecular interaction.[12] This interaction is also substantiated by the Si(2)–C(16) (1.919 (2) Å) bond distance, which is significantly longer than any of the other Si–C bonds which range from 1.862(2) to 1.874(2) Å. However, evidence for an intramolecular interaction in solution was not observed at room temperature, but the ^1H and ^{13}C NMR spectra of **5** in C_6D_5Cl were consistent with its X-ray structure. Coordination of aniline is maintained in such a non-polar solvent, as suggested by its resonances which are significantly shifted from those of free amine. In contrast, addition of THF to the amine cation **5** causes the release of *N*,*N*-dimethylaniline and its clean conversion into the corresponding THF adduct complex $[(2\text{-Me-Ind})Sc\{N(SiMe_3)_2\}(THF)_2]^+[B(C_6F_5)_4]^-$ (**6**), as shown by NMR and X-ray diffraction analysis. Alternatively, complex **6** can be prepared by reacting **4** with $[PhNMe_2H][B(C_6F_5)_4]$ in THF, and isolated in good yield after recrystallization from a mixture of THF and hexane.[13] Thus the reaction of **4** with $[PhNMe_2H][B(C_6F_5)_4]$ could be monitored by ^1H NMR spectroscopy in THF-d_8. The clean and quantitative consumption of **4** is completed within 45 min. The resulting NMR spectrum contains resonances for **6**-[d_8], identical to those of the isolated cation **6**, along with resonances corresponding to an equimolar amount of free 2-methylindene, and free *N*,*N*-dimethylaniline, showing that the protonolysis reaction is highly selective. The conversion of the neutral scandium complex **4** into **6**-[d_8] by using $[Ph_3C][B(C_6F_5)_4]$ in place of $[PhNMe_2H][B(C_6F_5)_4]$ was also observed by ^1H NMR spectroscopy in THF-d_8. The reaction proceeds *via* the clean and selective capture of one (2-Me-Ind)$^-$ anion by the Ph_3C^+ to give a mixture of the corresponding substituted indene 2-Me-((Ph_3C)Ind) and **6**-[d_8].[14]

In summary, we have shown that high activity and extremely high yields of 1,4-*cis* polybutadiene could be achieved under relatively smooth conditions, by using the new bis(indenyl) silylamide rare earth complexes in cooperation with a borate salt, and i-Bu_3Al. The cationization of these complexes, using $[PhNMe_2H][B(C_6F_5)_4]$, and $[Ph_3C][B(C_6F_5)_4]$, occurs by selective displacement of one indenyl ligand, affording new cationic mono(indenyl) amido rare earth compounds. Further studies in progress show that this activation process can be extended to other lanthanocene complexes for the generation of catalysts relevant to polymerization.

Acknowledgements

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Notes and references

‡ *Crystallographic data* for **4**: $C_{26}H_{36}Sc_1Si_2N_1$, $M = 463.70$, $T = 90(2)$ K, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.9022(17)$, $b = 15.712(2)$, $c = 14.570(2)$ Å, $\beta = 90.884(3)°$, $V = 2495.5(7)$ Å^3, $Z = 4$, $Dc = 1.234$ g cm^3, $\mu = 0.404$ mm^{-1}, reflections collected: 13713, independent reflections: 6624, ($R_{int} = 0.0482$), Final R indices [$I > 2\sigma I$]: $R_1 = 0.0396$, $wR_2 = 0.1037$, R indices (all data): $R_1 = 0.0523$, $wR_2 = 0.1071$. **5**: $C_{48}H_{38}F_{20}B_1Sc_1Si_2N_2$, $M = 1134.75$, $T = 90(2)$ K, triclinic, space group $P1^-$ (No. 2), $a = 12.125(3)$, $b = 13.378(5)$, $c = 14.834(4)$ Å, $\alpha = 96.813(7)$, $\beta = 92.136(4)$, $\gamma = 97.660(11)°$, $V = 2364.4(12)$ Å^3, $Z = 2$, $Dc = 1.594$ g cm^3, $\mu = 0.324$ mm^{-1}, reflections collected: 26223, independent reflections: 14514, ($R_{int} = 0.0300$), Final R indices [$I > 2\sigma I$]: $R_1 = 0.0456$, $wR_2 = 0.1214$, R indices (all data): $R_1 = 0.0649$, $wR_2 = 0.1371$. **6**: $C_{48}H_{43}F_{20}B_1Sc_1O_2Si_2N_1$, $M = 1157.78$, $T = 90(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 15.206(3)$, $b = 19.410(3)$, $c = 16.909(3)$ Å, $\beta = 91.299(2)°$, $V = 4989.4(15)$ Å^3, $Z = 4$, $Dc = 1.541$ g cm^3, $\mu = 0.311$ mm^{-1}, reflections collected: 25331, independent reflections: 11383, ($R_{int} = 0.0377$), Final R indices [$I > 2\sigma I$]: $R_1 = 0.0403$, $wR_2 = 0.0991$, R indices (all data): $R_1 = 0.0577$, $wR_2 = 0.1096$. Crystallographic data for **2** ($C_{26}H_{36}Gd_1Si_2N_1$), **3** ($C_{36}H_{40}Gd_1Si_2N_1$), and **7** ($C_{52}H_{71}B_1Gd_1O_3Si_2N_1$) can be found in the CIF file. CCDC reference numbers 670476 (**2**), 670551(**3**), 670550 (**4**), 670548 (**5**), 670549 (**6**), 670547 (**7**).

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6 Butadiene polymerization by using the ternary system $[(C_5Me_5)_2Gd(AlMe_4)]_2/[Ph_3C][B(C_6F_5)_4]$/i-$Bu_3Al$ (4 equiv.) at 20 °C; 100% yield; $M_n = 128\,100$; $M_w/M_n = 1.57$; 1,4-*cis*/1,4-*trans*/1,2 = 96.4/2.6/1.0; at −40 °C, $[(C_5Me_5)_2Gd(AlMe_4)]$ gave a nearly perfect *cis*-polybutadiene (1,4-*cis* > 99.9%), see ref. 5(*d*).

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13 Protonolysis of $(2\text{-Me-Ind})_2Gd\{N(SiMe_3)_2\}$ (**2**) with $[HNEt_3][BPh_4]$ in THF gave the mono(indenyl) silylamide cation $[(2\text{-Me-Ind})Gd\{N(SiMe_3)_2\}(THF)_3]^+[BPh_4]^-$ (**7**) as shown by X-ray diffraction analysis (see ESI†).

14 The reaction of $[Ph_3C][B(C_6F_5)_4]$ with $(C_5Me_4)_3Al$ which gives the aluminocenium cation $[(C_5Me_4)_2Al]^+[B(C_6F_5)_4]^-$, is to our knowledge, the only other similar example of such a cyclopentadienide abstraction reported in the research literature: S-J. Lee, P. J. Shapiro and B. Twamley, *Organometallics*, 2006, **25**, 5582.