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# Cationic borohydrido-neodymium complex: Synthesis, characterization and its application as efficient pre-catalyst for isoprene polymerisation<sup>†</sup>

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The cationic borohydrido lanthanide complex **1**, prepared from the reaction of  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  with  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ , is highly active towards isoprene polymerisation upon activation with  $\text{Al}(i\text{-Bu})_3$ , whereas the *in situ* prepared ternary catalytic combination  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}(i\text{-Bu})_3$ , albeit less active, displays higher *cis*-selectivity and better control in terms of macromolecular data.

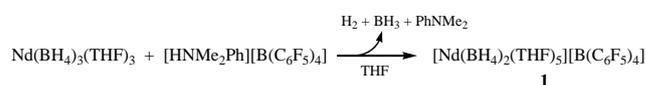
Catalysts based on rare-earth metals are known as highly effective towards the conjugated dienes polymerisation.<sup>1</sup> Among these catalysts, well-defined cationic species are of particular interest, due to their excellent activity along with *cis*-stereocontrol.<sup>2</sup> Such compounds are generally prepared by the straightforward reaction of an alkyllanthanide borate with a lanthanide alkyl,<sup>3</sup> allyl,<sup>4</sup> hydride,<sup>5</sup> amido,<sup>6</sup> or a chlorolanthanide/alkylaluminum intermediate.<sup>7</sup> However, the synthesis and isolation of these lanthanide initiators require hard experimental work-up, owing to their great sensitivity towards moisture and oxygen, together with a relative thermal stability.<sup>8</sup> It is thus of interest to discover more simple precursors and procedures that could be utilized successfully in catalytic combinations, and enabling controlled polymerisations.

We and other groups have demonstrated that the lanthanide trisborohydrides  $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ , considered as a true alternative to the trichlorides for organometallic syntheses since only recently,<sup>9</sup> could also initiate the polymerisation of a wide range of polar<sup>10</sup> and non polar<sup>11</sup> monomers. In particular, we established that combined with  $\text{MgR}_2$  co-catalysts,  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  affords the controlled polymerisation of isoprene in a *trans*-selective manner.<sup>12</sup>

In this communication, we report that upon straightforward reaction between  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  and  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ , the first borohydrido cationic compound,  $[\text{Nd}(\text{BH}_4)_2(\text{THF})_5][\text{B}(\text{C}_6\text{F}_5)_4]$ , **1**, could be isolated and fully characterized, including its X-Ray structure. Combined with  $\text{Al}(i\text{-Bu})_3$ , this compound reveals to be highly active towards the polymerisation of isoprene. The ternary catalytic system  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}(i\text{-Bu})_3$ , prepared *in situ* without isolation of **1**, behaves very similarly but with higher levels of *cis*-selectivity.

Ephritikhine and coll. reported a decade ago that the protonation of the monoborohydrido (COT) $\text{Nd}(\text{BH}_4)_2(\text{THF})_2$  derivative (COT =  $\text{C}_8\text{H}_8$ ) with  $\text{HNEt}_3\text{BPh}_4$  afforded the cationic (COT) $\text{Nd}(\text{THF})_2^+$  compound.<sup>9a</sup> Following this idea, we investigated by <sup>1</sup>H NMR monitoring the reaction of  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  with  $\text{HNEt}_3\text{BPh}_4$  in THF-D<sub>8</sub>. At room

temperature, the consumption of the starting material was quite low but traces of released H<sub>2</sub> ( $\delta$  ppm = 4.4 ppm) were an indication of the expected protonation reaction.<sup>13,14</sup> In the presence of one equivalent of  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  in THF-D<sub>8</sub>,  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  was this time immediately and completely consumed, along with unambiguous formation of H<sub>2</sub>. The experiment was then conducted at a bulk scale (Scheme 1), and after experimental work-up (see ESI), purple crystals of **1** could be isolated in good yield (68 %). Elemental analysis confirmed the chemical composition for a bisborohydrido compound, and corresponded to the formula  $[\text{Nd}(\text{BH}_4)_2(\text{THF})_5][\text{B}(\text{C}_6\text{F}_5)_4]$ .



Scheme 1 Synthesis of complex **1**

Crystals of **1** were grown from THF/pentane at  $-20$  °C. X Ray structure determination established the expected ionic pair structure, without any interaction between  $\text{Nd}(\text{BH}_4)_2(\text{THF})_5^+$  and its borate counteranion (Fig. 1).<sup>‡</sup>

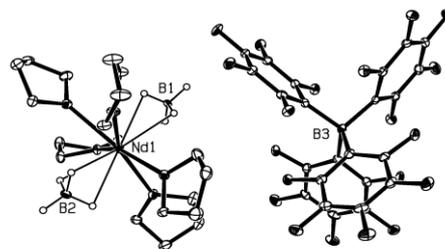


Fig. 1 ORTEP drawing of **1** (ellipsoid probability level 30 %). Hydrogen atoms except BH<sub>4</sub> omitted for clarity. Selected bond lengths [Å] and angles [°]: Nd1-B1 2.596(4); Nd1-B2 2.641(4); B1-Nd-B2 177.67 (13).

The cationic moiety adopts a distorted heptahedral arrangement and BH<sub>4</sub> ligands both exhibit an  $\eta^3\text{-H}_3\text{BH}$  terminal bonding mode. The molecular structure of the cationic  $\text{Nd}(\text{BH}_4)_2(\text{THF})_5^+$  is fully comparable to the samarium one found in the recently described bimetallic compound  $[\text{Sm}(\text{BH}_4)_2(\text{THF})_5]^+[\text{Cp}^*\text{Sm}(\text{BH}_4)_3]^-$ , which exhibited an ionic structure in the solid state only.<sup>15</sup> The Nd-B (BH<sub>4</sub>) distances in **1** (average 2.618 Å) are comparable or slightly shorter to those reported for monocyclopentadienyl bisborohydrido neodymium compounds.<sup>9</sup>

The ability of **1** to polymerise isoprene was studied in the presence of  $\text{Al}(i\text{-Bu})_3$ , as described for typical polymerisation experiments involving a cationic lanthanide precursor.<sup>16</sup> At 20 °C and in the presence of 10 equivalents of  $\text{Al}(i\text{-Bu})_3$ , the monomer conversion was nearly complete (82 % recovered

polymer), in only 30 min (entry 1; Table 1). The activity was high and the stereospecificity observed was fairly good (84 % *-cis*) but the GPC curve, albeit monomodal, was found somewhat broad, characteristic of a rather low initiation process (PDI 2.31). This was attributed to the poor solubility of crystalline **1** in toluene. These observations prompted us to study the polymerisation of isoprene with a catalytic system in

**15 Table 1** Polymerisation of isoprene with  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}(i\text{-Bu})_3$

Entry <sup>a</sup>	Activator (equiv.)	$\text{Al}(i\text{-Bu})_3$ (equiv.)	$[\text{I}]/[\text{Nd}]$	T (°C)	Time (h)	Yield (%)	average activity (kg/mol.h)	% <i>cis</i> <sup>h</sup>	% <i>trans</i> ; % 3,4 <sup>h</sup>	$M_{n,\text{exp}}$	$M_w/M_n$ (PDI)	Eff. (%) <sup>i</sup>
1 <sup>b</sup>	-	10	3125	20	0.5	82	350	84	10; 6	85000	2.31	51
2 <sup>c</sup>	1	7	3000	20	0.5	46	184	86	10; 4	121200	1.63	76
3 <sup>d</sup>	1	10	3000	20	0.75	25	68	92	3.4; 4.6	55700	1.34	61
4	1	10	1000	20	24	66	1.9	81	15; 4	47100	1.71	100
5	1	3.5	1000	20	1.5	84	38	78	18; 4	109400	1.91	52
6 <sup>e</sup>	1.5	10	1000	20	0.5	90	122	80	17; 3	62900	1.70	100
7 <sup>f</sup>	2	20	1500	20	48	50	1	90	6; 4	56400	1.74	91
8 <sup>g</sup>	1	8	3000	20	3.5	30	17.5	76	20; 4	99500	1.62	60
9	1	10	1000	50	24	78	3.25	76	19; 5	37000	1.87	143
10	1	50	1000	50	24	29	8	66	29; 5	10200	1.65	196
11	1	50	1000	75	24	87	2.5	46	51; 4	9500	1.90	630
12	1	10	1000	90	4	75	12.7	38	58; 4	36700	2.21	140

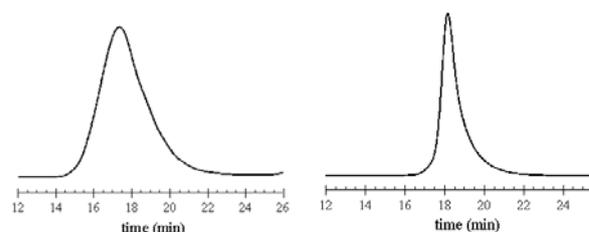
<sup>a</sup> 10 μmol Nd/1 mL toluene. <sup>b</sup> Pre-catalyst **1** (9.6 μmol), 0.05 mL toluene. <sup>c</sup> (100 μL + 0.4 mL) toluene. <sup>d</sup> (50 μL + 0.4 mL) toluene. <sup>e</sup> 5 μmol Nd / 0.025 mL toluene. <sup>f</sup> 0.1 mL toluene. <sup>g</sup> solvent = heptane 0.5 mL. <sup>h</sup> Determined by <sup>1</sup>H and <sup>13</sup>C NMR. <sup>i</sup> eff = 100 ×  $M_{n,\text{th}}/M_{n,\text{exp}}$ ,  $M_{n,\text{th}} = ([\text{I}]/[\text{Nd}]) \times \text{yield} \% \times 68$ ; efficiency factor calculated for one growing chain per metal.

As expected, a better control of macromolecular data is observed at 20 °C (monomodal curves, PDI 1.34-1.91). In the presence of 1 equiv.  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  per Nd, the results are comparable to those obtained from isolated **1**. The activity is sensibly lower (184 vs. 350 kg/mol.h) but this result is balanced by a narrower PDI value, indicating that the process is more controlled (entry 2). The isoprene concentration has a strong effect on the course of the polymerisation: when the reaction between the pre-catalyst and the ionic activator is carried out in a minimum of toluene (25 to 100 μl) in a preliminary stage (during ca. 10 min), and for high  $[\text{I}]/[\text{Nd}]$  ratios (3000), the *cis*-percentage can reach the value of 92 % while the activity remains high, whatever the quantity of toluene added subsequently (entry 3). In diluted conditions (entry 4: monomer/catalyst ratio = 1000, 1 mL toluene) the activity decreases to less than 2 kg/mol.h. Besides, the amount of co-catalyst seems to be directly related to the selectivity: in the presence of 3.5 equiv.  $\text{Al}(i\text{-Bu})_3$  the *cis*-rate decreases below 80 % (entry 5). It is however possible to increase the *cis*-selectivity up to 90 % for low monomer/catalyst ratios, by varying the quantity of borate activator (entries 6, 7); the highest activity (ca. 120 kg PI/mol Nd/h) is observed using 1.5 borate per Nd (entry 6). In heptane (entry 8): the system is less active and the *cis*-selectivity is lowered, in sharp contrast to what is generally observed in hydrocarbon solvents.<sup>17</sup> Raising the temperature allows to improve the monomer conversion, but to the detriment of the selectivity and the control of macromolecular data (entries 9-12). Nevertheless, it is noteworthy that in such conditions, and in the presence of large excesses of co-catalyst, low molecular weight polyisoprene can be obtained, involving probably some transfer between Nd and Al (see further, transfer reactions section).

In all cases, the SEC traces show a monomodal character,

which the cationic  $\text{Nd}(\text{BH}_4)_2^+$ , formed *in situ*, would not be isolated. Preliminary polymerisations experiments were then conducted with the ternary catalytic system  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}(i\text{-Bu})_3$ , under the same conditions as for **1** (the mixture was allowed to react at a given temperature for a given time. Representative results are reported Table 1, entries 2-12).

typical of a single-site catalysis. The PDI values remain in a range typical of a rather controlled process (< 1.9), at temperatures not exceeding 75 °C. Figure 2 shows two typical SEC traces, and one can observe the much narrower molecular weight distribution provided by the ternary catalytic system (right, entry 3) vs. isolated **1** (left, entry 1).



**60 Fig. 2** SEC curve of entries 1 (cationic precatalyst **1**, left) and 3 (ternary catalytic system, right) showing the monomodal character.

As reported in general in the literature for Nd-based catalysts, a high degree of control of macromolecular data (including narrow PDI values), together with full initiation efficiency of the lanthanide metal (*i.e.* calculated for one growing chain per metal; eff. = 100 ×  $M_{n,\text{th}}/M_{n,\text{exp}}$ ,  $M_{n,\text{th}} = ([\text{I}]/[\text{Nd}]) \times \text{yield} \%$ ), is still hard to obtain, particularly in the specific case of isoprene. In our case, the efficiency of this new catalytic system, considering the protonation of one  $\text{BH}_4$  group per metal, is much higher than previously described: from ca. 52 % (entry 4), to 100 % at 20 °C (entry 3).<sup>‡</sup>

The mastering of transfer reactions in polymerisation catalysis, so called “catalysed chain growth polymerisation”, is of interest because it allows the preparation of functionalised polymers and/or oligomers.<sup>18</sup> As far as we know, the very few reports concerning this topic and involving lanthanide catalysts all refer specifically to butadiene.<sup>1,19</sup> In the presence of large excesses of Al co-

catalyst at 50 °C (Table 2), we observed that  $M_n$  values strongly decrease when the  $\text{Al}(i\text{-Bu})_3$  amount varies from 30 to 100 equivalents. We assume that a non negligible part of the Al co-catalyst acts as a transfer agent, allowing a number of growing chains per metal up to ca. 10 (eff % = 970, entry 15). Interestingly, the PDI values remain quite narrow (1.5–1.7), indicating a rapid exchange between Al and Nd, but to the detriment of both the selectivity, as already reported with butadiene,<sup>20</sup> and the activity (entry 10, Al/Nd = 50, vs. entry 9, Al/Nd = 10, Table 1). Nevertheless, increasing the temperature to 75 °C allows to enhance the conversion, as well as the transfer process (eff. = 630 %, entry 11, Table 1).

**Table 2** Effect of the [Al]/[Nd] ratio

entry <sup>a</sup>	Al( <i>i</i> -Bu) <sub>3</sub> (equiv.)	Yield (%)	Time (h)	% <i>cis</i>	$M_{n,\text{exp}}$	$M_w/M_n$ (PDI)	Eff. (%) <sup>c</sup>
13	30	30	2	78	29800	1.68	200
14	40	40	6	75	22300	1.74	360
15	100 <sup>b</sup>	70	20	67	14400	1.55	970

<sup>a</sup> 1 Nd(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>/1 [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/1 mL toluene, [I]/[Nd] = 3000, 50 °C; <sup>b</sup> addition of Al co-catalyst in two stages: Nd(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub> + [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] + 1 mL toluene + 40 equiv. Al + isoprene + 60 equiv. Al. <sup>c</sup> Same as in Table 1.

In conclusion, The new borohydrido ionic [Nd(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>5</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] can be prepared straightforwardly from the simple precursor Nd(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub> and [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Combined with Al(*i*-Bu)<sub>3</sub> this cationic compound polymerises isoprene with a good activity but a more controlled process is obtained when the cation is prepared *in situ* by using the ternary catalytic system Nd(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>/[HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Al(*i*-Bu)<sub>3</sub>. This strongly supports the formation of the a cationic active species during the *in situ* polymerisation process. Depending on the experimental conditions, it is possible to reach up to 92 % of *cis*-selectivity, together with good control of  $M_n$  and PDI, and high initiation efficiency of the catalyst. In the presence of large excesses of Al co-catalyst, transfer to aluminum is evidenced, which opens the possibility of regulation of the molecular weight of the polymer, as well as a convenient route to functionalized polymers, without the necessity to expand the quantity of Nd-based initiator. This study clearly confirms the high potential of borohydrido Ln-based catalysts toward polymerisation. Further studies are in due course aimed at the synthesis and application of similar cyclopentadienyl-supported and related complexes via the substitution of the BH<sub>4</sub> moiety.

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## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Experimental details of the synthesis and analytical data of complex **1**, and of polymerisations reactions. CCDC reference number 660039. For crystallographic data in CIF see DOI: 10.1039/b000000x/.

<sup>‡</sup> Complex **1** (C<sub>44</sub>H<sub>48</sub>B<sub>3</sub>F<sub>20</sub>O<sub>5</sub>Nd, M = 1213.5 gmol<sup>-1</sup>) crystallizes in the monoclinic space group P21/c with a = 8.6142(2), b = 34.3484(8), c = 16.4956(4) Å, β = 96.9390(10) °, V = 4845.0(2) Å<sup>3</sup>, T = 100(2) K, ρ = 1.663 gcm<sup>-3</sup> for Z = 4. 59711 total reflections, 10233 independent reflections, R<sub>int</sub> = 0.0362. final R values = 4.37 %, w<sub>R</sub> = 4.99 % [I > 3.0σ(I)]; R = 6.28 %, w<sub>R</sub> = 5.32 % for (all reflections). CCDC 660039.

<sup>¶</sup> Efficiency of the metal is here expressed as commonly reported in the literature for Nd-based catalysts, even in the presence of Al co-catalyst excess,<sup>[1,18,20]</sup> i.e. by reference to Nd metal, despite the fact that Al may contribute via Al-Nd transfer (see next paragraph).

1 L. Friebe, O. Nuyken, W. Obrecht, *Adv. Polym. Sci.*, 2006, **204**, 1 and refs therein.

2 P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, *Chem. Rev.* 2006, **106**, 2404; A. Fischbach and R. Anwander, *Adv. Polym. Sci.*, 2006, **204**, 155 and refs therein; M. Shiotsuki, Y. Taniguchi, W. Dong, and T. Masuda, *Polym. Bull.* 2005, **54**, 173.

3 Selected references: L. Lukesova, B. D. Ward, S. Bellemin-Laponnaz, H. Wadeppohl and L. H. Gade, *Dalton Trans.*, 2007, 920; Z. Hou, Y. Luo and X. Li, *J. Organomet. Chem.*, 2006, **691**, 3114; S. Bambilra, D. van Leusen, C. G. J. Tazelaar, A. Meetsma and B. Hessen, *Organometallics*, 2007, **26**, 4, 1014.

4 R. Taube, S. Maiwald and J. Sieler, *J. Organomet. Chem.*, 2001, **621**, 327.

5 X. Li, J. Baldamus, M. Nishiura, O. Tardif and Z. Hou, *Angew. Chem. Int. Ed.*, 2006, **45**, 8184.

6 V. Monteil, R. Spitz and C. Boisson, *Polym. Int.*, 2004, **53**, 576.

7 W. Gao and D. Cui, *J. Am. Chem. Soc.*, 2008, **130**, 4984.

8 S. A. Cotton, *Coord. Chem. Rev.*, 1997, **160**, 93; W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233/234**, 131; B. Liu, D. Cui, J. Ma, X. Chen and X. Jing, *Chem. Eur. J.*, 2007, **13**, 834.

9 Selected refs: S. M. Cendrowski-Guillaume, M. Nierlich, M. Lance, M. Ephritikhine, *Organometallics* **1998**, **17**, 786; D. Barbier-Baudry, O. Blacque, A. Hafid, A. Nyassi, H. Sitzmann and M. Visseaux, *Eur. J. Inorg. Chem.*, 2000, 2333; C Qian, W. Nie and J. Sun, *J. Organomet. Chem.*, 2001, **626**, 17; M. Visseaux, P. Zinck, M. Terrier, A. Mortreux and P. Roussel, *J. All. Comp.*, 2008, **451**, 1-2, 352.

10 S.M. Guillaume, M. Schappacher and A. Soum, *Macromolecules*, 2003, **36**, 54; F. Bonnet, A. C. Hillier, A. Collins, S. R. Dubberley and P. Mountford, *Dalton Trans.*, 2005, 421; M. Visseaux, A. S. Madureira Bruno, F. Bouyer and D. Barbier-Baudry, *Appl. Organometal. Chem.*, 2006, **20**, 24; N. Barros, M. Schappacher, P. Dessuge, L. Maron and S. M. Guillaume, *Chem. Eur. J.*, 2008, **14**, 1881.

11 M. Visseaux, T. Chenal, A. Mortreux and P. Roussel, *J. Organomet. Chem.* 2006, **691**, 86; J. Thuilliez, R. Spitz and C. Boisson *Macromol. Chem. Phys.*, 2006, **207**, 19, 1727; P. Zinck, A. Valente, A. Mortreux and M. Visseaux, *Polymer*, 2007, **48**, 4609.

12 M. Terrier, M. Visseaux and A. Mortreux, *J. Pol. Sci. Pol. Chem (A)*, 2007, **45**, 2400.

13 P. J. Dyson, G. Laurency, C. André Ohlin, J. Vallance and T. Welton, *Chem. Commun.*, 2003, 2418.

14 The preparation of cationic **1** was preliminarily mentioned in M. Mainil, M. Visseaux, A. Mortreux, M. Destarac, T. Mathivet FR2906534A1; During the time of submission of this manuscript, Okuda and coll. published the synthesis of [Nd(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>5</sub>][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>], see D. Robert, M. Kondracka and J. Okuda *Dalton Trans.*, 2008, 2667.

15 F. Bonnet, M. Visseaux, A. Hafid, D. Baudry-Barbier, M. M. Kubicki and E. Vigier, *Inorg. Chem. Commun.*, 2007, **10**, 690.

16 B. Wang, D. Cui and K. Lv, *Macromolecules*, 2008, **41**, 1983-1988; S. Arndt, K. Beckerle, P. M. Zeimentz, T. P. Spaniol and J. Okuda, *Angew. Chem. Int. Ed.*, 2005, **44**, 7473.

17 D. J. Wilson, *Polym. Int.*, 1996, **39**, 3, 235.

- 
- 18 N. Ajellal, L. Furlan, C. M. Thomas, O. L. Casagrande Jr and J. F. Carpentier, *Macromol. Rapid Commun.*, 2006, **27**, 338; J. Gromada, L. le Pichon, A. Mortreux, F. Leising and J. F. Carpentier, *J. Organomet. Chem.*, 2003, **683**, 44.
- 5 19 J. F. Pelletier, A. Mortreux, X. Olonde and K. Bujadoux, *Angew. Chem.*, 1996, **35**, 1854; R. Kempe, *Chem. Eur. J.*, 2007, **13**, 2764.
- 20 L. Friebe, J. H. Müller, O. Nuyken, and W. Obrecht, *J. Macromol. Sci Pure Appl. Chem.*, 2006, **43**, 1, 11; S. Kaita, M. Yamanaka, A. C. Horiuchi and Y. Wakatsuki, *Macromolecules*, 2006, **39**, 1359.