

# Neutral *ansa*-bis(fluorenyl)silane neodymium borohydrides: synthesis, structural study and behaviour as catalysts in butadiene–ethylene copolymerisation†

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The reaction of silylene-bridged bis(fluorenyl)dipotassium salts with neodymium tris(borohydride) afforded new neutral *ansa*-bis(fluorenyl)silane neodymium borohydrides:  $(\text{Flu}_2\text{SiR}_2)\text{Nd}(\text{BH}_4)(\text{THF})$  [ $\text{R}_2 = \text{Me}_2, \text{Et}_2, (\text{CH}_2)_3, \text{Me}(\text{Ph}), \text{Flu} = \text{C}_{13}\text{H}_8$ ] that were better characterised and more soluble than the previously described anionic  $[(\text{Flu}_2\text{SiMe}_2)\text{Nd}(\text{BH}_4)_2]^-$ . The X-ray structures of three of these complexes were determined, and their solid-state geometrical parameters are very similar, despite the ring strain introduced by the silacyclobutane bridge in  $[\text{Flu}_2\text{Si}(\text{CH}_2)_3]\text{Nd}(\text{BH}_4)(\text{THF})$ . The main geometrical features were satisfactorily reproduced by DFT calculations. The catalytic activity of the title complexes in ethylene–butadiene copolymerisation reactions was assessed and compared to that of the reported activity of  $[(\text{Flu}_2\text{SiMe}_2)\text{Nd}(\text{BH}_4)_2]^-$  under similar conditions. From these results it can be concluded that the cyclo-copolymerisation of ethylene with butadiene is characteristic of a catalyst featuring silylene-bridged bis(fluorenyl) ligands around neodymium, and appears to be independent of the substituents at the silicon atom.

## Introduction

The development of  $\alpha$ -olefin–diene copolymers is a very challenging and thus very active field of research.<sup>1</sup> Several of these polymers have shown promising properties as new vulcanisable elastomers for the tyre industry because of the advantageous partial substitution of expensive butadiene by cheaper ethylene. However, copolymerisation of these two classes of monomers is not an obvious problem. There are not so many metal-based systems that are able to catalyse both the polymerisation of olefins and that of dienes. Among these, lanthanide-based organometallic complexes are probably the most promising systems, and over the past few years several *ansa*-bis(substituted Cp) neodymium complex-based catalysts have been developed.<sup>2–6</sup>

As a recent addition to this series, dimethylsilylene-bridged *ansa*-bis(fluorenyl) neodymium complexes have been prepared, like the structurally uncharacterised  $[(\text{Flu}_2\text{SiMe}_2)\text{NdCl}]$

( $\text{Flu} = \text{C}_{13}\text{H}_8$ ) as well as anionic complexes of type A:  $[(\text{Flu}_2\text{SiMe}_2)\text{Nd}(\text{BH}_4)_2]^{7-}$ , which has been characterised (Fig. 1). An interesting feature of the copolymer produced, when a combination of these new complexes with an alkylating agent as coactivator was used as a catalyst, was that cyclohexane units were present in the microstructure observed. Note that a mechanism rationalising the formation of these cycles has been proposed.<sup>4,7</sup>

The presence of these rings in the microstructure imparts beneficial properties to the copolymer in terms of relatively high  $T_g$  values and absence of melt transitions. However, the overall activity of the catalyst needs to be improved to meet industrial requirements. Since structure A appeared promising, we launched a research program aimed at studying the effects of the substitution pattern of the silylene-substituted bridge on catalytic activity and polymer microstructure. Herein, we wish to report on the synthesis of new silylene-bridged bis(fluorenyl)neodymium complexes as well as on their respective catalytic activity in the copolymerisation of ethylene with butadiene.

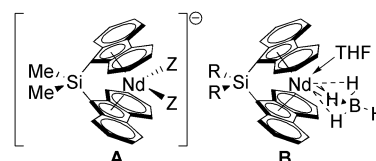


Fig. 1 Anionic (type A) and neutral (type B) *ansa*-bis(fluorenyl)silane neodymium borohydrides.

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† Electronic supplementary information (ESI) available: <sup>1</sup>H NMR spectra of **3b** and **3d**; computational details. CCDC reference numbers 772838 (**1a**), 772839 (**1b**), 772840 (**1c**), 772841 (**1d**), 772842 (**3a**), 772843 (**3b**) and 772844 (**3c**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00274g

‡ Deceased.

## Results and discussion

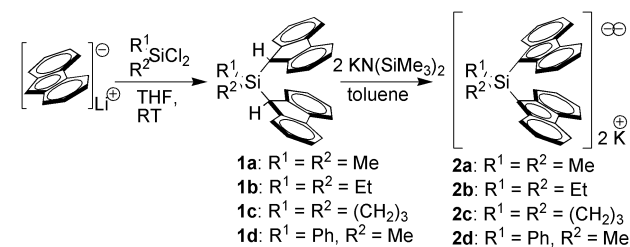
### Synthesis of the complexes

The first part of our study focused on the synthesis and the structural characterisation of neutral *ansa*-bis(fluorenyl)-neodymium complexes of type **B** ( $\text{Flu}_2\text{SiR}_2$ ) $\text{Nd}(\text{BH}_4)(\text{THF})$  (Fig. 1). Indeed, these derivatives are expected to be more easily accessible and also more soluble than their anionic congeners of type **A**.

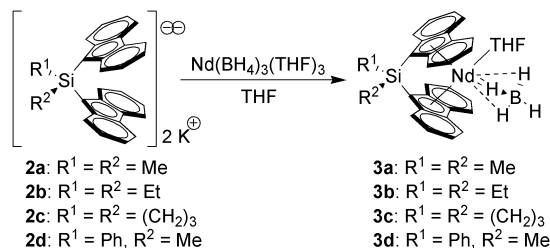
The synthesis of silyl-substituted bis(fluorene) compounds is relatively straightforward. In all cases, fluorenyllithium, which can be obtained on a large scale, was reacted with dichlorosilanes in THF at low temperature. After standard workup, compounds **1a–d** were obtained in fair to good yields. Compounds **1a–c** were further structurally characterised. Deprotonation of the fluorene ligands was performed with a non-nucleophilic base in order to avoid nucleophilic attack at silicon.<sup>8</sup> We found that  $\text{KN}(\text{SiMe}_3)_2$  was well suited for this purpose. Thus, reaction of two equivalents of  $\text{KN}(\text{SiMe}_3)_2$  with **1a–d** afforded silylene-bridged bis(fluorenyl)dipotassium salts **2a–d** which could be isolated as white powders (Scheme 1).

Neutral neodymium complexes can be synthesised by the reaction of a suitable neodymium precursor with **2a–d**. We selected neodymium(III) borohydride because of its better solubility than the chloride derivative. Furthermore, this precursor is easily available from commercial  $\text{NdCl}_3$ .<sup>9</sup> Thus, reaction of **2a–d** with  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  in THF afforded neutral complexes **3a–d** in fair to good yield after toluene workup (Scheme 2).

These complexes were characterised by proton NMR, elemental analysis, and X-ray crystal structures (for **3a–c**). Despite the paramagnetism of neodymium(III), the proton spectra could be fully assigned in most cases. In THF- $d_8$  solution at room temperature, there is a configurational instability at Nd due to rapid exchange of the coordinated THF ligand. This is evidenced by the occurrence of only four resonances for the fluorenyl protons in **3a–c**, in which the silylene bridge is symmetrical, and eight in complex **3d**, in which it is dissymmetrical. In toluene- $d_8$  at room temperature, no exchange of coordinated THF occurs and the dissymmetrical configuration of the  $\text{Nd}(\text{BH}_4)\text{THF}$  core is retained. This is established by the appearance of the fluorenyl signals in the spectrum of **3b** in toluene- $d_8$ , which are now split into eight resonances. Although we were not able to properly assign the signals in the spectrum of **3d** in toluene- $d_8$ , its



**Scheme 1** Synthesis of silylene-bridged bis(fluorenyl)dipotassium salts **2a–d**.



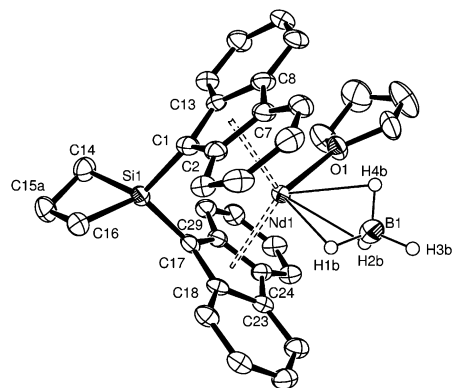
**Scheme 2** Synthesis of neutral *ansa*-bis(fluorenyl)silane neodymium borohydrides **3a–d**.

complexity is very likely due to the absence of exchange of the coordinated THF in this solvent.

### X-Ray crystal structures and theoretical calculations

In order to look for possible geometrical differences in complexes **3** due to the substituents on the silylene bridge, we undertook X-ray crystal analyses of complexes **3a–c** (no suitable crystals of **3d** could be grown). The main crystallographic data are presented in Table 1, whilst Fig. 2 shows complex **3c** as a representative example of compounds **3**.

The structures of **3a–c** are similar. The neodymium atom is chelated by the *ansa*-bis(fluorenyl) ligand. The Nd–C(ring) bonds are not equal, the shortest distances are Nd1–C1 and Nd1–C17 (2.65–2.69 Å), i.e. between Nd and the five-membered ring carbon atoms directly bonded to the silylene bridge, while the longest are between Nd and the other five-membered ring atoms (C7, C8, C23 and C24: 2.87–2.93 Å). Nonetheless, the neodymium atom can be described as  $\eta^5$ -bonded to the five-membered rings of the *ansa*-bis(fluorenyl) ligand. The borohydride ligand displays the usual tridentate coordination to neodymium, and the Nd–O bonds (2.44 Å) are also similar for the three complexes.



**Fig. 2** An ORTEP plot (50% ellipsoids) of one molecule of **3c** together with the numbering scheme used. C15 is disordered over two positions; only one is shown on the picture. Hydrogen atoms (except those on the borohydride) have been omitted for clarity. Selected distances (Å) and angles (°): Nd1–O1 2.444(4), Nd1–B1 2.602(8), Nd1–C1 2.643(6), Nd1–C17 2.671(5), Nd1–C13 2.727(5), Nd1–C18 2.743(5), Nd1–C2 2.756(6), Nd1–C29 2.822(5), Nd1–C8 2.855(6), Nd1–C7 2.860(6), Nd1–C23 2.906(5), Nd1–C24 2.931(6), Nd1–H1B 2.36(8), Nd1–H2B 2.36(8), Nd1–H4B 2.51(8), Si1–C1 1.851(6), Si1–C17 1.859(6), Si1–C16 1.871(6), Si1–C14 1.871(6), C1–Si1–C17 100.5(3), C16–Si1–C14 80.0(3)

**Table 1** Main crystallographic and data collection parameters for **3a–c**

Compound	<b>3a</b>	<b>3b</b>	<b>3c</b>
Molecular formula	C <sub>32</sub> H <sub>34</sub> BNdOSi	C <sub>34</sub> H <sub>38</sub> BNdOSi-½(C <sub>7</sub> H <sub>8</sub> )	C <sub>33</sub> H <sub>34</sub> BNdOSi
Molecular weight	617.73	691.85	629.74
Crystal habit	Red blocks	Reddish orange needles	Red blocks
Crystal dimensions (mm)	0.18 × 0.18 × 0.06	0.23 × 0.14 × 0.10	0.40 × 0.30 × 0.12
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	P <sub>2</sub> <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (no. 19)	P $\bar{1}$ (no. 2)	P <sub>2</sub> <sub>1</sub> /c (no. 14)
<i>a</i> (Å)	9.400(1)	9.198(1)	8.747(1)
<i>b</i> (Å)	11.887(1)	11.563(1)	34.629(1)
<i>c</i> (Å)	24.070(1)	15.325(1)	9.214(1)
$\alpha$ (°)	90	97.919(1)	90
$\beta$ (°)	90	93.629(1)	92.708(1)
$\gamma$ (°)	90	93.853(1)	90
<i>V</i> (Å <sup>3</sup> )	2689.5(4)	1606.4(2)	2787.8(4)
<i>Z</i>	4	2	4
<i>d</i> (g cm <sup>-3</sup> )	1.526	1.430	1.500
<i>F</i> (000)	1252	708	1276
$\mu$ (cm <sup>-1</sup> )	1.999	1.682	1.930
Maximum $\theta$	30.01	30.05	27.48
Reflections measured	23520	20537	22172
Unique data	7719	9365	6121
<i>R</i> <sub>int</sub>	0.0616	0.0300	0.0330
Reflections used	6287	8485	5494
<i>wR</i> <sub>2</sub>	0.1367	0.0792	0.1543
<i>R</i> <sub>1</sub>	0.0380	0.0275	0.0529
GoF	1.084	1.033	1.202
Flack parameter	−0.013(18)	n.a.	n.a.

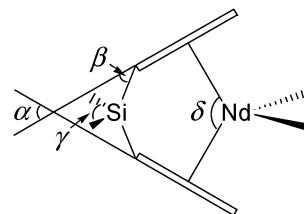
The “bite angle” on neodymium can be evaluated by two parameters: the dihedral angle  $\alpha$  between the two mean planes of the fluorenyl ligands, and the centroid–Nd–centroid angle ( $\delta$ ) around neodymium in the  $\eta^5$  configuration (Fig. 3). These two parameters are almost equal for the three complexes (73.8° to 75.6° for  $\alpha$  and 120°–121° for  $\delta$ ). Therefore, there are no significant geometrical differences between complexes **3a–c**.

### Computational details

Since 4f orbitals are much smaller than 6s and 5d orbitals, it is generally accepted that they are not involved in chemical bonding in lanthanide metal complexes. Therefore we adopted an effective core potential (ECP) for Nd, using the Stuttgart/Dresden ECP MWB49 basis set. This ECP treats the 5s<sup>2</sup>5p<sup>6</sup>6s<sup>0</sup> shells explicitly, whereas the [Kr]4d<sup>10</sup>4f<sup>3</sup> core of Nd(III) is fixed. This type of ECP is often used in calculations of metallocene derivatives of the lanthanides.<sup>10</sup> Geometry optimisations were performed with the Gaussian03<sup>11</sup> set of programs, using the B3LYP<sup>12</sup> hybrid DFT functional with the 6-31G\* basis set<sup>13,14</sup> and the above-mentioned ECP for Nd.

Table 2 presents a comparison between experimental and theoretical data. As can be seen, there is a good correlation between these data, the only slight divergence being some values of  $\beta$  (the bending angle between the Si–C<sub>1</sub> bond and the fluorenyl plane). However, this slight distortion (about 10% on average) can be explained if we consider that the B3LYP functional is known to slightly overestimate aromatic effects. Therefore the sp<sup>2</sup> character of the carbon atom C<sub>1</sub> is more important, leading to a smaller bending angle.

From these data we conclude that modifying the substituents at silicon only leads to a weak variation in the whole geometry of complexes. The most significant example is given by complex **3c**, which features a smaller  $\gamma$  angle (79.5°) than



**Fig. 3** Angles describing the geometry in complexes **3a–d**:  $\alpha$ , dihedral angle between the two mean planes of the fluorenyl ligands;  $\beta$ , out-of-plane bending angle of the silylene bridge;  $\gamma$ , bond angle between the alkyl or aryl substituents on the silylene bridge;  $\delta$ , centroid–Nd–centroid angle.

complexes **3a** and **3b** and the theoretical model **3d**. Indeed, in **3c**, the values of  $\alpha$  and  $\beta$  are very close to those of complexes **3a**, **b** and **d**. This situation probably results from the hyper-valent character of the silicon atom.

### Polymerisation results

In the case of group 4 metallocenes, it has been shown that introduction of substituents at different positions of ligands, including the bridging unit, can greatly influence the performance of the catalyst.<sup>15</sup> Recently, we showed that the *tert*-butyl substitution in positions 2 and 7 of the fluorenyl ligands modified the cyclisation selectivity in cyclo-copolymerisation of ethylene and butadiene.<sup>7</sup> In the present study, the effect of substituents of the silylene bridging unit on catalyst performance was assessed.

As previous studies showed that the ate-complex  $\{(\text{Me}_2\text{SiFlu}_2)\text{Nd}(\mu\text{-BH}_4)[(\mu\text{-BH}_4)\text{Li}(\text{THF})]\}_2$  (**4**) in combination with a dialkylmagnesium compound exhibited a good catalytic activity in the ethylene–butadiene copolymerisation process, complexes **3a–d** were also evaluated under similar experimental

**Table 2** Neodymium complexes geometries: X-ray and computational data

Complexes <b>3a–d</b> : (R <sup>1</sup> )(R <sup>2</sup> )SiFlu <sub>2</sub> Nd(BH <sub>4</sub> )(THF)	Dihedral angle: $\alpha$	Bending angle: $\beta$	R <sup>1</sup> –Si–R <sup>2</sup> bond angle: $\gamma$	Si–C1 bond length
R <sup>1</sup> = R <sup>2</sup> = Me ( <b>3a</b> )				
Experimental	75.6°	13.0°	104.1°	1.87 Å
Calculated	78.9°	11.6°	102.4°	1.89 Å
R <sup>1</sup> = R <sup>2</sup> = Et ( <b>3b</b> )				
Experimental	75.1°	13.1°	105.6°	1.87 Å
Calculated	78.7°	11.6°	104.2°	1.89 Å
R <sup>1</sup> = R <sup>2</sup> = (CH <sub>2</sub> ) <sub>3</sub> ( <b>3c</b> )				
Experimental	73.8°	13.6°	79.5°	1.84 Å
Calculated	79.1°	11.8°	78.8°	1.87 Å
R <sup>1</sup> = Me, R <sup>2</sup> = Ph ( <b>3d</b> )				
Calculated	79.7°	11.5°	102.8°	1.88 Å

conditions (see experimental section). *n*-Butyl-*n*-octyl-magnesium (BoMag) was used in a tenfold excess ([Mg]/[Nd] = 10) as activator. Indeed, dialkylmagnesiums have proven to be efficient alkylating and transfer agents for lanthanide metallocene catalysts.<sup>6,16,17</sup>

The measured activities of complexes **3a–d**, which are reported in Table 3, are similar to those of the reference complex **4**. All catalysts provided a polymer of high molecular weight with narrow molecular weight distribution except the catalyst based on **3c**. In that case, the strained 4-membered ring may not remain intact in the reaction conditions, and this would lead to several active species. However, the general bis(fluorenyl) structure of the catalytic species is maintained since the microstructure of polymers was not modified (run 4, Table 3 and Table 4).

### Microstructure and physical properties

The composition and the microstructures of the obtained copolymers were investigated by <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy, and the results are reported in Table 4. NMR studies showed that the copolymers displayed similar microstructures: they exhibit a high proportion of rings and vinyl groups resulting from the 2,1-insertion of butadiene, together with *trans*-1,4 butadiene and linear ethylene units. A slightly higher *trans*-1,4 selectivity was observed for the ate-complex **4** in comparison with **3a**. This kind of microstructure was previously observed on copolymers obtained with the [4/BoMag] system.<sup>7</sup> The cyclo-copolymerisation of ethylene with butadiene is therefore characteristic of a catalyst featuring silylene-bridged bis(fluorenyl) ligands around neodymium and appears to be independent of the substituents at the silicon atom.

C. Boisson *et al.*<sup>4,7</sup> proposed a four-step mechanism for the cyclisation process involving one molecule of 1,3-butadiene and two molecules of ethylene (Scheme 3). The first step involves a 2,1-insertion of one molecule of butadiene to form an  $\eta^3$ -allylneodymium complex (**A**). The second and the third steps, which are similar, rely on the insertion of one molecule of ethylene to yield an alkyl complex (**B**), in which the resulting vinyl unit is coordinated to neodymium. Note that at this stage an intramolecular insertion of this vinyl unit into the neodymium–carbon bond would result in the formation of a cyclobutane unit, which is highly disfavoured for evident thermodynamic reasons related to the ring strain. Therefore, the insertion of a second ethylene unit is favoured, yielding an intermediate (**C**) in which the vinyl unit is still coordinated to the neodymium. At this stage the intramolecular insertion is then kinetically favoured to form an alkyl neodymium complex featuring a 1,2-cyclohexane ring in the polymer chain.

According to this mechanism, the partial pressure of butadiene is a critical factor for the formation of cyclic structure; if a butadiene unit is inserted instead of an ethylene during the ring-forming process, it would lead to a classical 1,2-vinyl pattern. Run 6 shows that with a lower butadiene feed, the 1,2 vs. 1,4-addition ratio does not vary, as the *trans*-1,4 molar ratio does not change. In contrast, the ring vs. vinyl ratio increases with lower butadiene weight fraction.

This kind of microstructure has an important impact on the macroscopic properties. Indeed, the presence of rings modifies chain flexibility, as inserted rings reduce the number of degrees of freedom of the polymer chain. DSC analyses of the obtained copolymers were performed, and the measured glass-transition temperatures (*T*<sub>g</sub>) are reported in Table 4. The obtained copolymers present high *T*<sub>g</sub> values

**Table 3** Activity in ethylene/butadiene copolymerisation with **3a–d**/BoMag<sup>a</sup>




Run	Compd.	Butadiene in feed (mol%)	<i>n</i> (Nd) (μmol)	Yield (g)	Time (min)	<i>M</i> <sub>n</sub> (PDI) <sup>c</sup> (g mol <sup>-1</sup> )	Activity (kg mol <sup>-1</sup> h <sup>-1</sup> )
1 <sup>b</sup>	<b>4</b>	30	20.0	7.5	180	33 300 (1.68)	123.0
2	<b>3a</b>	30	20.0	7.19	180	32 000 (1.8)	119.8
3	<b>3b</b>	30	19.5	6.43	173	24 200 (1.86)	114.4
4	<b>3c</b>	30	18.7	5.67	171	21 400 (3.44)	106.4
5	<b>3d</b>	30	21.0	6.33	180	33 100 (1.82)	100.5
6	<b>3b</b>	15	16.8	8.84	180	25 900 (1.65)	175.4
7	<b>3c</b>	15	22.0	7.27	114	36 700 (4.10)	173.9
8	<b>3d</b>	15	19.6	7.87	180	20 100 (1.73)	133.8
9	<b>3d</b>	60	19.5	2.42	180	11 400 (3.88)	41.4

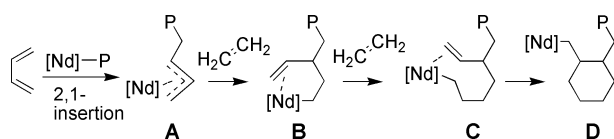
<sup>a</sup> Polymerisation conditions : toluene (200 mL), BoMag 0.2 mmol ([Mg]/[Nd] = 10), 80 °C, 4 bar. <sup>b</sup> According to ref. 7. <sup>c</sup> *M*<sub>n</sub>: number-average molecular weight; PDI: polydispersity index.



**Table 4** Microstructure of the copolymers

Run	Compd.	Butadiene in feed (mol%)	$\eta$ (Nd) ( $\mu$ mol)	Yield (g)	Time (min)	$M_n$ (PDI) ( $\text{g mol}^{-1}$ )	Activity ( $\text{kg mol}^{-1} \text{h}^{-1}$ )
1 <sup>b</sup>	<b>4</b>	30	20.0	7.5	180	33 300 (1.68)	123.0
2	<b>3a</b>	30	20.0	7.19	180	32 000 (1.8)	119.8
3	<b>3b</b>	30	19.5	6.43	173	24 200 (1.86)	114.4
4	<b>3c</b>	30	18.7	5.67	171	21 400 (3.44)	106.4
5	<b>3d</b>	30	21.0	6.33	180	33 100 (1.82)	100.5
6	<b>3b</b>	15	16.8	8.84	180	25 900 (1.65)	175.4
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8	<b>3d</b>	15	19.6	7.87	180	20 100 (1.73)	133.8
9	<b>3d</b>	60	19.5	2.42	180	11 400 (3.88)	41.4

<sup>a</sup> Polymerisation conditions: same as in Table 3. <sup>b</sup> Rings (according to ref. 7): 1,2-T:  1,2-C:  1,4-T: 

**Scheme 3** Mechanism of the formation of 1,2-cyclohexane structures in ethylene-butadiene copolymerisation with **3a-d**.

compared to linear polybutadiene ( $-106\text{ }^{\circ}\text{C}$ ) or polyethylene ( $-125\text{ }^{\circ}\text{C}$ ).<sup>18</sup>

It is known that  $T_g$  increases with 1,2-vinyl weight fraction<sup>19</sup> in polybutadiene. Based on theoretical and experimental studies, a linear relation has been proposed:<sup>20</sup>  $T_g = -106 + 91 \times (\text{vinyl weight fraction})$ . According to this, a  $T_g$  of  $-45\text{ }^{\circ}\text{C}$ , similar to that of the obtained copolymers (run 2–5), can be achieved with a polybutadiene including 67% 1,2-vinyl units. In comparison, the obtained copolymer for run 3 exhibits weight fractions of 20% for 1,2-vinyl units. So the presence of cyclic microstructures and ethylene units in the copolymer also contributes to the increase of  $T_g$ .

## Conclusions

A series of neutral silylene bridged *ansa*-bis(fluorenyl) neodymium borohydride complexes were prepared and characterised. In combination with a dialkylmagnesium compound, all complexes showed high activity in cyclo-copolymerisation of ethylene with butadiene. Various substituents were introduced on the silicon atom of the bridging unit, but few influences were observed either on the crystal structure of organo-metallic complexes or on the performance of catalysts in polymerisation.

## Experimental section

### General

All reactions involving air-sensitive compounds were performed under a protective atmosphere of dry nitrogen or argon with dry, oxygen-free solvents. Dichlorodiethylsilane was distilled before use, and all other commercially available reagents were obtained from the suppliers and used without further purification.  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  was prepared as previously described.<sup>9</sup> NMR spectra of all synthesised compounds were measured at ambient temperature ( $20\text{ }^{\circ}\text{C}$ ) with a Bruker Avance 300 spectrometer operating at 300 MHz for  $^1\text{H}$  and 75.5 MHz

for  $^{13}\text{C}$ . Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane. The microstructure of polymers was determined by Nuclear Magnetic Resonance (NMR) using a Bruker DRX 400 spectrometer. Spectra were measured with a 5mm QNP probe at 363 K. A 2:1 volume mixture of tetrachloroethylene and hexadeuterobenzene was used as the solvent. Gel Permeation Chromatography (GPC) samples were prepared in 1,2,4-trichlorobenzene. Solutions were injected at  $150\text{ }^{\circ}\text{C}$  into a Waters Alliance GPCV 2000 instrument equipped with a Waters viscosimeter and 3 Styragel columns (HT 6E and HT 2). The system was calibrated with polystyrene standards using universal calibration. Thermal studies were performed by Differential Scanning Calorimetry (DSC) with a Setaram 131 Calorimeter. Samples were heated from  $-130\text{ }^{\circ}\text{C}$  to  $120\text{ }^{\circ}\text{C}$  in order to erase their thermal past, then cooled to  $-130\text{ }^{\circ}\text{C}$ , and heated again at a rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ . Microanalytical data were obtained through the Centre de Microanalyse de l'Université de Dijon.

### Preparation of the compounds

**Synthesis of fluorenyllithium.** (FluLi):<sup>21</sup> Fluorene (16.6 g, 100 mmol) was dissolved in 80 mL of toluene, and 1.05 eq. BuLi (2.5 M in hexanes, 42 mL) was added dropwise at  $0\text{ }^{\circ}\text{C}$ . The reaction mixture was warmed to room temperature and stirred at  $80\text{ }^{\circ}\text{C}$  for 2 h, whereupon a yellow solid precipitated. After cooling down to room temperature, the precipitate was filtered, washed with toluene and hexane, and dried under vacuum to afford 13.7 g of FluLi as a yellow powder (80 mmol, 80%).  $^1\text{H}$  NMR ( $\text{THF-d}_8$ ):  $\delta = 5.95$  (s, 1H), 6.41 (t, 2H,  $J_{\text{H-H}} = 7\text{ Hz}$ ), 6.78 (t, 2H,  $J_{\text{H-H}} = 7\text{ Hz}$ ), 7.28 (d, 2H,  $J_{\text{H-H}} = 7\text{ Hz}$ ), 7.89 (d, 2H,  $J_{\text{H-H}} = 7\text{ Hz}$ ).

### General procedure (GP1) for the synthesis of the *ansa*-bis(fluorenyl)silanes **1a-d**

Fluorenyllithium was dissolved in THF, and 0.5 eq. of dichlorosilane was added with stirring at  $-80\text{ }^{\circ}\text{C}$ . The resulting solution was warmed to room temperature. After 18 h,  $\text{NH}_4\text{Cl}$  was added to quench any residual fluorenyllithium. The solution was evaporated, and the orange solid was redissolved in  $\text{CH}_2\text{Cl}_2$ , dried on  $\text{MgSO}_4$  and purified by filtration on silica gel. The clear solution was evaporated to a light yellow solid that was further purified by recrystallisation from petroleum ether. The product was dried at  $60\text{ }^{\circ}\text{C}$  under vacuum overnight, affording **1a-d** as white solids. **1a-d** were further

characterised by X-ray structures; single crystals were obtained by slow evaporation of  $\text{CHCl}_3$  solutions at room temperature.

**Difluorenyldimethylsilane (1a).** 1.63 g of **1a** (4.2 mmol, 81%) was prepared according to GP1 from 1.79 g FluLi (10.4 mmol), and 0.63 mL  $\text{Me}_2\text{SiCl}_2$  (0.67 g, 5.2 mmol) in 50 mL THF.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  = -0.56 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ), 4.18 (s, 2H, Si-CH), 7.15 (t, 4H,  $J_{\text{H-H}}$  = 8 Hz), 7.27 (t, 4H,  $J_{\text{H-H}}$  = 8 Hz), 7.38 (d, 4H,  $J_{\text{H-H}}$  = 8 Hz), 7.80 (d, 4H,  $J_{\text{H-H}}$  = 8 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = -6.9 ( $\text{CH}_3$ ), 40.5 (C9), 120.3, 124.4, 125.8, 126.40 (C1-C8), 140.9, 145.1 (C10-C13). MS (IC of  $\text{NH}_3$ ): 389 [M + 1], 100%.

**Difluorenyldiethylsilane (1b).** 1.19 g of **1b** (2.8 mmol, 66%) was prepared according to GP1 from 1.5 g FluLi (8.7 mmol), and 0.65 mL  $\text{Et}_2\text{SiCl}_2$  (0.68 g, 4.3 mmol) in 45 mL THF.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.38 (m, 10H,  $\text{CH}_3\text{-CH}_2\text{-Si}$ ), 3.91 (s, 2H, Si-CH), 7.17 (t, 4H,  $J_{\text{H-H}}$  = 8 Hz), 7.25 (d, 4H,  $J_{\text{H-H}}$  = 7 Hz), 7.26 (t, 4H,  $J_{\text{H-H}}$  = 7 Hz), 7.76 (d, 4H,  $J_{\text{H-H}}$  = 8 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.1 (2 Si- $\text{CH}_2$ ), 7.3 (2 - $\text{CH}_3$ ), 38.7 (C9), 120.5, 124.8, 125.9, 126.6 (C1-C8), 141.2, 145.5 (C10-C13). MS (IC,  $\text{NH}_3$ , 70 eV): 417 [M + 1], 100%.

**1,1-Difluorenylsilacyclobutane (1c).** 1.75 g (4.4 mmol, 57%) of **1c** was prepared according to GP1 from 2.65 g FluLi (15.4 mmol) and 0.91 mL of 1,1-dichlorosilacyclobutane (1.08 g, 7.7 mmol) in 60 mL THF.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.96 (t, 4H, - $\text{CH}_2\text{-Si}$ ,  $J_{\text{H-H}}$  = 8.2 Hz), 1.68 (m, 2H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ,  $J_{\text{H-H}}$  = 8.2 Hz), 3.72 (s, 2H, C9), 7.13 (d, 4H,  $J_{\text{H-H}}$  = 7 Hz), 7.27 (t, 4H,  $J_{\text{H-H}}$  = 7 Hz), 7.35 (t, 4H,  $J_{\text{H-H}}$  = 7 Hz), 7.83 (d, 4H,  $J_{\text{H-H}}$  = 7 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 15.0 (- $\text{CH}_2\text{-Si}$ ), 16.6 ( $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 40.3 (C9), 120.8, 124.9, 126.4, 127.0 (C1-C8), 141.2, 144.8 (C10-C13). MS (IC,  $\text{NH}_3$ , 70 eV): 401 [M + 1], 100%.

**Difluorenyl(methyl)phenylsilane (1d).** 2.67 g of **1d** (5.9 mmol, 82%) was prepared according to GP1 from 2.5 g of FluLi (14.5 mmol) and 1.17 mL dichloro(methyl)phenylsilane (1.38 g, 7.2 mmol) in 70 mL THF.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = -0.27 (s, 3H, Si- $\text{CH}_3$ ), 4.70 (s, 2H, Si-CH), 6.55 (d, 2H,  $J$  = 7.4 Hz), 6.92 (t, 2H,  $J$  = 7.5 Hz, Flu), 7.16 (t, 1H,  $J$  = 7.5 Hz), 7.22 (t, 2H,  $J$  = 7.4 Hz), 7.37 (8H), 7.80 (m, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = -10.07 ( $\text{CH}_3\text{-Si}$ ), 39.57 (C9), 120.10, 124.39, 125.68, 126.23 (C1-C8), 126.72 (CH), 131.6 ( $\text{C}_{\text{ipso}}$ ), 134.03 (CH), 140.99, 141.10, 144.35, 144.39 (C10-C13). MS (IC,  $\text{NH}_3$ , 70 eV) 451 [M + 1], 100%.

#### General procedure (GP2) for the synthesis of *ansa*-bis(fluorenylsilane) dianions **2a-d**

A solution of **1a-d** in toluene was added to a solution of  $\text{KN}(\text{TMS})_2$  (2.1 eq.) in toluene at room temperature. The reaction mixture was heated at 50 °C for 16 h, whereupon dianions **2a-d** precipitated as yellow-orange powders that were isolated, washed with toluene to remove any remaining  $\text{KN}(\text{SiMe}_3)_2$ , and dried under vacuum.

**Dipotassium (dimethylbis(9-fluorenyl)silane)diide (2a).** 1.0 g of **2a** (2.2 mmol, 91%) was prepared according to GP2 from 0.92 g of **1a** (2.35 mmol) and 0.98 g of  $\text{KN}(\text{SiMe}_3)_2$  (5.2 mmol) in 16 mL of toluene.  $^1\text{H}$  NMR (THF- $d_8$ )  $\delta$  = 0.9 (s, 6H,

$\text{Si}(\text{CH}_3)_2$ ), 6.5 (t, 4H,  $J_{\text{H-H}}$  = 7 Hz), 6.9 (t, 4H,  $J_{\text{H-H}}$  = 7 Hz), 7.9 (d, 4H,  $J_{\text{H-H}}$  = 7 Hz), 8.0 (d, 4H,  $J_{\text{H-H}}$  = 7 Hz).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta$  = 2.6 ( $\text{CH}_3\text{-Si}$ ), 37.4 (C9), 119.4, 120.3, 125.7, 127.4 (C1-C8), 142.7, 144.1 (C10-C13).

**Dipotassium (diethylbis(9-fluorenyl)silane)diide (2b).** 1.2 g of **2b** (2.4 mmol, 92%) was prepared according to GP2 from 1.11 g **1b** (2.67 mmol) and 1.10 g  $\text{KN}(\text{SiMe}_3)_2$  (5.5 mmol) in 20 mL of toluene.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  = 1.31 (t, 6H,  $\text{CH}_3$ ), 1.97 (q, 4H,  $\text{CH}_2$ ), 6.66 (t, 4H,  $J_{\text{H-H}}$  = 7 Hz), 7.01 (t, 4H,  $J_{\text{H-H}}$  = 7 Hz), 8.04 (d, 4H,  $J_{\text{H-H}}$  = 7 Hz), 8.09 (d, 4H,  $J_{\text{H-H}}$  = 7 Hz).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta$  = 0.1 ( $\text{CH}_2\text{-Si}$ ), 5.9 ( $\text{CH}_3$ ), 41.7 (C9), 118.1, 122.0, 123.3, 124.8 (C1-C8), 142.6, 146.0 (C10-C13).

**Dipotassium (bis(9-fluorenyl)-1,1'-silacyclobutanediide) (2c).** 410 mg of **2c** (0.86 mmol, 85%) was prepared according to GP2 from 401 mg of **1c** (1.0 mmol) and 430 mg of  $\text{KN}(\text{SiMe}_3)_2$  (2.16 mmol) in 10 mL of toluene;  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  = 7.97 (d, 4H,  $J_{\text{H-H}}$  = 8 Hz), 7.94 (d, 4H,  $J_{\text{H-H}}$  = 8 Hz), 6.94 (t, 4H), 6.57 (t, 4H), 2.41 (m, 2H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 1.85 (t, 4H,  $\text{CH}_2\text{-Si}$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ )  $\delta$  = 17.9 (- $\text{CH}_2\text{-Si}$ ), 23.0 ( $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 45.3 (C9), 111.5, 119.4, 120.1, 121.5 (C1-C8), 145.7, 140.3 (C10-C13).

**Dipotassium (methylphenylbis(9-fluorenyl)silane)diide (2d).** 470 mg of **2c** (0.89 mmol, 90%) was prepared according to GP2 from 450 mg of **1d** (1.0 mmol) and 438 mg of  $\text{KN}(\text{SiMe}_3)_2$  (2.2 mmol) in 10 mL toluene.  $^1\text{H}$  NMR (THF- $d_8$ )  $\delta$  = 1.25 (s, 3H, Si- $\text{CH}_3$ ), 6.55 (d, 4H), 6.75 (t, 4H), 7.22 (m, 3H), 7.68 (d, 4H), 7.90 (m, 2H), 7.95 (d, 4H).

#### General procedure (GP3) for the synthesis of the *ansa*-bis(fluorenyl)silane neodymium borohydrides **3a-d**.

An equimolecular mixture of dianions **2a-d** and  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  in THF was stirred 1 h at room temperature, whereupon a white precipitate ( $\text{KBH}_4$ ) appeared. It was then eliminated by centrifugation, and 20 mL of toluene was added to the dark red solution. After stirring overnight, the solution was evaporated to a brown solid, which was redissolved in toluene and centrifuged to eliminate more  $\text{KBH}_4$ . The clear solution was evaporated to dryness, the residue was washed with petroleum ether and dried under vacuum to give complexes **3a-d**. **3a-c** were further characterised by X-ray structures; pale-red single crystals were obtained by recrystallisation from a toluene-petroleum ether solution at -20 °C.

**[Dimethylbis(9-fluorenyl)silane)diyl](borohydrido)(tetrahydrofuran)neodymium (3a).** According to GP3, starting from 464 mg **2a** (1.0 mmol) and 404 mg of  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (1.0 mmol) in 16 mL of THF, **3a** (380 mg) was obtained as a red-brown powder. Yield: 0.55 mmol (55%).  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  = -2.4 (b, 8H), 3.4 (b, 4H), 5.0 (b, 4H), 13.1 (b, 6H, - $\text{CH}_3$ ). Anal (%), found: C, 61.07; H, 5.70; calcd. for  $\text{C}_{32}\text{H}_{34}\text{BNdOSi}$  = 617.75, C: 62.22, H: 5.55.

**[Diethylbis(9-fluorenyl)silane)diyl](borohydrido)(tetrahydrofuran)neodymium (3b).** According to GP3, starting from 308 mg of **2b** (0.63 mmol) and 250 mg of  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (0.63 mmol) in 10 mL of THF, **3b** (270 mg) was obtained as a red-brown powder that contained toluene. Anal(%): found, C: 64.95, H: 6.37; calcd. for  $\text{C}_{34}\text{H}_{38}\text{BNdOSi}$  = 645.80, C: 63.23,

H: 5.95; calcd. for  $C_{34}H_{38}BNdOSi \cdot 0.5(C_7H_8) = 696.87$ , C: 65.10; H, 6.12. Yield (as hemitoluene solvate): 0.39 mmol (62%).  $^1H$  NMR (toluene- $d_8$ )  $\delta = -11.8$  (b, 4H, THF),  $-10.9$  (b, 2H),  $-9.9$  (b, 2H),  $-5.2$  (b, 4H, THF),  $-5.2$  (b, 2H, Flu),  $-4.7$  (b, 2H),  $-4.1$  (b, 2H),  $-3.8$  (b, 2H), 9.8 (b, 3H,  $CH_3$ ), 9.9 (b, 2H), 10.8 (b, 2H,  $CH_2$ ), 11.9 (b, 2H), 13.1 (b, 3H,  $CH_3$ ), 20.6 (b, 2H,  $CH_2$ ).  $^1H$  NMR (THF- $d_8$ ):  $\delta = -6.9$  (b, 4H),  $-4.3$  (b, 4H), 0.9 (b, 4H), 8.4 (b, 4H), 11.4 (b, 6H,  $-CH_3$ ), 16.2 (b, 4H,  $-CH_2-$ ).

**[Bis(9-fluorenyl)-1,1'-silacyclobutanediyl](borohydrido)(tetrahydrofurano)neodymium (3c).** According to GP3, starting from 465 mg (0.85 mmol) of **2c** and 345 mg (0.85 mmol) of  $Nd(BH_4)_3(THF)_3$  in 15 mL of THF, **3c** (357 mg) was obtained as a red-brown powder that contained toluene. Anal (%): found, C: 64.03, H: 5.84; calcd. for  $C_{33}H_{34}BNdOSi = 629.76$ , C: 62.94, H: 5.44; calcd. for  $C_{33}H_{34}BNdOSi \cdot 0.5(C_7H_8) = 675.83$ , C: 64.87; H, 5.67. Yield (as hemitoluene solvate): 0.54 mmol (63%).  $^1H$  NMR (THF- $d_8$ ):  $\delta = -3.0$  (b, 4H),  $-2.2$  (b, 4H), 2.4 (s, 1.5H, toluene), 7.1 (b, 4H), 7.2 (m, 2.5H, toluene), 9.9 (b, 2H), 10.8 (b, 2H,  $CH_2-CH_2-CH_2$ ), 12.0 (b, 4H, Flu), 14.8 (b, 4H,  $Si-CH_2$ ), 28.9 (b, 2H,  $-CH_2-$ ), 99.1 (vb, 4H,  $Nd-BH_4$ ).

**[Methylphenylbis(9-fluorenyl)silanediy](borohydrido)(tetrahydrofurano)neodymium (3d).** According to GP3, starting from 348 mg (0.66 mmol) of **2d** and 266 mg (0.66 mmol) of  $Nd(BH_4)_3THF_3$  in 10 mL THF, **3d** (380 mg) was obtained as a dark-red powder that contained toluene. Yield (as hemitoluene solvate): 0.51 mmol (78%).  $^1H$  NMR (THF- $d_8$ )  $\delta = -7.9$  (b, 2H),  $-5.9$  (b, 2H),  $-5.2$  (b, 2H),  $-4.8$  (b, 2H),  $-3.5$  (b, 2H),  $-1.4$  (b, 2H), 2.3 (s, 1.5H, toluene), 7.3–7.2 (m, 2.5H, toluene), 7.8 (b, 2H), 8.3 (b, 2H), 10.1 (b, 1H,  $Ph-Si$ ), 11.0 (b, 2H), 16.1 (b, 3H,  $Si-CH_3$ ), 20.7 (b, 2H).

## X-ray experimental section

Crystals for X-ray analysis were immersed in Paratone-N oil in a drybox and mounted on a fiberglass needle in a cold stream of dinitrogen. Data collection was performed at 150 K on a Nonius KappaCCD diffractometer, using graphite-monochromated  $Mo-K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ).

**1a**, chemical formula:  $C_{28}H_{24}Si$ ,  $M$ : 388.56, crystal system: orthorhombic,  $a$  ( $\text{\AA}$ ): 18.538(1),  $b$  ( $\text{\AA}$ ): 35.874(1),  $c$  ( $\text{\AA}$ ): 12.751(1),  $V$  ( $\text{\AA}^3$ ): 8479.8(8), space group:  $Aba2$ ,  $Z$ : 16,  $T$ : 150.0(1) K, reflections measured: 24 164,  $R_{int}$ : 0.0512, reflections used: 5763, final  $R1$ : 0.0404,  $wR2$  (all data): 0.1191, Flack parameter: 0.04(12).

**1b**, chemical formula:  $C_{30}H_{28}Si$ ,  $M$ : 416.61, crystal system: orthorhombic,  $a$  ( $\text{\AA}$ ): 17.026(1),  $b$  ( $\text{\AA}$ ): 9.952(1),  $c$  ( $\text{\AA}$ ): 13.230(1),  $V$  ( $\text{\AA}^3$ ): 2241.7(3), space group:  $Pbcn$ ,  $Z$ : 4,  $T$ : 150.0(1) K, Reflections measured: 14 437,  $R_{int}$ : 0.0473, reflections used: 1797, final  $R1$ : 0.0892,  $wR2$  (all data): 0.2523.

**1c**, chemical formula:  $C_{29}H_{24}Si$ ,  $M$ : 400.57, crystal system: triclinic,  $a$  ( $\text{\AA}$ ): 8.740(1),  $b$  ( $\text{\AA}$ ): 9.839(1),  $c$  ( $\text{\AA}$ ): 13.230(1),  $\alpha$  ( $^\circ$ ): 104.023(1),  $\beta$  ( $^\circ$ ): 105.022(1),  $\gamma$  ( $^\circ$ ): 102.433(1),  $V$  ( $\text{\AA}^3$ ): 1046.8(2), space group:  $P\bar{1}$ ,  $Z$ : 2,  $T$ : 150.0(1) K, reflections measured: 7940,  $R_{int}$ : 0.0195, reflections used: 4019, final  $R1$ : 0.0485,  $wR2$  (all data): 0.1304.

**1d**, chemical formula:  $C_{33}H_{26}Si$ ,  $M$ : 450.63, crystal system: triclinic,  $a$  ( $\text{\AA}$ ): 9.3890(1),  $b$  ( $\text{\AA}$ ): 10.038(1),  $c$  ( $\text{\AA}$ ): 12.922(1),  $\alpha$  ( $^\circ$ ): 92.983(1),  $\beta$  ( $^\circ$ ): 90.812(1),  $\gamma$  ( $^\circ$ ): 99.215(1),  $V$  ( $\text{\AA}^3$ ): 1200.2(2), space group:  $P\bar{1}$ ,  $Z$ : 2,  $T$ : 150.0(1) K, reflections measured: 13 437,  $R_{int}$ : 0.0221, reflections used: 5451, final  $R1$ : 0.0423,  $wR2$  (all data): 0.1176.

## Polymerisation procedure

Polymerisation reactions were performed in a 250 mL glass reactor, stirred with a stainless steel blade. A solution of the alkylating agent (butyloctylmagnesium; BoMag) in toluene (200 mL) was transferred *via* cannula over the Nd complexes **3a–d**. The concentration of **3a–d** was  $100 \mu\text{mol L}^{-1}$  and that of BoMag was  $1 \text{ mmol L}^{-1}$  (ratio  $[Mg]/[Nd] = 10$ ). The mixture was stirred for 1 min, and transferred to the reactor under a stream of argon. The argon was then pumped out before introducing the monomers. For low concentrations of butadiene in the feed ( $\leq 30 \text{ mol\%}$ ), the reactor was charged with the gaseous monomers (ethylene–butadiene mixture). Temperature and pressure were then progressively increased up to  $80 \text{ }^\circ\text{C}$  and 4 bar respectively and kept constant. For higher concentrations of butadiene, the latter was dissolved in the toluene solution and then heated up to  $80 \text{ }^\circ\text{C}$ . Pure ethylene was finally added in order to obtain the required composition. At the end of polymerisation, the mixture was quenched with 1 mL of methanol, then the polymer was stabilised with 2,6-di-*tert*-butyl-4-methylphenol, precipitated by adding 600 mL EtOH and dried under vacuum at  $60 \text{ }^\circ\text{C}$ . Activities were measured *via* the mass of polymer obtained.

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