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Scandium Aminopyridinates: Synthesis, Structure and Isoprene Polymerization

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Alkane elimination reactions of $[Sc(CH_2SiMe_3)_3(thf)_2]$ or $[Sc(CH_2Ph)_3(thf)_3]$ with aminopyridines (**1a** = (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine, **1b** = [6-(2,4,6-triisopropylphenyl)pyridin-2-yl]-(2,4,6-trimethylphenyl)amine, **1c** = (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amine) led to selective formation of dialkyl complexes of scandium stabilized by one aminopyridinato (Ap) ligand. The reaction of these compounds with anilinium borate leads to the elimination of one of the two alkyl functions and affords organoscandium cations. The amine elimination reaction of $[Sc\{N(SiHMe_2)_2\}_3(thf)]$ with the aminopyridine **1a** yields the corresponding mono(aminopyridinato) complex. Single-crystal X-ray analyses were carried out for $[Ap^*Sc(CH_2Ph)_2(thf)]$ (**3a**), $[Ap^*Sc(CH_2Ph)(thf)_3][B(C_6H_5)_4]$ (**4a**) and $[Ap^*Sc\{N(SiHMe_2)_2\}_2]$ (**6a**) (Ap^*-H = **1a**). The aminopyridinato-stabilized dialkylscandium complexes $[ApScR_2(thf)]$ (R = CH_2SiMe_3, CH_2Ph) are initiators for controlled 3,4-selective isoprene polymerization after activation with perfluorinated tetraphenyl borates. Variation of the polymerization temperature as well as the addition of different alkylaluminium compounds influence the microstructure of the obtained polymer. Bis(dimethylsilyl)amides of scandium polymerize isoprene in the presence of anilinium borate and alkylaluminium compounds with high *cis*-1,4-selectivity.

Introduction

Isoprene polymerization catalyzed by organolanthanoid cations has gained a lot of attention recently after the initial reports published by Okuda and co-worker as well as Hou and co-worker simultaneously.[1] Rare earth metal-alkyl(halide) complexes of the type $[(\mathbf{L})LnR_2(D)]$ (R = CH_2SiMe_3, $AlMe_4$, *o*-$CH_2C_6H_4NMe_2$, μ^3-C_3H_5, Cl, D = thf) where **L** is a cyclopentadienyl[2] or an anionic N-ligand,[3,4] are known to catalyse or initiate isoprene polymerization.[5] Very interesting in terms of stereoselectivity are the precursors $[\{Me_2Si(C_5Me_4)\text{-}(PHCy)\}YCH_2SiMe_3]_2$ (Cy = cyclohexyl)[1b] or $[(PhC(NC_6H_4iPr_2\text{-}2,6)_2)Y(o\text{-}CH_2C_6H_4\text{-}NMe_2)_2]$[4] which show, in the combination with $[Ph_3C][B(C_6F_5)_4]$, very high regio- and stereoselectivities (3,4-selectivity: >99%, mmmm > 99%). Furthermore, the yttrium amidinate complex switches the stereoselectivity drastically from 3,4-isospecific to *cis*-1,4-selective by addition of $AlMe_3$. Recently Zimmermann et al. described half-sandwich complexes of the type $[(C_5Me_5)Ln(AlMe_4)_2]$ (Ln = Y, La, Nd) which, upon activation with fluorinated borates or boranes, are highly active catalysts for the living *trans*-1,4-selective (up to 99.5%) polymerization of isoprene.[2b] Although 3,4-polyisoprene is used as an important component of high-performance rubber, for example in tires,[6] the number of 3,4-selective catalyst systems is smaller in contrast to systems which preferably yield *cis*-1,4-polyisoprene (natural rubber),[2d,3e,4,7,8] most likely since isoprene prefers to coordinate in most of the catalytically active systems in the thermodynamically more stable *cis*-1,4-mode.[3a,9]

Herein we report the synthesis and the structure of dialkyl and bis(dimethylsilylamide) complexes of scandium stabilized by aminopyridinato (Ap) ligands[10,11] and their catalytic properties in the isoprene polymerization in the presence of borates. Furthermore, the influence of the aminopyridinato ligand, the polymerization temperature, the catalyst concentration and various alkylaluminium compounds on the polymerization will be discussed.

Results and Discussion

Metal Complex Synthesis and Structure

Similarly to the synthesis of aminopyridinato-dialkylyttrium complexes $[ApY(CH_2SiMe_3)_2(thf)]$[12] the corresponding scandium complexes were successfully prepared (Scheme 1). Only very recently the first (homoleptic) aminopyridinato-scandium complex was described.[13] The reaction of the aminopyridines **1a**–**c** with one equivalent of $[Sc(CH_2SiMe_3)_3(thf)_2]$ yielded after tetramethylsilane elimination the corresponding scandium compounds **2a**–**c** (Scheme 1, left) which were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The ^1H NMR spectra of the compounds **2a**–**c** exhibit the characteristic splitting pattern of each aminopyridinato ligand as it was observed for the already described analogous yttrium compounds. In contrast to the yttrium derivatives the methylene

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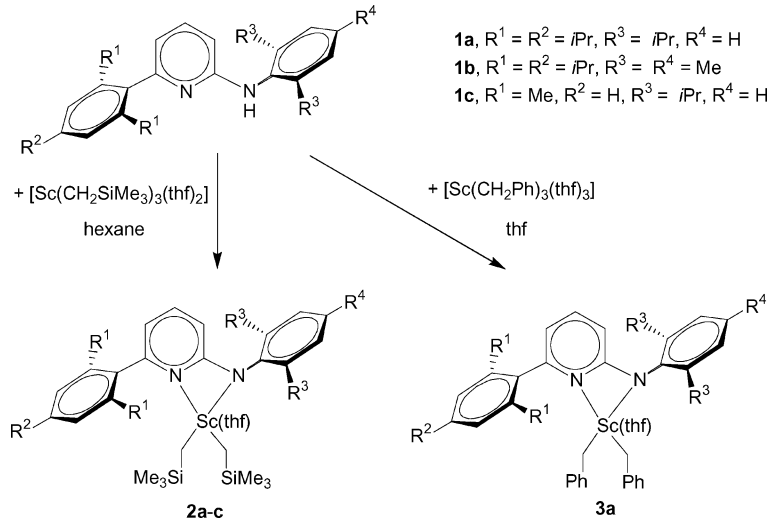


Scheme 1. Synthesis of Ap-stabilized dialkyl compounds **2a**, **2b**, **2c** and **3a**.

groups of the alkyl ligand exhibit an AB-system (doublets at δ = 0.01 and 0.09 ppm for **2a**; –0.01 and 0.07 ppm for **2b** and 0.01 and 0.07 ppm for **2c**) in the ^{1}H NMR spectrum. This effect can be attributed to the smaller coordination sphere of the scandium ion and hindered rotation of the aminopyridinato ligands therewith. The aminopyridine **1a** reacts also with one equivalent of the tribenzyl complex $[Sc(CH_2Ph)_3(thf)_3]$ to afford after toluene elimination the aminopyridinato-stabilized dibenzyl complex **3a**. Suitable single crystals for X-ray structure analysis of this compound were obtained by cooling a saturated pentane solution to 0 °C. The compound **3a** crystallizes in the monoclinic space group *C*2/*c*. The molecular structure is depicted in Figure 1, the crystallographic details are summarized in Table 5. The metal centre has a coordination number of five and is coordinated by one aminopyridinato ligand, one thf ligand and two benzyl ligands which show different coordination modes in the solid state. One of the two benzyl ligands has an η^1-coordination [Sc1–C1–C2 121.88(16)°], while the other ligand exhibits η^2-coordination indicated by the Sc1–C8–C9 angle of 88.50(15)° and a shortened distance of the scandium atom to the *ipso*-carbon atom of this ligand [Sc1–C9 2.657(2) Å].

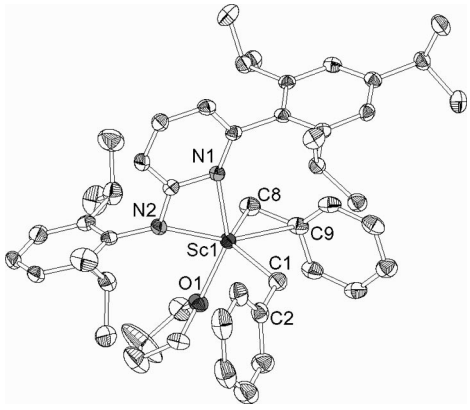
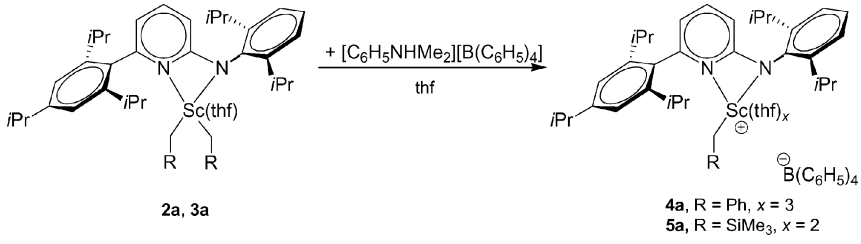


Figure 1. ORTEP diagram of the molecular structure of **3a** in the solid state (ellipsoids set at 50% probability level). H Atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Sc1–N1 2.286(2), Sc1–N2 2.1290(19), Sc1–C1 2.245(3), Sc1–C8 2.256(3), Sc1–C9 2.657(2), N1–Sc1–N2 61.31(7), Sc1–C1–C2 121.88(16), Sc1–C8–C9 88.50(15).

The dialkyl complexes **2a** and **3a** react with one equivalent of anilinium borate to afford after alkane elimination the organoscandium cations **4a** and **5a** respectively which were isolated in the presence of thf (Scheme 2). The composition of the compounds was determined by NMR spectroscopy and elemental analyses. Furthermore, compound **4a** was characterized by an X-ray structure analysis. Suitable single crystals were obtained by slow diffusion of pentane into a thf/toluene (1:1) solution of **4a**. The compound crystallizes in the triclinic space group $P\bar{1}$ as yellow plates. Crystallographic details are summarized in Table 5 and the molecular structure of **4a** is presented in Figure 2.



Scheme 2. Synthesis of organoscandium cations **4a** and **5a**.

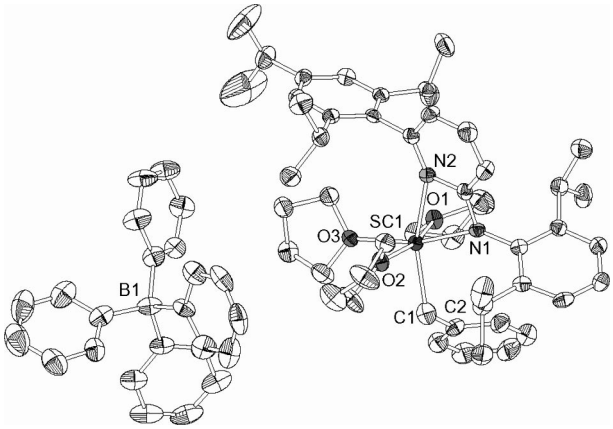
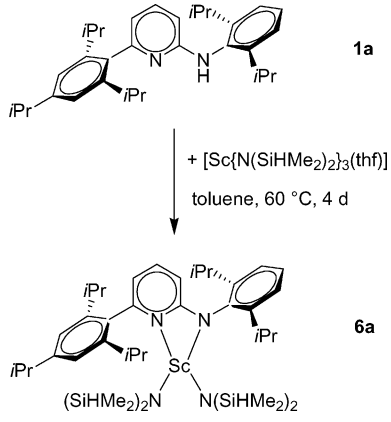


Figure 2. ORTEP diagram of the molecular structure of **4a** in the solid state (ellipsoids set at 50% probability level). H Atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Sc1–C1 2.234(6), Sc1–N1 2.188(4), Sc1–N2 2.358(4), Sc1–O1 2.177(3), Sc1–O2 2.192(3), Sc1–O3 2.217(3), Sc1–C1–C2 121.2(4), O1–Sc1–C1 95.15(17), O2–Sc1–C1 89.51(17), O3–Sc1–C1 95.94(18).

The cation of **4a** shows a distorted octahedral coordination of the scandium atom indicated by O–Sc–C_{benzyl} angles of 89.51(17) and 95.94(18)°. The metal atom is coordinated by three thf, one benzyl [η^1-coordination, Sc1–C1–C2 121.2(4)°] and one aminopyridinato ligand. The thf ligands show a meridonal arrangement and the methylene group of the benzyl ligand is in *trans*-position to the pyridine nitrogen atom of the aminopyridinato ligand.

As we reported recently, the bulky aminopyridines **1a**,**b** react with triamide precursors, namely [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (Ln = Y, La).[14] Similarly the compound [Sc{N(SiHMe$_2$)$_2$}$_3$(thf)] reacts with the aminopyridine **1a** in toluene at 60 °C within four days to afford the diamide **6a** (Scheme 3).



Scheme 3. Synthesis of the aminopyridinato-stabilized diamide **6a**.

Figure 3 depicts the molecular structure of **6a**, crystallographic details are summarized in Table 5. The structure of **6a** demonstrates that the thf ligand present in the starting compound was eliminated due to steric demand of the aminopyridinato ligand. The metal atom displays a distorted tetrahedral geometry and is coordinated by four nitrogen atoms [N1–Sc–N4 116.33(5)°, N3–Sc–N4 107.36(6)°, N2–Sc–N3 109.49(6)°] [two from the aminopyridinato and two from the bis(dimethylsilyl)amido ligand respectively]. Both scandium to nitrogen bond lengths between the {N(SiHMe$_2$)$_2$} groups and the scandium atom of **6a** [2.0573(15) and 2.0409(14) Å] are only marginally shorter than the average of Sc–N bond lengths of 2.069(2) Å in [Sc{N(SiHMe$_2$)$_2$}$_3$(thf)].[15] Both {N(SiHMe$_2$)$_2$} ligands exhibit an asymmetrical coordination to the metal centre which is caused by a Sc···(Si–H) interaction of both bis(dimethylsilyl)amido ligands respectively. As a result, the Sc–N–Si angles within each of amido ligands are different [Sc–N3–Si1 100.93(7)° vs. Sc–N3–Si2 129.36(9)° and Sc–N4–Si3 99.40(7)° vs. Sc–N4–Si4 131.32(8)°]. This bending towards the scandium centre also results in different Sc–Si distances of each {N(SiHMe$_2$)$_2$} ligand [Sc–Si1 2.9003(6) and Sc–Si3 2.8642(6) Å vs. Sc–Si2 3.4117(6) and Sc–Si4 3.4208(6) Å]. The very short Sc–Si3 distance of 2.8642(6) Å is the shortest observed up to now for an agostic Sc–Si interaction and is very close to the known distance of Sc–Si σ-bonds in [(C$_5$H$_5$)$_2$Sc{Si(SiMe$_3$)$_3$}thf][16] with 2.863(2) Å and [(C$_5$Me$_5$)$_2$Sc(SiH$_2$SiPh$_3$)][17] with 2.797(1) Å. Proton NMR spectra of **6a** were recorded in [D$_8$]toluene in the temperature range of 23 to 100 °C (Figure 4). The room temperature ^{1}H NMR spectrum reveals two doublets for the methyl groups of the silylamide group but only one septet for the SiH protons. The same splitting pattern was observed at –80 °C. Above 20 °C, the signals for the SiMe groups begin to broaden and at 100 °C only one doublet is observed.

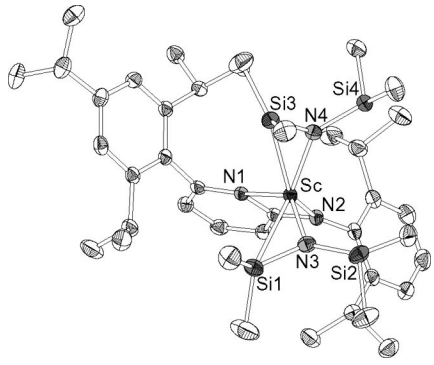


Figure 3. ORTEP diagram of the molecular structure of **6a** in the solid state (ellipsoids set at 50% probability level). H Atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Sc–N1 2.2548(14), Sc–N2 2.1320(14), Sc–N3 2.0573(15), Sc–N4 2.0409(14), Sc–Si1 2.9003(6), Sc–Si2 3.4117(6), Sc–Si3 2.8642(6), Sc–Si4 3.4208(6), Si1–N3–Si2 129.45(9), Sc–N3–Si1 100.93(7), Sc–N3–Si2 129.36(9), Si3–N4–Si4 128.64(9), Sc–N4–Si3 99.40(7), Sc–N4–Si4 131.32(8), N1–Sc–N4 116.33(5), N3–Sc–N4 107.36(6), N2–Sc–N3 109.49(6).

The rate constants for this exchange were determined by NMR simulation using the program DNMR3.[18] From the Eyring equation, the activation parameters for this process were calculated ($\Delta G^{\ddagger}$ = 73.9 ± 0.9 kJ mol^{-1}; $\Delta H^{\ddagger}$ = 49.2 ± 0.3 kJ mol^{-1}; $\Delta S^{\ddagger}$ = 71.9 ± 1.0 J mol^{-1} K^{-1}, T_c = 348 K; Figure 5). The activation energy of $\Delta G^{\ddagger}$ = 73.9 kJ mol^{-1} for this process is similar to that found in

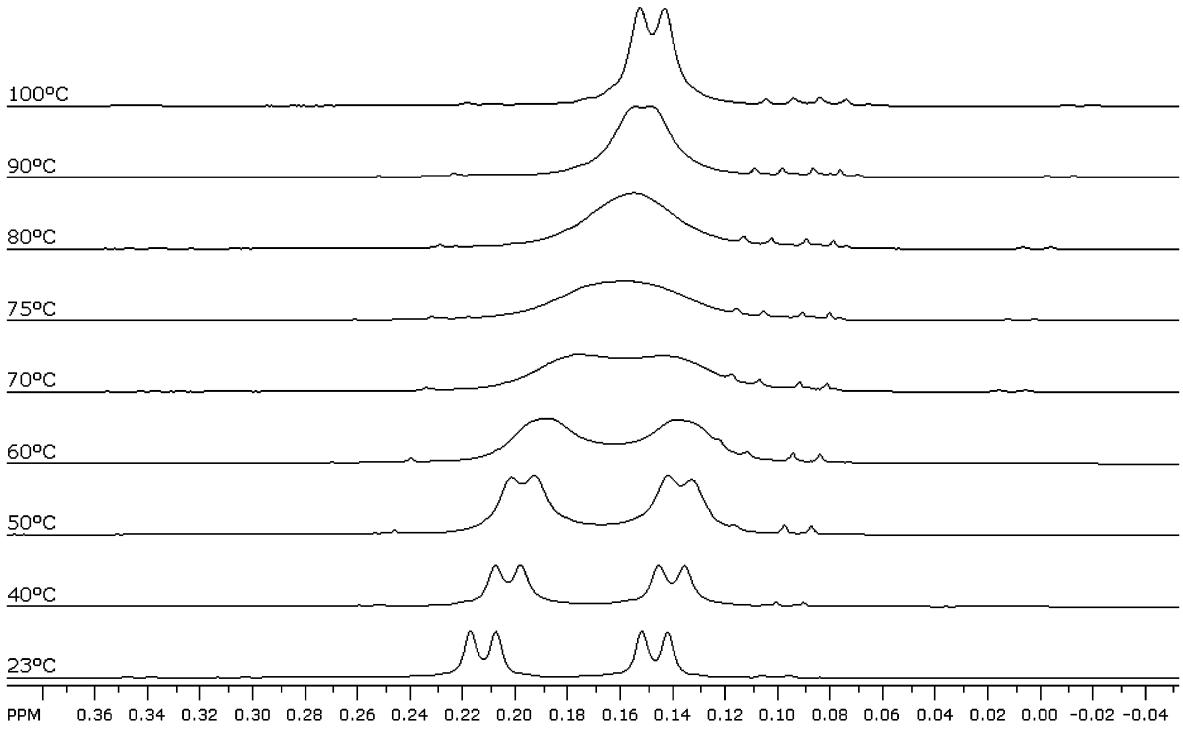


Figure 4. ^{1}H NMR spectra of **6a** in [D_8]toluene at different temperatures.

[(etbmp)Sc{N(SiHMe$_2$)$_2$}(thf)] (etbmp = 1,4-dithiabutanediyl-bis(6-*tert*-butyl-4-methylphenol) with $\Delta G^{\ddagger}$ = 69.79 kJ mol^{-1} and T_c = 330 K).[19]

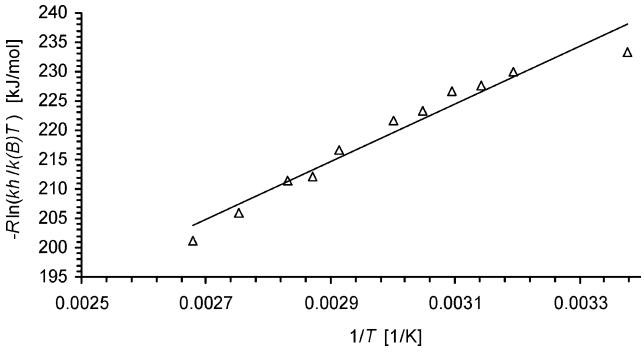


Figure 5. Eyring plot ($-R\ln(kh/k_BT) = -\Delta S^{\ddagger} + \Delta H^{\ddagger}/T$) for the coalescence of the SiMe signals.

Polymerization of Isoprene

The complexes **2**, **3a** and **6a** were tested as precatalysts for the polymerization of isoprene. The microstructure of the obtained polyisoprene was determined by ^{1}H and ^{13}C NMR spectroscopy. The results of the polymerization experiments are summarized in Tables 1, 2, 3, and 4. The bis(trimethylsilylmethyl)scandium compounds **2a**–**c** polymerize isoprene in a 3,4-selective fashion (>93%) after activation with perfluorinated anilinium borate in chlorobenzene or toluene. A narrow molecular weight distribution of 1.26 to 1.33 is observed (Table 1, run 1–3). A marked decrease of the 3,4-polyisoprene content and broadening of the molecular weight distribution is observed when triisobutylaluminium (10 equiv.) was mixed with the polymerization catalyst. (Table 1, run 5–7). Detailed investigations of the influence of different alkylaluminium compounds or TIBAO (tetraisobutylalumoxane) on the microstructure of the obtained polymer were performed (Table 1, run 8–10). Switching from Al*i*Bu$_3$ to the short-chain aluminium compounds AlEt$_3$ and AlMe$_3$ results in a decrease of 3,4-polyisoprene content and increase of *cis*-1,4-polyisoprene content in the direct relation to the size of the alkyl groups at the aluminium metal; the molecular weight distributions are very broad due to a bimodal distribution. A similar influence of the aluminium alkyls on the microstructure of the polymer was also reported by Zhang et al. for an yttrium-amidinate isoprene polymerization catalyst.[4] When the polymerization temperature was increased to 40 °C for the system **2a**/[$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$]/Al*i*Bu$_3$ a decrease of the 3,4-polyisoprene content to 62% together with a broadening of the molecular weight distribution were observed (Table 1, run 11). Decrease of the polymerization temperature (0 °C) for this system leads to an increased 3,4-polyisoprene content going along with an isotactically enrichment (mm ≈ 100%, mmmm ≈ 30% and 35%, Table 1, run 12, 13). At a lower temperature (–14 °C) a relatively narrow molecular weight distribution was observed, indicative of the deactivation of other polymerization-active species or absence of such species at low temperature.

Table 1. Polymerization of isoprene with complexes **2** under various conditions.[a]

Run	Cat.	Alkyl-Al	T [°C]	Yield [%]	$M_n \times 10^{-3}$[b]	M_w/M_n[b]	Microstructure [%][c] 3,4:*cis*-1,4
1[d]	**2a**	–	20	94	135	1.26	93:7
2	**2b**	–	20	100	141	1.27	97:3
3	**2c**	–	20	94	192	1.33	96:4
4[e]	**2a**	–	20	81	58	4.47	83:17
5	**2a**	Al*i*Bu$_3$	20	100[f]	137	3.84	80:20
6	**2b**	Al*i*Bu$_3$	20	98	144	3.08	91:9
7	**2c**	Al*i*Bu$_3$	20	100	144	2.59	89:11
8	**2a**	TIBAO	20	100	104	2.00	96:4
9	**2a**	AlEt$_3$	20	96	32	6.84[g]	81:19
10	**2a**	AlMe$_3$	20	90	25	6.10[g]	33:67
11	**2a**	Al*i*Bu$_3$	40	100	31	6.10[g]	62:38
12	**2a**	Al*i*Bu$_3$	0	100	147	3.54	96[h]:4
13	**2a**	Al*i*Bu$_3$	–14	100	225	1.75	96[i]:4
14	**2a**	–	0	99	80	2.35	96:4
15	–	Al*i*Bu$_3$	20	–	–	–	–

[a] Conditions: 10 mL C_6H_5Cl, dialkyl compounds **2a**–**c**: 10 μmol, anilinium borate: $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ 10 μmol, isoprene: 10 mmol, [Al]/[complex] = 10, reaction time: 20 h. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C spectroscopy, no *trans*-1,4-polyisoprene was found. [d] 10 mL toluene used as solvent. [e] $[Ph_3C][B(C_6F_5)_4]$ was used as the activator, polymerization time 2 h. [f] 98% conversion after 30 min. [g] Bimodal distribution. [h] mm = 100%, mmmm = 30%. [i] mm = 100%, mmmm = 35%.

Table 2. Polymerization of isoprene with complex **2a** with different catalyst/monomer ratios.[a]

Run	Concentration **2a** [μmol]	$M_n \times 10^{-3}$[b]	M_w/M_n[b]	Microstructure [%][c] 3,4:*cis*-1,4
1	5	157	1.96	96:4
2	10	115	1.55	94:6
3	15	75	1.30	94:6

[a] Conditions: 10 mL C_6H_5Cl, anilinium borate: $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$, [**2a**]/[B] = 1, isoprene: 10 mmol, reaction time: 20 h. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C spectroscopy, no *trans*-1,4-polyisoprene was found.

Table 3. Polymerization of isoprene with complex **3a** under various conditions.[a]

Run	Alkyl-Al (equiv.)	T [°C]	Yield [%]	$M_n \times 10^{-3}$[b]	M_w/M_n[b]	Microstructure [%][c] 3,4:*cis*-1,4
1	–	20	–	–	–	–
2[d]	–	20	–	–	–	–
3[e]	–	20	97	130	1.68	95[f]:5
4[e]	Al*i*Bu$_3$ (10)	20	100	33	9.48	81:19
5	Al*i*Bu$_3$ (10)	20	98	78	5.32[g]	76:24
6	Al*i*Bu$_3$ (5)	20	99	73	2.85	73:27
7	Al*i*Bu$_3$ (2)	20	100	139	2.10	77:23
8	Al*i*Bu$_3$ (1)	20	100	119	1.76	81:19
9	AlEt$_3$ (10)	20	99	63	3.86[g]	37:63
10	AlMe$_3$ (10)	20	96	67	4.51[g]	10:90
11	Al*i*Bu$_3$ (10)	0	100	153	3.43[g]	>99:0
12	Al*i*Bu$_3$ (10)	–14	100	129	2.40	>99:0

[a] Conditions: 10 mL C_6H_5Cl, **3a** 10 μmol, anilinium borate: $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ 10 μmol, isoprene: 10 mmol, reaction time: 20 h. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C spectroscopy, no *trans*-1,4-polyisoprene were found. [d] $B(C_6F_5)_3$ was used as the activator. [e] $[Ph_3C][B(C_6F_5)_4]$ was used as the activator, 20 mL C_6H_5Cl. [f] mm = 100%, mmmm = 35%. [g] Bimodal distribution.

To investigate the isoprene polymerization catalyzed by **2a** in more detail, the polymerizations were carried out at different monomer to catalyst ratios. The results are summarized in Table 2. A plot of the concentration of **2a** against the average number molecular weight (M_n) affords a linear dependence, indicative of controlled polymerization (Figure 6).

The aminopyridinato-stabilized dibenzyl complex **3a** showed no activity in the polymerization of isoprene in the presence of anilinium borate or tris(pentafluorophenyl)-borane (Table 3, run 1–2). However, if $[Ph_3C][B(C_6F_5)_4]$ is used as an activator a high stereo- and regioselectivity (95% 3,4-isoprene, mm = 100%, mmmm = 35%, Table 3, run 3) and a narrow molecular weight distribution of 1.68 is ob-

Table 4. Polymerization of isoprene with bis(dimethylsilylamide)scandium complexes.[a]

Run	Cat.	Yield [%]	$M_n \times 10^{-3}$[b]	M_w/M_n[b]	Microstructure [%][c] 3,4:*cis*-1,4
1[d]	$[Sc\{N(SiHMe_2)_2\}_3(thf)]$	97	183	2.73	6:94
2[e]	$[Sc\{N(SiHMe_2)_2\}_3(thf)]$	91	64	2.81	7:93
3[d]	**6a**	100	206	2.22	22:78
4[e]	**6a**	100	241	2.32	4:96

[a] Conditions: 10 mL C_6H_5Cl, Cat. 10 μmol, anilinium borate: $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ 10 μmol, isoprene: 10 mmol, reaction time: 20 h. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C spectroscopy, no *trans*-1,4-polyisoprene was found. [d] Al*i*Bu$_3$ (10 equiv.) used for alkylation/activation. [e] $AlMe_3$ (10 equiv.) used for alkylation/activation.

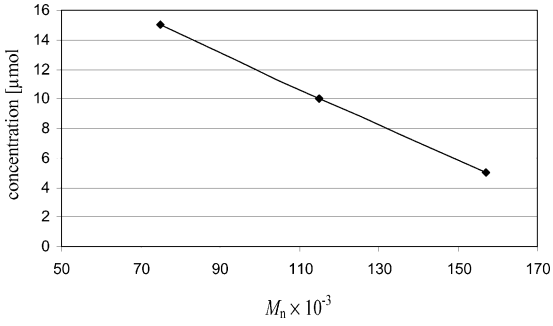


Figure 6. Plot of concentration of **2a** vs. average number molecular weight (M_n) of the obtained polyisoprene.

served for the polymer. Isotactically enriched 3,4-polymerization of isoprene has been rarely described.[1b,4,8g] Addition of alkylaluminium compounds (Table 3, run 4–13) to the system **3a**/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ also leads to a polymerization active system with the same trend as it was observed for **2** as a precatalysts (the use of $[Ph_3C][B(C_6F_5)_4]$ as an activator leads to a similar selectivity like it was observed for the system **3a**/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$/$AlR_3$, but it highly increases the molecular weight distribution, Table 3, run 4). The influence on the *cis*-1,4-selectivity in the presence of $AlMe_3$ is even more pronounced (67% *cis*-1,4-polyisoprene with **2a** vs. 90% with **3a**). If less than 10 equiv. of Al*i*Bu$_3$ were used a significantly narrower molecular weight distribution was observed. The presence of bimodal distributions for the system **3a**/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]/AlR_3$ (R = Me, Et, *i*Bu) suggests also the presence of several polymerization-active species; because of its close relation to the amidinato-yttrium system used by Zhang et al.[4] (addition of $AlMe_3$ switches the regio- and stereoselectivity), where a heterotrinuclear Y/Al complex is formed, it is suggested that a similar species might be one of these active species in our system (Table 3, run 4, 9–11). The thf-stabilized organoscandium cation **4a** does not polymerize isoprene, even not in the presence of 10 equiv. of Al*i*Bu$_3$.

We cannot completely rule out the formation of aminopyridinato-aluminium complexes under the polymerization conditions, but aminopyridinato ligand transfer from the lanthanide to the aluminium atom is usually observed in significant rates for neutral rare earth complexes and not for cations.[12,14]

The diamide **6a** is also an effective precatalyst for the polymerization of isoprene. After alkylation with 10 equiv. of alkylaluminium compounds ($AlMe_3$ or Al*i*Bu$_3$) the compound **6a** yields *cis*-1,4-enriched polyisoprene in the presence of $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ (Table 4, run 3, 4). Aminopyridinato-stabilized yttrium- or lanthanum diamides react with alkylaluminium compounds by transfer of the aminopyridinato ligand from the rare earth metal to the aluminium atom.[14] ^1H NMR spectroscopic investigations of the reaction of **6a** with an excess of trimethylaluminium (6 equiv.) reveal that the diamide **6a** react immediately with the alkylaluminium compound. The proton NMR spectrum showed the formation of a new aminopyridinato ligand containing species and one equivalent of $[Me_2Al\{\mu\text{-}N(SiHMe_2)_2\}]_2$. Furthermore, two equivalents of unreacted $AlMe_3$ were detected. This led to the conclusion that a bis(aluminate)scandium species of the type $[ApSc(AlMe_4)_2]$ had been formed. A similar formation of a bis(aluminate) complex was described by Anwander et al. in the reaction of $[Cp^*Ln\{N(SiHMe_2)_2\}_2]$ (Cp^* = pentamethylcyclopentadienyl, Ln = Y, Lu) with $AlMe_3$.[20] Unfortunately, we did not succeed to separate these species from the byproduct $[Me_2Al\{\mu\text{-}N(SiHMe_2)_2\}]_2$ in order to prove clearly the existence of the aminopyridinato-bis(aluminate) complex. The NMR tube reaction of **6a** with trimethylaluminium also displayed the formation of $[ApAlMe_2]$ by ligand transfer[11g,14] (11% after 3.5 h, 40% after 10 d).

Further investigations revealed that the triamide $[Sc\{N(SiHMe_2)_2\}_3(thf)]$ showed similar *cis*-1,4-selectivity under the same conditions for the polymerization of polyisoprene (Table 4, runs 1, 2). A similar system ($[Nd\{N(SiMe_3)_2\}_3]$/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$/Al*i*Bu$_3$) also showed 1,4-*cis*-selectivity for the polymerization of butadiene.[21]

Conclusions

Mono(aminopyridinato)scandium complexes of the type $[ApScR_2(thf)_x]$ (R = CH_2SiMe_3, CH_2Ph, x = 1; R = $N(SiHMe_2)_2$, x = 0) were synthesized and characterized. The dialkyl complexes are active and selective catalysts for the controlled 3,4-selective polymerization of isoprene after activation by borates. Addition of alkylaluminium compounds to the catalyst system leads to drastical changes in the microstructure of the polymer which are depending from the steric demand of the alkyl ligand of the aluminium

and the polymerization temperature. The stereo- and regioselectivity can be improved by polymerization at low temperatures. The highest stereo- and regioselectivity was observed for the catalyst/activator system **3a**/[Ph_3C][$B(C_6F_5)_4$] (3,4-content 95%, mm = 100%, mmmm = 35%, M_w/M_n = 1.68), whereas the system **2a**/[$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$] shows the narrowest molecular weight distribution (3,4-content 93%, M_w/M_n = 1.26). The ternary systems **6a**/AlR_3/[$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$] and [Sc{$N(SiHMe_2)_2$}$_3$(thf)]/AlR_3/[$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$] (R = Me, *i*Bu) polymerize isoprene *cis*-1,4-selective.

Experimental Section

General Procedures Synthesis and Structure: All reactions and manipulations involving air-sensitive compounds were performed under dry and oxygen free argon by using standard Schlenk and glovebox techniques. Non-halogenated solvents were dried with sodium/benzophenone ketyl and halogenated solvents with CaH_2. Deuterated solvents were obtained from Cambridge Isotope Laboratories, degassed, dried with molecular sieves and distilled prior to use. Starting materials **1a**–**c**,[12,22] tetraisobutylaluminoxane ([$iBu_2Al]_2O$, TIBAO),[23] [$Sc(CH_2SiMe_3)_3(thf)_2$],[24] [$Sc(CH_2Ph)_3(thf)_3$],[25] [Sc{$N(SiHMe_2)_2$}$_3$(thf)],[15] [$C_6H_5NH(CH_3)_2$][$B(C_6H_5)_4$][26] were synthesized according to literature methods. All other chemicals were purchased from commercial sources in purities >97% and used without further purification, if not otherwise stated. NMR spectra were obtained with either a Varian INOVA 300 or a Varian INOVA 400 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were carried out with a Vario elementar EL III apparatus. The molecular weights (M_w/M_n) of the polymers were determined by gel-permeation chromatography (GPC) on an Agilent 1200 series (column: PLgel Mixed-C) at 30 °C using thf as eluent and a flow rate of 1 mL/min against polystyrene standards. X-ray crystal structure analyses were performed with a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[27] SHELXL-97[28] and WinGX.[29] Crystallographic details are summarized in Table 5. CCDC-734318 (for **6a**), -734319 (for **3a**), -734320 (for **4a**) contain 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.

Synthesis of the Complexes

Synthesis of 2a: To a mixture of [$Sc(CH_2SiMe_3)_3(thf)_2$] (451 mg, 1.00 mmol) and **1a** (457 mg, 1.00 mmol) was added hexane (20 mL) at room temperature. The reaction mixture was stirred for 1 h and filtered. Removal of all volatiles under vacuum yielded 610 mg (80%) of **2a** as a yellow crystalline material. $C_{44}H_{67}N_2OScSi_2$ (747.2): calcd. C 70.73, H 9.85, N 3.75; found C 70.57, H 10.12, N 3.48. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.01 (d, ^2J(H,H) = 11 Hz, 2 H, $CH_AH_BSiMe_3$), 0.09 (d, ^2J(H,H) = 11 Hz, 2 H, $CH_AH_BSiMe_3$), 0.14 (s, 18 H, $CH_2Si(Me_3)$), 1.08 (br., 4 H, β-CH_2, THF), 1.16 (d, ^3J(H,H) = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.20 (d, ^3J(H,H) = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.23 (d, ^3J(H,H) = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.36 (d, ^3J(H,H) = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.61 (d, ^3J(H,H) = 6.8 Hz, 6 H, $CH(CH_3)_2$), 2.93 (sept, ^3J(H,H) = 6.8 Hz, 1 H, 15-H), 3.16 (sept, ^3J(H,H) = 6.8 Hz, 2 H, 13,14/22,23-H), 3.44 (sept, ^3J(H,H) = 6.8 Hz, 2 H, 13,14/22,23-H), 3.81 (br., 4 H, α-CH_2, THF), 5.63 (d, ^3J(H,H) = 8.5 Hz, 1 H, 3-H), 6.16 (d, ^3J(H,H) = 7.1 Hz, 1 H, 5-H), 6.74 (dd, ^3J(H,H) = 8.5, ^3J(H,H) = 7.1 Hz, 1 H, 4-H), 7.16–7.30 (m, 5 H, 9,11,18,19,20-H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.7, 23.3, 24.1, 24.5, 24.7, 25.3, 27.0, 28.6, 31.0, 35.1, 45.3, 71.5, 106.4, 112.3, 121.2, 124.3, 125.2,

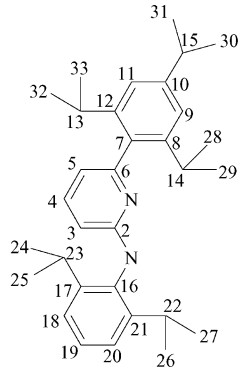
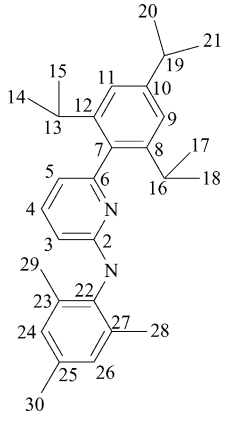


Table 5. Details of the X-ray crystal structure analyses.

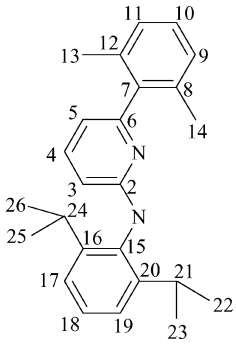
Compound	**3a**	**4a**	**6a**
Formula	$C_{50}H_{65}N_2OSc\times C_5H_{12}$	$C_{75}H_{94}BN_2O_3Sc$	$C_{40}H_{71}N_4Si_4Sc$
Crystal system	monoclinic	triclinic	monoclinic
Space group	*C*2/*c*	$P\bar{1}$	$P2_1/n$
a [Å]	36.4750(12)	13.6470(11)	11.6110(5)
b [Å]	12.9730(6)	15.2080(13)	18.8400(8)
c [Å]	23.8620(9)	19.1700(15)	21.6160(9)
α [°]	90	101.638(6)	90
β [°]	118.169(4)	98.954(6)	103.936(3)
γ [°]	90	113.099(6)	90
Z	4	2	4
μ [mm^{-1}]	0.186	0.152	0.295
Cell volume [Å^3]	9953.9(7)	3460.5(5)	4589.3(3)
Crystal size [mm^3]	0.55×0.29×0.21	0.35×0.35×0.11	0.24×0.13×0.12
T [K]	133(2)	133(2)	133(2)
θ range [°]	1.79–26.05	1.52–24.00	1.45–26.19
Reflections unique	9361	10851	8654
Reflections obsd. [$I>2\sigma(I)$]	5866	5776	7552
Parameters	532	742	458
wR_2 (all data)	0.123	0.206	0.109
R value [$I>2\sigma(I)$]	0.052	0.088	0.040

135.8, 139.6, 144.3, 144.4, 146.7, 149.6, 156.0, 170.0 ppm. ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ = –4.9 ppm.

Synthesis of 2b: The compounds [Sc(CH_2SiMe_3)$_3$(thf)$_2$] (451 mg, 1.00 mmol) and **1b** (415 mg, 1.00 mmol) were dissolved in hexane (20 mL). The resulting mixture was stirred for 1 h and filtered. The solvent was removed in vacuo to yield **2b** as a yellow crystalline compound (420 mg, 60%). $C_{41}H_{67}N_2OScSi_2$ (705.1): calcd. C 69.84, H 9.58, N 3.97; found C 69.44, H 9.56, N 3.92. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = –0.01 (d, ^2J(H,H) = 11 Hz, 2 H, CH_AH$_B$SiMe$_3$), 0.07 (d, ^2J(H,H) = 11 Hz, 2 H, CH$_A$$H_B$SiMe$_3$), 0.16 (s, 18 H, CH$_2SiMe_3$), 1.03 (br., 4 H, β-C$H_2$, THF), 1.19 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.35 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.59 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 2.18 (s, 6 H, 28,29-H), 2.21 (s, 3 H, 30-H), 2.92 (sept, ^3J(H,H) = 6.8 Hz, 1 H, 19-H), 3.15 (sept, ^3J(H,H) = 6.8 Hz, 2 H, 13,16-H), 3.74 (br., 4 H, α-CH_2, THF), 5.64 (d, ^3J(H,H) = 8.5 Hz, 1 H, 3-H), 6.20 (d, ^3J(H,H) = 7.1 Hz, 1 H, 5-H), 6.84 (m, 3 H, 4-H, 9,11/24,26-H), 7.29 (s. 2 H, 9,11/24,26-H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.9, 19.0, 21.0, 23.3, 24.5, 24.6, 27.1, 31.0, 35.1, 45.3, 71.2, 104.2, 112.0, 121.1, 129.5, 133.0, 133.3, 135.8, 140.0, 143.7, 146.7, 149.6, 156.1, 167.9 ppm. ^{29}Si NMR (79 MHz, C_6D_6, 298 K): δ = –4.8 ppm.



Synthesis of 2c: [Sc(CH_2SiMe_3)$_3$(thf)$_2$] (270 mg, 0.60 mmol) and **1c** (215 mg, 0.60 mg) were dissolved in hexane (20 mL). The mixture was stirred for 1 h and filtered. All volatiles were removed under reduced pressure yielding **2c** (196 mg, 51%) as a yellow crystalline material. $C_{37}H_{55}N_2OScSi_2$ (649.0): calcd. C 68.47, H 9.16, N 4.32; found C 68.30, H 9.00, N 4.40. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.01 (d, ^2J(H,H) = 11 Hz, 2 H, CH_AH$_B$SiMe$_3$), 0.07 (d, ^2J(H,H) = 11 Hz, 2 H, CH$_A$$H_B$SiMe$_3$), 0.17 (s, 18 H, CH$_2SiMe_3$), 1.09 (br., 4 H, β-C$H_2$, THF), 1.16 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH(CH_3)$_2$), 1.21 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH(CH_3)$_2$), 2.40 (s, 6 H, 13,14-H), 3.42 (sept, ^3J(H,H) = 6.9 Hz, 2 H, 21,24-H), 3.82 (br., 4 H, α-CH_2,



THF), 5.58 (d, ^3J(H,H) = 8.6 Hz, 1 H, 3-H), 5.86 (d, ^3J(H,H) = 7.1 Hz, 1 H, 5-H), 6.80 (dd, ^3J(H,H) = 8.6, ^3J(H,H) = 7.1 Hz, 1 H, 4-H), 7.03–7.20 (m, 6 H, 9,10,11,17,18,19-H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.8, 20.9, 24.1, 24.7, 25.2, 28.4, 44.5, 71.5, 105.6, 109.2, 124.2, 125.3, 127.8, 128.7, 135.9, 139.9, 140.8, 143.9, 144.3, 156.0, 169.5 ppm. ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ = –5.0 ppm.

Synthesis of 3a: [Sc(CH_2Ph)$_3$(thf)$_3$] (428 mg, 0.80 mmol) and **1a** (365 mg, 0.80 mmol) were dissolved in thf (20 mL) and stirred at room temperature for about 1 h. All volatiles were removed under reduced pressure and the residue was extracted with hexane (40 mL). Removal of the solvent affords **3a** as a yellow spectroscopically pure compound (364 mg, 60%). $C_{50}H_{65}N_2OSc$ (755.0): calcd. C 79.54, H 8.68, N 3.71; found C 79.07, H 9.06, N 3.75. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.79 (br., 4 H, β-CH_2, THF), 1.13 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.19 (d, ^3J(H,H) = 6.5 Hz, 12 H, CH(CH_3)$_2$), 1.32 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.52 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH(CH_3)$_2$), 2.02 (dd, ^3J(H,H) = 8.8 Hz, 4 H, CH_2Ph), 2.90 (sept, ^3J(H,H) = 6.8 Hz, 1 H, 15-H), 3.23 (sept, ^3J(H,H) = 6.7 Hz, 2 H, 13,14/22,23-H), 3.31 (br., 4 H, α-CH_2, THF), 3.39 (sept, ^3J(H,H) = 6.8 Hz, 2 H, 13,14/22,23-H), 5.74 (d, ^3J(H,H) = 8.5 Hz, 1 H, 3-H), 6.28 (d, ^3J(H,H) = 7.1 Hz, 1 H, 5-H), 6.58 (d, ^3J(H,H) = 7.5 Hz, 4 H, *o*-H), 6.76 (t, ^3J(H,H) = 7.1 Hz, 2 H, *p*-H), 6.88 (t, ^3J(H,H) = 7.8 Hz, 1 H, 4-H), 7.05 (t, ^3J(H,H) = 7.4 Hz, *m*-H), 7.16 (m, 3 H, 18,19,20-H), 7.33 (s, 2 H, 9,11-H). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 22.6, 24.0, 24.4, 24.7, 24.9, 27.2, 28.6, 31.3, 34.0, 60.1, 71.5, 105.8, 112.3, 119.1, 121.2, 124.2, 124.6, 125.5, 129.0, 135.5, 139.9, 143.5, 144.4, 147.2, 150.1, 150.2, 155.7, 169.3 ppm.

Synthesis of 4a: To a mixture of **3a** (76 mg, 0.10 mmol) and [$C_6H_5NH(CH_3)_2$][B(C_6H_5)$_4$] (44 mg, 0.10 mmol) were added thf (1.0 mL) and toluene (1.0 mL). The reaction mixture was shaken for 5 min to obtain a clear solution. Slowly diffusion of pentane into this solution over a period of 3 d affords **4a**·(OC_4H_8) as yellow crystalline plates which where decanted and washed twice with hexane (2 × 10 mL); yield 54 mg (40%). [$C_{51}H_{74}N_2O_3Sc$][$C_{24}H_{20}B$](OC_4H_8) (1199.4): calcd. C 79.11, H 8.57, N 2.34; found C 79.10, H 8.39, N 2.50. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ = 1.12–1.16 (m, 12 H, CH(CH_3)$_2$), 1.22 (br., 12 H, β-CH_2, THF), 1.31–1.35 (m, 12 H, CH(CH_3)$_2$), 1.40 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH(CH_3)$_2$), 2.11 (br., 2 H, CH_2Ph), 2.85 (sept, ^3J(H,H) = 6.7 Hz, 2 H, 13,14/22,23-H), 3.02 (sept, ^3J(H,H) = 6.9 Hz, 1 H, 15-H), 3.24 (br., 2 H, 13,14/22,23-H), 3.47 (br., 12 H, α-CH_2, THF), 5.85 (d, ^3J(H,H) = 8.7 Hz, 1 H, 3-H), 6.37 (d, ^3J(H,H) = 7.1 Hz, 1 H, 5-H), 6.53 (d, ^3J(H,H) = 7.6 Hz, 2 H, *o*-Benzyl), 6.86 (t, ^3J(H,H) = 7.3 Hz, 1 H, *p*-Benzyl), 7.07–7.37 (m, 20 H, *m*-Benzyl, 4,9,11,18,19,20-H, BC_6H_5), 7.83 (br., 8 H, *o*-BC_6H_5) ppm. ^{13}C NMR (100 MHz, C_6D_5Br, 298 K): δ = 22.9, 24.1, 24.6, 25.7, 26.3, 27.8, 30.5, 34.5, 40.3, 67.4, 68.1, 108.1, 112.7, 113.5, 116.7, 121.2, 125.0, 125.0, 129.1, 134.3, 135.3, 137.2, 137.8, 139.8, 142.2, 143.6, 146.6, 147.3, 150.8, 154.2, 164.5 (q, ^1J(C,B) = 49.3 Hz, BC_6H_5), 169.6 ppm.

Synthesis of 5a: The compounds **2a** (75 mg, 0.10 mmol) and [$C_6H_5NH(CH_3)_2$][B(C_6H_5)$_4$] (44 mg, 0.10 mmol) were dissolved in thf (5 mL). The mixture was stirred for 20 min. After removal of all volatiles the mixture was washed twice with hexane (2 × 10 mL) and the remaining yellow solid was dried in vacuo to yield **5a** as a yellow powder (74 mg, 70%). [$C_{44}H_{70}N_2O_2ScSi$][$C_{24}H_{20}B$] (1051.3): calcd. C 77.69, H 8.63, N 2.66; found C 78.05, H 8.95, N 2.31. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.02 (s, 9 H, CH$_2$SiMe_3), 0.36 (br., 2 H, CH_2SiMe$_3$), 1.00–1.22 (m, 38 H, β-CH_2, THF, CH(CH_3)$_2$), 2.66 (br., 2 H, 13,14/22,23-H), 2.79 (sept, ^3J(H,H) = 6.9 Hz, 1 H, 15-H), 3.00 (br., 2 H, 13,14/22,23-H), 3.30 (br., 8 H,

α-CH_2, THF), 5.59 (d, ^3J(H,H) = 8.6 Hz, 1 H, 3-H), 6.06 (d, ^3J(H,H) = 7.1 Hz, 1 H, 5-H), 7.05–7.28 (m, 18 H, 4,9,11,18,19,20-H, BC_6H_5), 7.95 (br., 8 H, *o*-BC_6H_5) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 3.4, 23.7, 24.6, 24.7, 25.5, 25.6, 26.5, 29.2, 31.2, 35.1, 40.6, 72.7, 108.5, 113.4, 121.7, 122.6, 125.4, 126.5, 127.3, 129.7, 137.4, 139.3, 141.7, 142.5, 147.2, 151.4, 154.9, 165.4 (q, ^1J(C,B) = 49.5 Hz, BC_6H_5), 169.7 ppm.

Synthesis of 6a: The compounds [Sc{N(SiHMe_2)$_2$}$_3$(thf)] (797 mg, 1.55 mmol) and **1a** (708 mg, 1.55 mmol) were dissolved in toluene (20 mL). The reaction mixture was stirred at 60 °C for 4 d. All volatiles were removed and the residue was extracted with hexane (40 mL). The solvent was removed in vacuo to yield 925 mg (78%) of a yellow crystalline compound. $C_{40}H_{71}N_4ScSi_4$ (765.3): calcd. C 62.78, H 9.35, N 7.32; found C 62.26, H 9.49, N 7.02. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.17 (d, ^3J(H,H) = 2.3 Hz, 12 H, Si(CH_3)$_2$), 0.23 (d, ^3J(H,H) = 2.2 Hz, 12 H, Si(CH_3)$_2$), 1.11–1.15 (m, 12 H, CH(CH_3)$_2$), 1.27 (d, ^3J(H,H) = 6.9 Hz, 6 H, 30,31-H), 1.40–1.42 (m, 12 H, CH(CH_3)$_2$), 2.83 (sept, ^3J(H,H) = 6.9 Hz, 1 H, 15-H), 2.95 (sept, ^3J(H,H) = 6.8 Hz, 2 H, 13,14/22,23-H), 3.60 (sept, ^3J(H,H) = 6.8 Hz, 2 H, 13,14/22,23-H), 4.92 (br., ^1J(Si,H) = 162 Hz, 4 H, Si*H*), 5.63 (d, ^3J(H,H) = 8.6 Hz, 1 H, 3-H), 6.02 (d, ^3J(H,H) = 7.0 Hz, 1 H, 5-H), 6.67 (t, ^3J(H,H) = 7.8 Hz, 1 H, 4-H), 7.14–7.28 (m, 5 H, 9,11,18,19,20-H) ppm. ^{1}H NMR (300 MHz, [D_8]toluene, 373 K): δ = 0.15 (d, ^3J(H,H) = 2.8 Hz, 24 H, Si(CH_3)$_2$) 1.09 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.11 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.26 (d, ^3J(H,H) = 6.9 Hz, 6 H, 30,31-H), 1.34 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.38 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 2.85 (sept, ^3J(H,H) = 6.9 Hz, 1 H, 15-H), 2.94 (sept, ^3J(H,H) = 6.8 Hz, 2 H, 13,14/22,23-H), 3.52 (sept, ^3J(H,H) = 6.8 Hz, 2 H, 13,14/22,23-H), 4.86 (sept, ^3J(H,H) = 2.8, ^1J(Si,H) = 164 Hz, 4 H, Si*H*), 5.66 (dd, ^3J(H,H) = 8.6, ^1J(H,H) = 0.9 Hz, 1 H, 3-H), 6.01 (dd, ^3J(H,H) = 7.0, ^1J(H,H) = 0.9 Hz, 1 H, 5-H), 6.80 (dd, ^3J(H,H) = 7.0, ^3J(H,H) = 8.6 Hz, 1 H, 4-H), 6.96–7.22 (m, 5 H, 9,11,18,19,20-H) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 2.1, 2.8, 24.1, 24.2, 24.3, 25.4, 25.7, 28.3, 30.9, 34.7, 107.2, 111.5, 121.0, 124.3, 125.6, 135.3, 139.3, 142.7, 144.1, 146.4, 149.3, 156.3 168.6; ppm. ^{29}Si NMR (60 MHz, [D_8]toluene, 298 K): δ = –19.3 ppm.

NMR Tube Reaction of 2a with [$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$]: The compounds **2a** (15 mg, 20 μmol) and [$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$] (16 mg, 20 μmol) were dissolved in deuterated bromobenzene (0.5 mL) and thf (30 μL) was added. After 5 min the solution was transferred into a NMR tube equipped with a young valve. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ = 0.00 (s, 12 H, $SiMe_4$), 0.11 (s, 9 H, CH_2SiMe_3), 0.31 (br., 2 H, CH_2SiMe_3), 1.10–1.13 (m, 12 H, CH(CH_3)$_2$), 1.30–1.34 (m, 12 H, CH(CH_3)$_2$), 1.36 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH(CH_3)$_2$), 1.64 (br., β-CH_2, THF), 2.78 (s, 6 H, NMe_2), 2.88 (br., 2 H, 13,14/22,23-H), 2.98 (sept, ^3J(H,H) = 6.9 Hz, 1 H, 15-H), 3.22 (br., 2 H, 13,14/22,23-H), 3.67 (br., α-CH_2, THF), 5.78 (d, ^3J(H,H) = 8.6 Hz, 1 H, 3-H), 6.32 (d, ^3J(H,H) = 7.1 Hz, 1 H, 5-H), 6.72 (d, ^3J(H,H) = 8.1 Hz, 2 H, *o*-$C_6H_5NMe_2$), 6.83 (t, ^3J(H,H) = 7.3 Hz, 1 H, *p*-$C_6H_5NMe_2$), 7.11 (dd, ^3J(H,H) = 8.6, ^3J(H,H) = 7.1 Hz, 1 H, 4-H), 7.23 (s, 2 H, 9,11-H), 7.27–7.33 (m, 5 H, 18,19,20-H, *m*-$C_6H_5NMe_2$) ppm. ^{13}C NMR (100 MHz, C_6D_5Br, 298 K): δ = 0.0, 3.6, 23.0, 24.2, 24.5, 24.7, 25.8, 26.4, 27.9, 30.6, 34.6, 40.4, 67.5, 108.2, 112.8, 113.6, 116.8, 121.3, 125.1, 129.2, 134.4, 135.4, 137.2, 137.8, 139.7, 139.9, 142.3, 143.7, 146.7, 147.5, 149.9, 150.9, 154.3, 169.7 ppm. ^{19}F NMR (376 MHz, C_6D_5Br, 298 K): δ = –132.4 (br. d, ^3J(F,F) = 12.0 Hz, *o*-F), –162.7 (t, ^3J(F,F) = 21.0 Hz, *p*-F), –166.7 (t, ^3J(F,F) = 18.9 Hz, *m*-F) ppm.

NMR Tube Reaction of 6a with $AlMe_3$: The complex **6a** (25 mg, 33 μmol) was dissolved in a NMR tube equipped with a young valve in C_6D_6 (0.5 mL). After the addition of 6 equiv. trimethylaluminium (19 μL, 0.2 mmol) the tube was sealed and shaken. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = –0.34 (s, 24 H, AlMe_4), –0.13–0.07 (br., 30 H, AlMe_3, NAlMe_2), 0.19 (d, ^3J(H,H) = 3.0 Hz, 24 H, Si(CH_3)$_2$), 1.08 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH(CH_3)$_2$), 1.12 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.26 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH(CH_3)$_2$), 1.31 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH(CH_3)$_2$), 1.32 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$), 2.76–2.95 (m, 3 H, 13,14/22,23-H, 15-H), 3.37 (sept, ^3J(H,H) = 6.7 Hz, 2 H, 13,14/22,23-H), 4.74 (sept, ^1J(Si,H) = 211, ^3J(H,H) = 3 Hz, 4 H, Si*H*), 5.68 (d, ^3J(H,H) = 8.6 Hz, 1 H, 3-H), 6.13 (d, ^3J(H,H) = 7.1 Hz, 1 H, 5-H), 6.80 (dd, ^3J(H,H) = 7.1, ^3J(H,H) = 8.6 Hz, 1 H, 4-H), 7.17 (s, 2 H, 9,11-H), 7.23 (s, 3 H, 18,19,20-H) ppm.

Polymerization of Isoprene: A detailed polymerization procedure (Table 1, run 4) is described as a typical example. In a glove box the complex **2a** (8 mg, 10 μmol) was dissolved in C_6H_5Cl (8 mL) and isoprene (680 mg, 1 mL, 10 mmol) was added. The mixture was placed in a water bath (20 C). Then $AlMe_3$ (100 μmol, 50 μL, 2.0 M in hexane) and a solution of [$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$] (8 mg, 10 μmol) in C_6H_5Cl (2 mL) were added. After stirring for 20 h at room temperature the mixture was poured into a large quantity of acidified 2-propanol containing 0.1% (w/w) 2,6-di-*tert*-butyl-4-methylphenol as a stabilizing agent. The precipitated polymer was decanted, washed with 2-propanol and dried in vacuo at 60 °C to a constant weight to afford 680 mg of polyisoprene (100%). The microstructure of the polymer was examined by ^{13}C NMR spectroscopy in $CDCl_3$.

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