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Reversible Chain Transfer between Organoyttrium Cations and Aluminum: Synthesis of Aluminum-Terminated Polyethylene with Extremely Narrow Molecular-Weight Distribution

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Abstract: Aminopyridinato-ligand-stabilized organoyttrium cations are accessible in very good yield through alkane elimination from trialkyl yttrium complexes with sterically demanding aminopyridines, followed by abstraction of one of the two alkyl functions using ammonium borates. At 80 °C and in the presence of small amounts of aluminum alkyl compounds, very high ethylene polymerization activities are observed if very bulky aminopyridinato ligands are used. During these polymerizations a reversible polyethylene chain transfer is observed between the organoyttrium cations and aluminum alkyls. The chain-transfer catalyst system described here is able to produce relatively long-chain (up to 4000 g mol^{-1}) Al-terminated polyethylene with a molecular-weight distribution <1.1. In the synthesis of higher molecular PE a slight increase in polydispersity with increasing chain length (15600 g mol^{-1}, ~1.4) is observed owing to reduced reversibility caused by higher viscosity and precipitation of polymer chains (temperature of 80–100 °C).

Keywords: aluminum · chain transfer · lanthanides · polymerization · yttrium

Introduction

The unusually large coordination sphere and high Lewis acidity of the lanthanides give rise to unique coordination chemistry, for instance between Ln and main-group alkyls.[1,2] The optimization of such coordinative interactions between "[Cp_2SmPE]" (Cp = cyclopentadienyl, PE = polyethylenyl) and "[PE_2Mg]" allows the synthesis of well-defined PE materials and diblock copolymers by reversible chain transfer.[3] Lanthanide alkyls like "[Cp_2SmPE]" are usually less efficient in ethylene insertion than organolanthanide cations.[4] Early and late transition-metal PE chain-transfer catalysts on the other hand are limited to rather low-molecular-weight polymers. Such systems transfer efficiently at room temperature and are able to polymerize with a polydispersity less than 1.1, up to a molecular weight of 1200 g mol^{-1}.[5] We report here on aminopyridinato-ligand-stabilized[6] organoyttrium cations and the reversible PE chain transfer between these cations and aluminum to synthesize aluminium-terminated PE chains with a very narrow molecular-weight distribution. The rather high thermal stability of these cations in combination with suppressed β-H transfer allows for the synthesis of relatively high-molecular-weight Al-terminated PE, functionalized polyethylene blocks to build novel polymer architectures.[7] More than 50 years ago, Karl Ziegler and co-workers discovered the Aufbaureaktion[8]—the insertion of ethylene into an aluminum–alkyl bond at very high ethylene pressures. The "Nickeleffekt"[9] and subsequent explorations of the influence of other metals with regard to ethylene insertion led to transition-metal-catalyzed ethylene polymerization.[10] We report here on a lanthanide-catalyzed version of the Aufbaureaktion.

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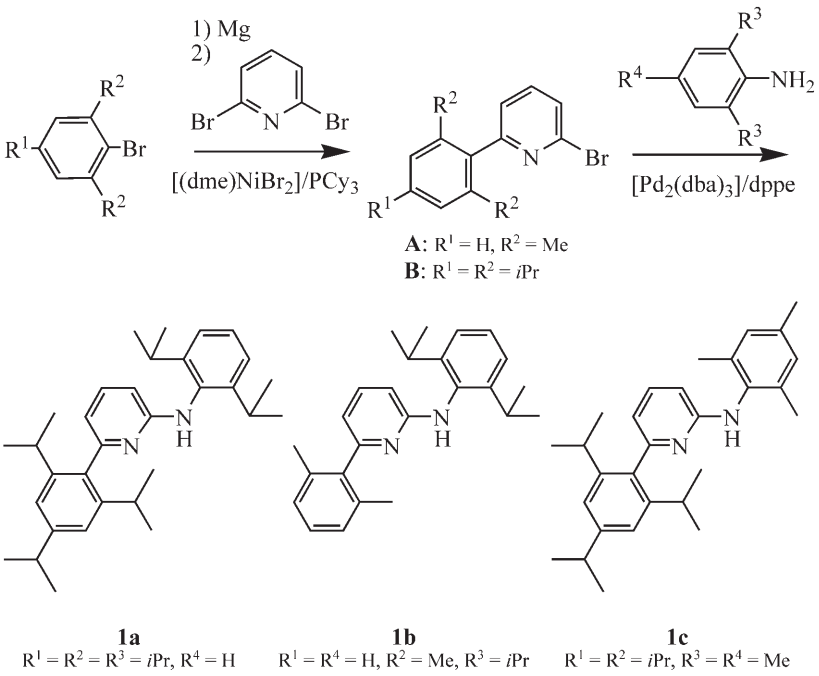
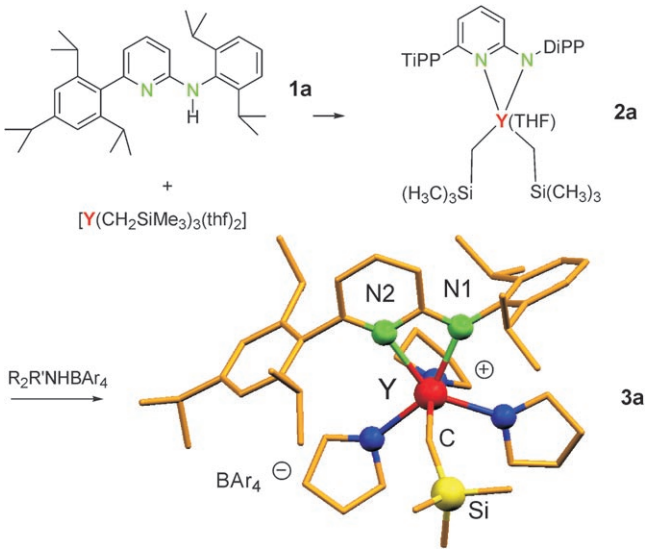
Results and Discussion

Synthesis and structure of the organoyttrium cations: The reaction of the sterically demanding aminopyridine[11] **1a** (Scheme 1) with one equivalent $[Y(CH_2SiMe_3)_3(thf)_2]$ leads to the dialkyl **2a** in good yield (Scheme 2). The proton and ^{13}C NMR signals of the CH_2 groups of the two alkyl ligands show coupling constants of $^2J(^{89}Y,^1H) = 3$ or $^1J(^{89}Y,^{13}C) = 39.74$ Hz, as well as $^2J(^{29}Si,^1H) = 8.3$ or $^1J(^{29}Si,^{13}C) = 46.5$ Hz. The ^{29}Si NMR spectrum of **2a** shows a doublet at −4.3 ppm with a coupling constant $^2J(^{89}Y,^{29}Si) = 1.9$ Hz. The reaction of **2a** with ammonium borates leads selectively and quantitatively to an elimination of one of the two alkyl ligands. The organoyttrium cation **3a** obtained in the presence of THF by using the anilinium borate $[C_6H_5NH(CH_3)_2]^+[B(C_6H_5)_4]^-$ was characterized by X-ray crystal structure analysis. The molecular structure is shown in Scheme 2. Crystallographic details are summarized in Table 1.

The mean Y−C bond length (2.382(4) Å) of **3a** is slightly shorter than the expected value of a Y−C bond of a $-CH_2Si(CH_3)_3$ ligand (2.401 Å)[12] and goes along with the shortening expected because of the cationic nature of the yttrium center. The mean Y-C-Si angle (143.8(2)°) of **3a** is around 10° larger than the mean observed value of these ligands (134.3°).[13] NMR spectroscopic investigations of the organoyttrium cation **3a** revealed similar coupling patterns as for



Scheme 1. Synthesis of sterically demanding aminopyridines **1a**–**1c**.



Scheme 2. Synthesis of **2a** and **3a** and molecular structure of the cation of **3a** (TiPP = 2,4,6-tri(isopropyl)phenyl, DiPP = 2,6-di(isopropyl)phenyl, R = CH_3, R′ = C_6H_5, Ar = C_6H_5). Two independent cations were found per asymmetric unit; selected bond lengths [Å] and angles [°]: Y−N1 2.302(3), Y−N2 2.421(3), Y−C 2.382(4); N1-Y-N2 57.41(11) Y-C-Si 143.8(2). The compounds **2b** and **2c** as well as **3b** and **3c** are synthesized analogously to **2a** and **3a** using **1b** and **1c**, respectively, (Scheme 1) instead of **1a**.

Abstract in German: *Aminopyridinato-Ligand-stabilisierte Organoyttrium-Kationen sind in sehr guten Ausbeuten via Alkaneliminierung ausgehend von sterisch anspruchsvollen Aminopyridinen und Trialkylyttrium-Komplexen und anschließender Abstraktion einer der beiden Alkylfunktionen durch Ammoniumborate zugänglich. Bei erhöhter Temperatur (80 °C) und in Gegenwart geringer Mengen von Alkylaluminium-Verbindungen werden für solche Kationen sehr hohe Aktivitäten in der Olefinpolymerisation beobachtet, wenn sterisch äußerst anspruchsvolle Aminopyridinato-Liganden zum Einsatz kommen. Während der Polymerisation erfolgt ein reversibler Polyethylen-Kettentransfer zwischen den Organoyttrium-Kationen und den eingesetzten Alkylaluminium-Verbindungen. Das hier beschriebene Kettentransfer-Katalysatorsystem eignet sich, um relativ langkettiges (bis zu 4000 g mol^{-1}) Al terminiertes Polyethylen mit Molekulargewichtsverteilungen < 1.1 herzustellen. Bei der Darstellung von höhermolekularem PE nehmen die Verteilungen mit der Kettenlänge zu (15600 g mol^{-1}, ~1.4), da durch eine erhöhte Viskosität und das "Ausfallen" von Polymerketten (Temperaturen von 80–100 °C) eine reduzierte Reversibilität beobachtet wird.*

Table 1. Details of the X-ray crystal structure analyses of **3a**, **3c**, and **4**.

Compound	**3a**	**3c**	**4**
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.258(2)	11.8440(6)	9.201(1)
b [Å]	20.221(3)	14.7060(7)	10.786(1)
c [Å]	27.745(4)	18.8650(10)	20.025(2)
α [°]	71.180(2)	76.945(4)	99.345(2)
β [°]	80.953(2)	84.642(4)	101.742(2)
γ [°]	86.622(2)	84.478(4)	93.622(2)
V [Å^3]	6952.6(18)	3177.4(3)	1910.4(3)
crystal size [mm^3]	0.5×0.4×0.2	0.6×0.5×0.3	0.4×0.3×0.1
ρ_{calcd} [g cm^{-3}]	1.156	1.176	1.038
μ [cm^{-1}] ($Mo_{K\alpha}$)	9.02	9.82	0.80
T [K]	100(1)	193(1)	100(1)
θ range [°]	2.39–29.15	1.43–25.75	2.29–28.08
reflections unique	27688	11992	6856
refl. obs. [$I>2\sigma(I)$]	17070	9619	4253
no. of parameters	1523	694	402
wR^2 (all data)	0.1887	0.1609	0.1297
R value [$I>2\sigma(I)$]	0.0636	0.0681	0.0597

2a. Furthermore, the good thermal stability of **3a** was observed by NMR spectroscopy; over a period of several days at room temperature no decomposition was detected.

As in the synthesis of **2a**, reaction of **1b** or **1c** (Scheme 1) with $[Y(CH_2SiMe_3)_3(thf)_2]$ led to the corresponding dialkyls **2b** and **2c**, respectively. Nearly quantitative yields were observed by NMR spectroscopy. These dialkyls formed organoyttrium cations in the presence of ammonium borates. The reactions of **2b** and **2c** with $[PhNMe_2H][B(C_6H_5)_4]$ gave rise to **3b** and **3c**, respectively (Schemes 1 and 2). The structure of **3c** was determined by X-ray crystallography (Figure 1); crystallographic details are listed in Table 1.

In analogy to the trialkyl yttrium $[Y(CH_2SiMe_3)_3(thf)_2]$, the aluminum trialkyl $[Al\{CH_2CH(CH_3)_2\}_3]$ reacts almost quantitatively with one equivalent of **1a** to give rise to the aminopyridinato-ligand-stabilized aluminum dialkyl **4**. The structure of **4** was determined by X-ray crystallography (Figure 2); crystallographic details are listed in Table 1.

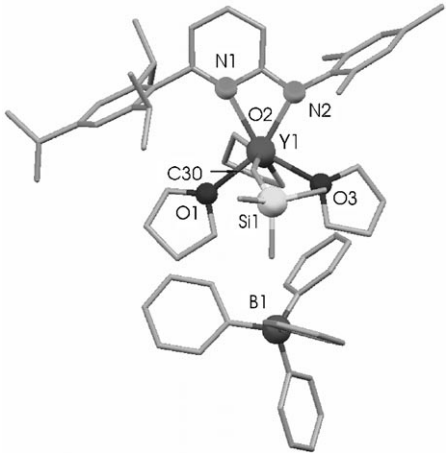


Figure 1. Molecular structure of **3c**. Selected bond lengths [Å] and angles [°]: C30–Y1 2.376(4), N1–Y1 2.427(3), N2–Y1 2.273(3), Y1–O3 2.322(3), Y1–O2 2.374(3), Y1–O1 2.361(3); O2-Y1-C30 159.34(13), O3-Y1-O1 109.88(10), N2-Y1-N1 57.81(10).

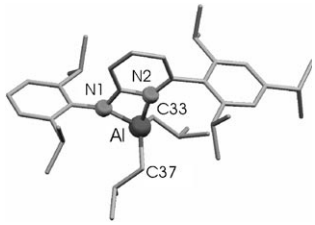


Figure 2. Molecular structure of **4**. Selected bond lengths [Å] and angles [°]: Al–N1 1.935(2), Al–N2 1.991(2), Al–C33 1.965(3), Al–C37 1.963(3); N1-Al-N2 68.77(8), C33-Al-C37 120.34(12).

Organoyttrium-catalyzed ethylene polymerization, dependence of the activity on the steric bulk of the aminopyridinato ligand: The Ap-ligand-stabilized (Ap = aminopyridinato) organoyttrium cations can polymerize ethylene with very high activity[14] in the presence of small amounts of aluminum alkyls (Table 2, entry 1). The presence of aluminum alkyl is essential to observe polymerization activity (Table 4, entry 1). The efficient steric shielding of the metal center and/or the Y–N bonds seems to be important to observe the very high activities.

Table 2. Ethylene polymerization activity—dependence of the steric bulk of the Ap ligand.[a]

Entry	Ligand	$m_{Pol.}$ [g]	Activity [$kg_{PE}mol_{cat}^{-1}$ $h^{-1}bar^{-1}$]	M_w [$gmol^{-1}$]	M_w/M_n
1	**1a**	13.4	1072	66500[b]	3.2
2	**1b**	5.0	400	46100[b] (10800[c])	4.3 (1.5)
3	**1c**	5.4	432	263900[b] (16300[c])	28.8 (2.4)

[a] Conditions: Dialkyl (**2a–c**): 10 μmol, ammonium borate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{31}$–$C_{18}H_{35}$), Y/B = 1/1.1, aluminum alkyl: TIBAO (tetraisobutylalumoxane), Y/Al = 1/20, 260 mL toluene, temperature: 80 °C, pressure: 5 bar, time: 15 min. [b] Bimodal. [c] M_w of the main fraction (>90 %).

The reduction of the steric demand of the Ap ligand (**1b** compared with **1a** for instance (Scheme 1); 2,6-dimethylphenyl instead of 2,4,6-triisopropylphenyl substituents at the pyridine ring of the Ap ligand) goes along with a decrease of the ethylene polymerization activity by about 60 %. The same behavior was found for the inversion of the substitution patterns of the sterically less demanding version (**1c** versus **1b**; 2,4,6-trimethylphenyl at the amido N atom instead at the pyridine ring (Scheme 1)). Coordination chemical studies show that less bulky aminopyridinato ligands like **1b** and **1c** have the tendency to form bisaminopyridinato complexes.[11b] We did not observe such species during the formation of the corresponding cations **3b** and **3c** but can not completely rule out that under catalytic conditions bisaminopyridinato complexes are formed by ligand redistribution and PE elimination. Such species can no longer catalyze chain growth since they do not have a metal–carbon bond into which to insert ethylene, and thus may contribute to the slightly decreased activity.

Temperature dependence of the organoyttrium-catalyzed ethylene polymerization: Since the organoyttrium cations based on **1a** showed the highest ethylene polymerization activity, we proceeded to explore these catalyst systems in more detail. An extremely unusual temperature dependence was observed (Table 3, Figure 3).

Table 3. Temperature dependence of the ethylene polymerization using organoyttrium cations based on **1a**.[a]

Entry	T [°C]	$m_{pol.}$ [g]	Activity [$kg_{PE}mol_{cat}^{-1}$ $h^{-1}bar^{-1}$]	M_w [$g\,mol^{-1}$]	M_w/M_n
1	30	0.5	40	67900[b] (1950)[c]	43.0 (1.3)
2	50	2.5	200	76400[d]	19.1
3	80	13.4	1072	66500[d]	3.2
4	100	10.1	808	15600	1.4

[a] Conditions: **2a**: 10 μmol, ammonium borate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{31}$–$C_{18}H_{35}$), Y/B = 1/1.1, aluminum alkyl: TIBAO, Y/Al = 1/20, 260 mL toluene, pressure: 5 bar, time: 15 min. [b] Contains a small amount of high molecular PE. [c] M_w of the main fraction (>95%). [d] Bimodal distribution.

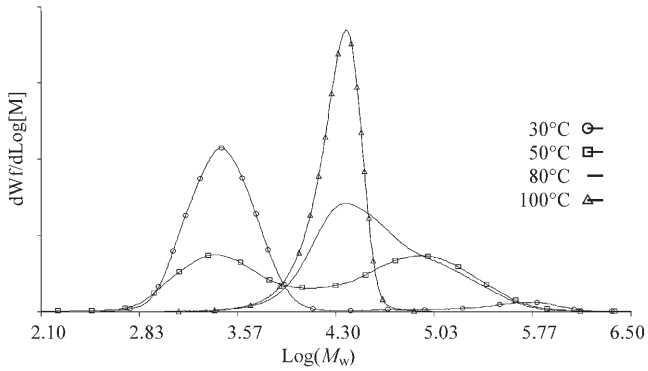
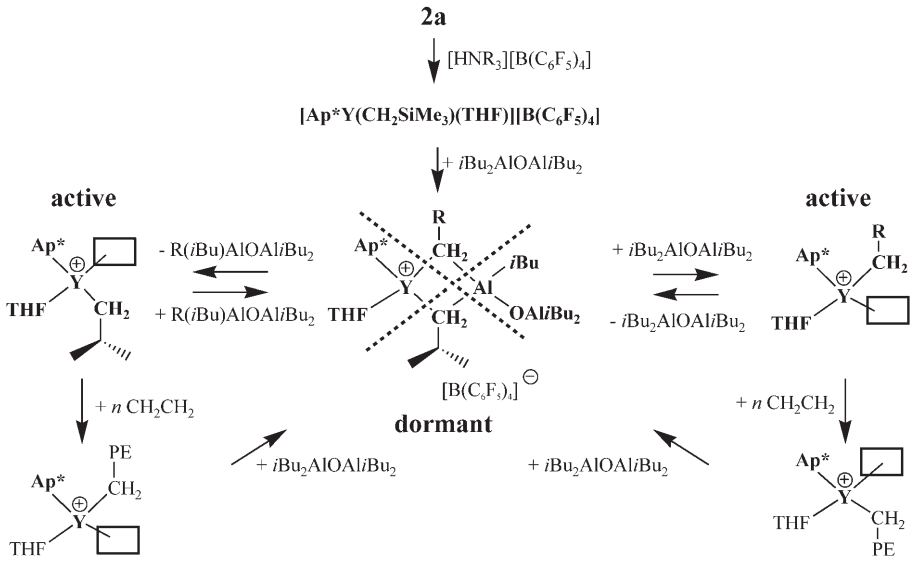


Figure 3. Molecular-weight distribution (SEC) of the polymerization experiments listed in Table 3.

At 30°C a mainly monomodal distribution with a relatively low molecular weight was observed. At 50°C a polymer with a bimodal distribution is observed. One of the distributions shows a molecular weight similar to the main fraction of the 30°C run, the second has a significantly higher M_w. At 80°C an overlapping bimodal distribution can be seen, also with an increase of the mean molecular weight with increasing temperature. At 100°C the polymerization under the given conditions (Table 3) again produces a monomodal distribution.



Scheme 3. Proposed mechanism for the organoyttrium cation catalyzed ethylene polymerization.

The overall trend from 30 to 80°C is an unusual increase in activity together with an increase in the molecular weight. These observations could be explained by a reversible chain transfer[3] between the organoyttrium cation—responsible for chain growth—and the aluminum center—responsible for chain storage in combination with (partial) precipitation of PE (Scheme 3). At 30°C, relatively slow chain growth proceeds (blocking of the active side by strongly bonded aluminum alkyls at low temperature), giving rise to a short, narrowly distributed and soluble Al-terminated main fraction. At 50 and 80°C, chain growth proceeds much faster, and since the same number of chains is grown, longer chains that precipitate are produced. Substantial amounts of precipitated polymer were observed at 50 and 80°C, whereas only traces were obtained for the 30°C run. After precipitation, two fractions are observed (bimodal distribution: the fraction still soluble under the applied conditions and the precipitated fraction, the fraction that most likely continues to grow). The improved solubility at 80°C relative to 50°C leads to overlapping bimodal distribution at this temperature and to a monomodal distribution at 100°C (Figure 3). NMR spectroscopy of the polymers obtained (after hydrolytic workup) revealed saturated polymers with isopropyl end groups (Figure 4). Even at 100°C nearly no β-H elimination takes place, indicating that chain transfer is much faster than β-H elimination. Increasing the aluminum-to-yttrium ratio (Table 4) is accompanied by an increase in the intensity of the end-group proton NMR signal relative to the PE signal (Figure 5). The PE signal also becomes very narrow, indicating a very narrow molecular weight distribution if the appropriate aluminum-to-yttrium ratio is used.

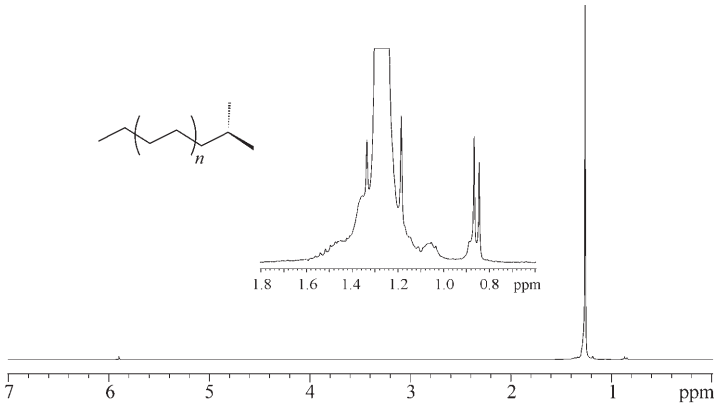


Figure 4. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of isopropyl-terminated PE (Table 3, entry 4).

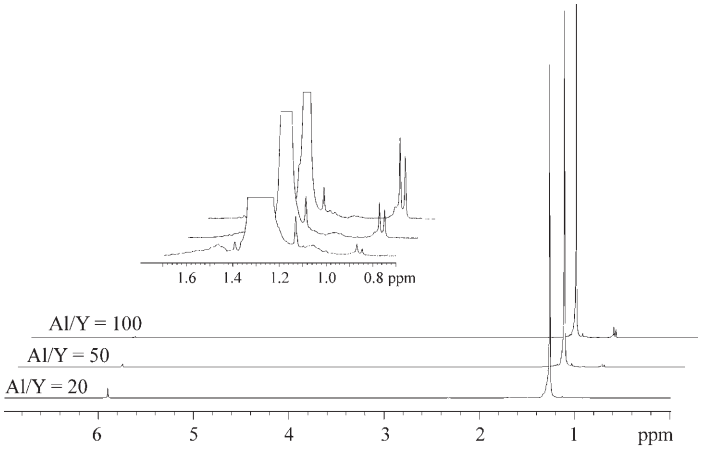


Figure 5. ^{1}H NMR spectra ($C_2D_2Cl_4$, 120 °C) of PE produced by polymerization runs (Table 4).

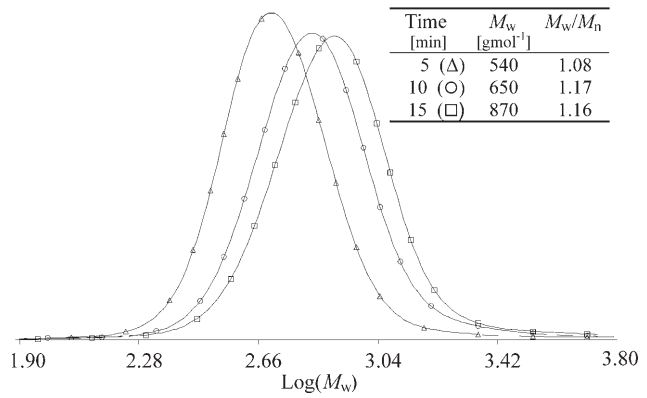


Figure 6. Time-dependent increase in the molecular weight of the polymers (SEC). Conditions: **2a**: 10 μmol, ammonium borate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{31}$–$C_{18}H_{35}$), Y/B = 1/1.1, aluminum alkyl: TIBAO, Y/Al = 1/150, 260 mL toluene, pressure: 5 bar.

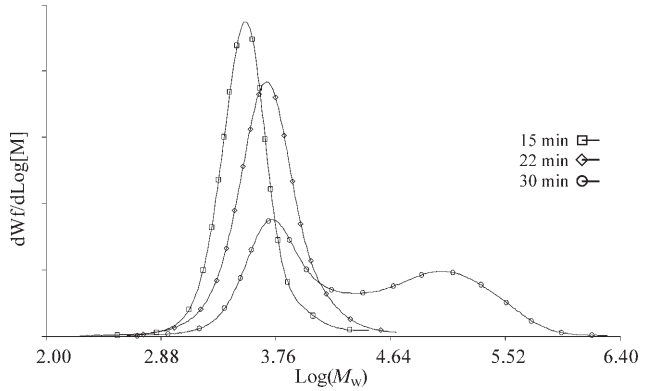


Figure 7. Influence of polymer precipitation on the molecular-weight distribution (SEC); before (15 min), at the beginning of (22 min,) and after (30 min) precipitation (Table 4, entries 4, 6, and 7).

Time dependence of the chain growth: In the organoyttrium-cation-catalyzed ethylene polymerization, two major periods can be distinguished. In the first "homogeneous" period, slow continuous ethylene consumption together with an increase of the molecular weight but without significant broadening[15] of the distribution (Figure 6) is observed.

With ongoing chain growth, partial polymer precipitation occurs together with a strong increase in ethylene uptake; this is the second "heterogeneous" period. In Figure 7 the molecular-weight distributions before, at, and after the precipitation point are shown. It can be seen that polymerization continues up to the precipitation point without significant broadening of the molecular weight. Beyond the precipitation point a bimodal distribution is observed. It seems (as mentioned above) that only the precipitated chain grows, while the molecular weight of the lower M_n fraction is barely raised with increasing time. This indicates that with reduced reversibility due to higher viscosity, fast multiple ethylene insertion into the active organoyttrium species (Scheme 3) occurs, which then precipitates with an attached polymer chain and continues to grow heterogeneously.

Dependence of the ethylene polymerization on the aluminum alkyl used and the aluminum-to-yttrium ratio: Reaction temperature, polymerization time, and the aluminum-to-yttrium ratio can be tuned to ensure that the Al-terminated PE stays soluble during the polymerization process and allows for the synthesis of very narrowly distributed polymers (Table 4, entries 4 and 5, Figure 8). The stability of the organoyttrium cations in combination with a nearly suppressed β-H elimination at even 100 °C allows for the synthesis of relatively long-chain polymers with a polydispersity <1.1. Increasing viscosity and precipitation of the Al-terminated polymer chains results in a reduction of the reversibility of the chain transfer and thus broader polydispersities are observed.

The Mortreux system, which allows operation at elevated temperatures, shows mainly α-olefin side products at 100 °C.[3a] Transition-metal-based chain-transfer catalyst systems[5] are intended to work at room temperature, which restricts the production of long-chain polymers, most likely because of solubility problems. Molecular weights with a dispersity of around 1.1 up to a M_w of about 1200 g mol^{-1} are

Table 4. Ethylene polymerization catalyzed by **2a** as a function of the aluminium-to-yttrium ratio.[a]

Entry	Al:Y [mol/mol]	$m_{pol.}$ [g]	Activity [$kg_{PE}\,mol_{cat}^{-1}\,h^{-1}\,bar^{-1}$]	M_w [$g\,mol^{-1}$]	M_w/M_n
1	0	0	0	n.d.	n.d.
2	5	13.5	1080	88100	2.3
3	20	13.4	1072	66500[b]	3.2
4	50	4.7	376	3940	1.09
5	100	2.1	168	1460	1.05
6	50[c]	7.5	409	5920	1.4
7	50[d]	14.5	580	73900	7.7
8	100[d]	6.0	240	5830	1.3

[a] Conditions: **2a**: 10 μmol, ammonium borate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{31}$–$C_{18}H_{35}$), Y/B = 1/1.1, aluminum alkyl: TIBAO, 260 mL toluene, pressure: 5 bar. [b] Bimodal. [c] 22 min run time. [d] 30 min run time.

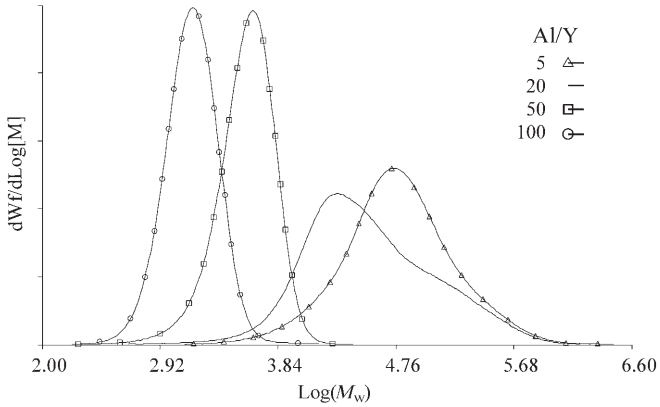


Figure 8. Molecular-weight distribution (SEC) of the polymerization experiments listed in Table 4, entries 2–5.

described for these catalyst systems, which corresponds to about 43 ethylene insertions per growing chain.

As shown in Table 5, the organoyttrium-cation-catalyzed chain growth on aluminum is not limited to TIBAO themselves, but can be carried out with a wide variety of aluminum alkyls. However, the use of partially hydrolyzed aluminum alkyls seems to have a strong beneficial effect on the ethylene polymerization activity. This behavior can best be explained by the stronger coordination of the aluminum trialkyls to the organoyttrium cation,[1,2] relative to the less electron-rich aluminoxanes. This results in a shift of the equilibrium between "free" organoyttrium, able to insert ethylene, and the yttrium–aluminum complex responsible for chain transfer (Scheme 3). Aluminum cations stabilized by aminopyridinato ligands are nearly inactive in ethylene polymerization. The activation of **4** with ammonium borates (10 μmol, ammonium borate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{31}$–$C_{18}H_{35}$), Al/B = 1/1.1, aluminum alkyl: TIBAO, Al/Al = 1/20, 260 mL toluene, pressure: 5 bar, 15 min) under the same conditions applied for **2a** (Table 3, entry 3) results in an activity of 8 $kg_{PE}\,mol_{cat}^{-1}\,h^{-1}\,bar^{-1}$. In other words, the yttrium-free catalyst system is not able to accomplish the chain growth that leads to the polymeric materials described above. By varying the substituents at the aluminum alkyl and the workup, alcohol derivatives are accessible. For examples, see Figures 9–11.

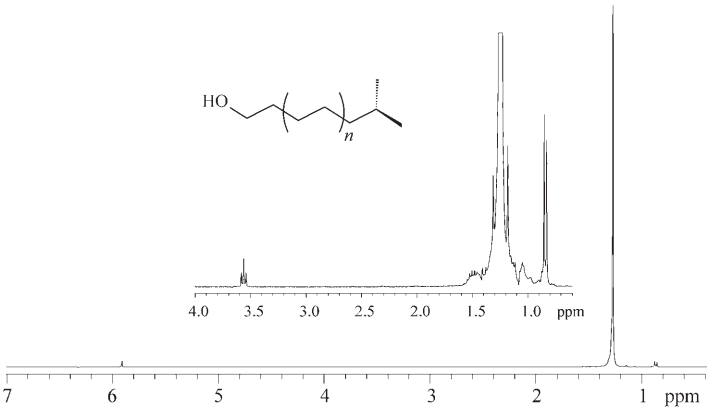


Figure 9. ^1H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of PE after oxidative workup (Table 4, entry 6).

Table 5. Ethylene polymerization catalyzed by **2a**: influence of the aluminum alkyl.[a]

Entry	Al-alkyl [mol/mol]	Al/Y [g]	$m_{pol.}$ [$kg_{PE}\,mol_{cat}^{-1}\,h^{-1}\,bar^{-1}$]	Activity [$gmol^{-1}$]	M_w	M_w/M_n
1	TOA	100	0.5	40	n.d.	n.d.
2	TIBA	100	0.9	80	n.d.	n.d.
3	TIBA[a]	100	4.3	129	2660	1.2
4	TOAO	100	1.9	152	2580	1.1
5	TIBAO	100	2.1	168	1460	1.05
6	TPPAO	5	4.6	368	111000	2.1
7	TPPAO	50	1.9	152	2770	1.2

[a] Conditions: **2a**: 10 μmol, ammonium borate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{31}$–$C_{18}H_{35}$), Y/B = 1/1.1, 260 mL toluene, pressure: 5 bar, time: 15 min. [a] 100 °C, 10 bar, 20 min.

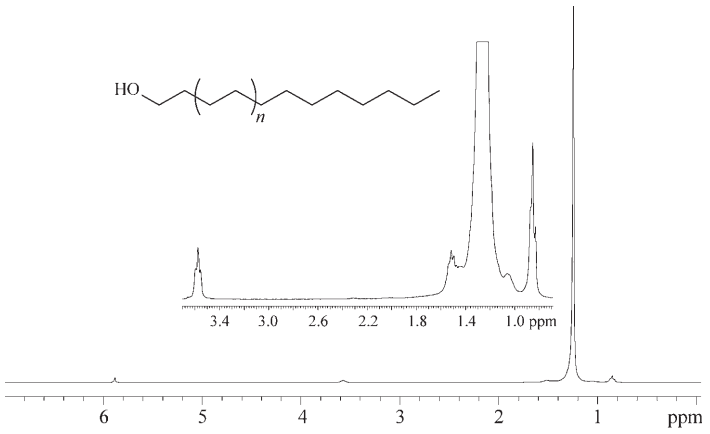


Figure 10. ^1H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of PE after oxidative workup (Table 5, entry 4).

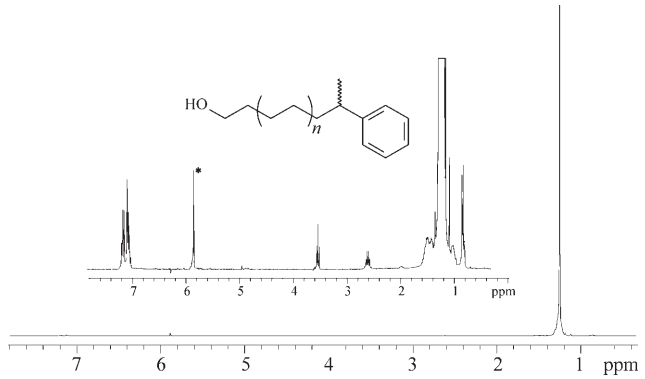


Figure 11. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of PE after oxidative workup (Table 5, entry 6).

Conclusion

Aminopyridinato-ligand-stabilized organoyttrium cations can show very high ethylene polymerization activity in the presence of small amounts of aluminum alkyl compounds (trialkyls and aluminoxanes) at elevated temperature. Reversible polyethylene chain transfer between the organoyttrium cations and the aluminum compounds can be observed. Since β-H elimination is nearly suppressed even at 100 °C, relatively high-molecular-weight Al-terminated polymer chains with a very narrow polydispersity can be produced.

Experimental Section

General: All manipulations of air- or moisture-sensitive compounds were carried out under N_2 using glove-box, standard Schlenk, or vacuum-line techniques. Solvents and reagents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy, or sodium ketyl of benzophenone under nitrogen immediately before use. Toluene (Aldrich, anhydrous, 99.8 %) was passed over columns of Al_2O_3 (Fluka), BASF R3–11 supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over BASF R3–11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å).

NMR spectra were recorded on a Varian Gemini 400 (^{1}H: 400 MHz, ^{13}C: 100.5 MHz) or Varian VXR-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 25 °C and 120 °C, were referenced internally using the residual solvent resonances, and the chemical shifts (δ) reported in ppm. The polymer samples were prepared by dissolving 15 mg of the polymer in 0.5 mL CD_2Cl_2 at 100 °C for 3 h before measuring.

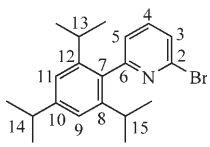
Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1 % weight/volume) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (M_w = 50000 g mol^{-1}) and polystyrene (M_w = 100000–500000 g mol^{-1}) standards. The reported values are the average of at least two independent determinations.

Ligand and complex synthesis: *N*,*N*-dimethylanilinium(tetrapentafluorophenyl)borate ([$PhNMe_2H$][$B(C_6F_5)_4$], Strem), *N*,*N*,*N*-trialkylammonium(tetrapentafluorophenyl)borate ([R_2NMeH][$B(C_6F_5)_4$], R = $C_{16}H_{31}$–$C_{18}H_{35}$, 6.2 wt % $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals), trimethylaluminum (TMA, 2.0 M in toluene, Aldrich), tri-isobutylaluminum (TIBA, 25 wt % in toluene, Aldrich), tri-*n*-octylaluminum (TOA, 25 wt % in toluene, Aldrich) and TIBA (Witco) were used as received.

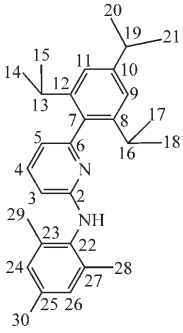
$[Y(CH_2SiMe_3)_3(thf)_2]$,[16] *N*,*N*-dimethylanilinium(tetraphenyl)borate ([$C_6H_5NH(CH_3)_2$] [$B(C_6H_5)_4$]),[17] tetra-isobutylaluminoxane ([*i*-$Bu_2Al]_2O$, TIBAO),[18] tetra-*n*-octylaluminoxane ([$Oct_2Al]_2O$, TOAO),[18] tetra-(2-phenyl-)propylaluminoxane ([$CH_3CH(Ph)CH_2]_2Al]_2O$, TPPAO),[18] **1a**, and **1b**[11a] were prepared according to published procedures.

Preparation of 1-MgBr-[2,4,6-*i*Pr$_3$C$_6$H$_2$]: Magnesium turnings (0.94 g, 38.7 mmol) were added to 1-Br-[2,4,6-*i*$Pr_3C_6H_2$] (35.2 mmol, 9.97 g) in THF (30 mL) and activated using 1,2-dibromoethane. When the resulting suspension was stirred, an exothermic reaction took place and an ice bath was used to cool the mixture if it became too vigorous. After about 2 h the reaction mixture was cooled, stirred overnight, and filtered. The filtrate was used directly in the preparation of **B**.

Preparation of B: 2,6-Dibromopyridine (7.91 g, 33.4 mmol), THF (35 mL), tricyclohexylphosphine (0.075 mmol), and [(dme)$NiBr_2$] (0.012 g, 0.0375 mmol) were added together in a Schlenk flask under argon. The Grignard reagent described above was then added to the stirred suspension resulting in a beige precipitate. The reaction mixture was kept at 50 °C for 72 h. Water and $CHCl_3$ were added and the resulting suspension transferred to a separating funnel. The organic phase was collected and the residue extracted with $CHCl_3$ (2×). The combined organic phases were washed with a saturated NaCl solution and dried over Na_2SO_4. The solvent was removed to afford a white precipitate, which was recrystallized from hexane (20 mL) (7.05 g, yield 58 %). M.p. 232–233 °C; ^{1}H NMR (250.13 MHz, $CDCl_3$, 298 K): δ = 1.00–1.30 (m, 18H; CH_3), 2.44 (sept, 2H; $H^{13,15}$), 2.88 (sept, 1H; H^{14}), 7.02 (s, 2H; $H^{9,11}$), 7.21 (d, ^3J = 7.4 Hz, 1H; H^5), 7.43 (d, ^3J = 8.0 Hz, 1H; H^3), 7.59 ppm (dd, ^3J = 8.0, ^3J = 7.4 Hz, 1H; H^4); ^{13}C NMR (62.9 MHz, $CDCl_3$, 298 K): δ = 23.8 (s; CH_3), 24.1 (s; CH_3), 24.2 (s; CH_3), 30.4 (s; $C^{13,15}$), 34.4 (s; C^{14}), 120.8 (s; $C^{9,11}$), 123.9 (s; $C^{3,5}$), 125.9 (s; $C^{3,5}$), 134.9 (s; C^7), 137.9 (s; C^4), 141.5 (s; C^2), 146.1 (s; $C^{8,12}$), 149.3 (s; C^{10}), 161.3 ppm (s; C^6); elemental analysis calcd (%) for $C_{20}H_{26}BrN$ (360.3): C 66.67, H 7.27, N 3.89; found: C 67.56, H 7.48, N 3.78.

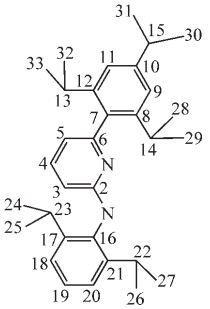


Preparation of 1c: Compound **B** (2.75 g, 7.63 mmol), 1,3-bis(diphenylphosphino)propane (0.12 g, 0.28 mmol), tris(dibenzylideneacetone) dipalladium(0) (0.13 g, 0.14 mmol), and sodium *tert*-butoxide (0.83 g, 8.6 mmol) were loaded into a Schlenk tube. After adding 2,4,6-trimethylphenylamine (1.03 g, 7.63 mmol) in toluene (30 mL) the resulting mixture was heated at about 95 °C for 24 h. The reaction mixture was cooled to room temperature, and subsequently water (50 mL) and diethyl ether (50 mL) were added. The organic phase was separated and the remaining residue extracted with diethyl ether (3×20 mL). The combined organic phases were washed with a saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting red solid was purified by using column chromatography (SiO_2/CH_2Cl_2). Recrystallization at −30 °C from pentane or hexane afforded white crystalline materials (2.05 g, 65 %). ^{1}H NMR (250.13 MHz, $CDCl_3$, 298 K): δ = 1.12 (d, ^3J = 6.9 Hz, 6H; $H^{14,15,17,18}$), 1.18 (d, ^3J = 6.9 Hz, 6H; $H^{14,15,17,18}$), 1.26 (d, ^3J = 7.0 Hz, 6H; $H^{20,21}$), 2.20 (s, 6H; $H^{28,29}$), 2.30 (s, 3H; H^{30}), 2.69 (sept, ^3J = 6.9 Hz, 2H; $H^{13,16}$), 2.91 (sept, ^3J = 7.0 Hz, 1H; H^{19}), 5.92 (dd, ^3J = 8.3 Hz, ^4J = 0.8 Hz, 1H; H^3), 5.97 (br, 1H; H^{NH}), 6.61 (dd, ^3J = 7.2, ^4J = 0.8 Hz, 1H; H^5), 6.95 (s, 2H; $H^{9,11/24,26}$), 7.05 (s, 2H; $H^{9,11/24,26}$), 7.37 ppm (dd, ^3J = 8.3, ^3J = 7.2 Hz, 1H; H^4); ^{13}C NMR (62.9 MHz, $CDCl_3$, 298 K): δ = 18.2 (s; $C^{28,29}$), 20.9 (s; C^{30}), 24.0 (s; $C^{14,15/17,18/20,21}$), 24.1 (s; $C^{14,15/17,18/20,21}$), 24.5 (s; $C^{14,15/17,18/20,21}$), 30.3 (s; $C^{13,16}$), 34.5 (s; C^{19}), 103.1 (s; C^3), 114.8 (s; C^5), 120.7 (s; $C^{9,11/24,26}$), 129.2 (s; $C^{9,11/24,26}$), 134.3 (s; C^7), 136.3 (s; C^{10}), 136.7 (s; $C^{8,12/27,29}$), 137.4 (s; C^{25}), 146.0 (s; $C^{8,12/27,29}$), 148.3 (s; C^4), 157.7 (s; C^6), 158.6 ppm (s; C^2) (two sig-

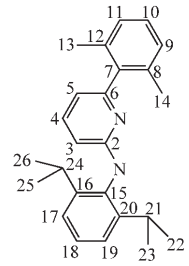


nals seem to be isochronic); elemental analysis calcd (%) for $C_{29}H_{38}N_2$ (414.63): C 84.01, H 9.24, N 6.76; found: C 84.10, H 9.35, N 6.20.

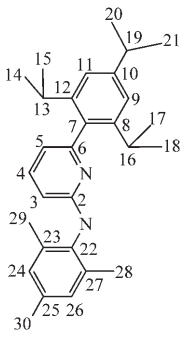
Synthesis of bis(trimethylsilylmethyl)-aminopyridinato-yttrium(tetrahydrofurane) complexes 2a–2c: The desired amino pyridine ligand Ap′H (0.1 mmol: **1a**, 45.6 mg; **1b**, 41.5 mg; **1c**, 33.0 mg; Scheme 1) was dissolved in toluene (2 mL) and slowly added to an ice-cooled solution of $[Y(CH_2SiMe_3)_3(thf)_2]$ (49.5 mg, 0.1 mmol) in toluene (2 mL). After the mixture had been stirred for 30 min, all volatiles were removed to yield the corresponding, spectroscopically pure $[Ap'Y(CH_2SiMe_3)_2(thf)]$ (based on ^{1}H NMR, **2a–2c**, Scheme 2) as a pale yellow residue in almost quantitative yield.



2a: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = −0.42 (d, 4H, ^2J(Y,H) = 3.0 Hz; H^{YCH2}), 0.18 (s, 18H; H^{SiMe3}), 1.05 (br, 4H; β-CH_2, THF), 1.16 (d, 6H, ^3J(H,H) = 6.8 Hz; $H^{28,29,32,33}$), 1.18 (d, 6H, ^3J(H,H) = 6.8 Hz; $H^{30,31}$), 1.24 (d, 6H, ^3J(H,H) = 6.8 Hz; $H^{24,25,26,27}$), 1.32 (d, 6H, ^3J(H,H) = 6.8 Hz; $H^{24,25,26,27}$), 1.56 (d, 6H, ^3J(H,H) = 6.8 Hz; $H^{28,29,32,33}$), 2.88 (sept, 1H, ^3J(H,H) = 6.8 Hz; H^{15}), 3.11 (sept, 2H, ^3J(H,H) = 6.8 Hz; $H^{13,14}$), 3.42 (sept, 2H, ^3J(H,H) = 6.8 Hz; $H^{22,23}$), 3.60 (br, 4H; α-CH_2, THF), 5.65 (d, 1H, ^3J(H,H) = 8.4 Hz; H^3), 6.09 (d, 1H, ^3J(H,H) = 7.2 Hz; H^5), 6.75 (dd, 1H, ^3J(H,H) = 8.4, ^3J(H,H) = 7.2 Hz; H^4), 7.10 (m, 2H; $H^{18,20}$), 7.16 (m, 1H; H^{19}), 7.25 ppm (m, 2H; $H^{9,11}$); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.1 (s; C^{SiMe3}), 23.6 (s; $C^{28,29,32,33}$), 24.3 (s; $C^{24,25,26,27}$), 24.4 (s; $C^{28,29,32,33}$), 24.9 (s; $C^{24,25,26,27}$), 25.2 (s; β-CH_2, THF), 26.7 (s; $C^{30,31}$), 28.8 (s; $C^{22,23}$), 30.9 (s; $C^{13,14}$), 35.0 (s; C^{15}), 39.8 (d, ^1J(Y,C) = 39.7, ^1J(Si,C) = 46.5 Hz; C^{YCH2}), 69.2 (s; α-CH_2, THF), 106.7 (d, ^3J(Y,C) = 1.6 Hz; C^3), 111.2 (s; C^5), 121.2 (s; $C^{9,11}$), 124.2 (s; $C^{18,20}$), 124.9 (s; C^{19}), 136.0 (s; C^7), 139.4 (s; C^4), 144.0 (s; $C^{17,21}$), 144.5 (d, ^2J(Y,C) = 0.9 Hz; C^{16}), 146.7 (s; $C^{8,12}$), 149.6 (s; C^{10}), 156.0 (d, ^2J(Y,C) = 1.0 Hz; C^6), 169.6 ppm (d, ^2J(Y,C) = 2.6 Hz; C^2).

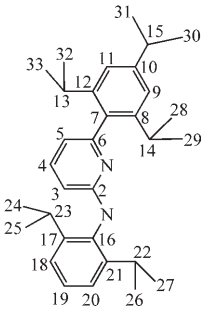


2b: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = −0.46 (d, 4H, ^2J(Y,H) = 3.3 Hz; H^{YCH2}), 0.21 (s, 18H; H^{SiMe3}), 1.16 (br, 4H; β-CH_2, THF), 1.18 (d, 6H, ^3J(H,H) = 7.0 Hz; $H^{22,23,25,26}$), 1.22 (d, 6H, ^3J(H,H) = 7.0 Hz; $H^{22,23,25,26}$), 2.36 (s, 6H; $H^{13,14}$), 3.39 (sept, 2H, ^3J(H,H) = 7 Hz; $H^{21,24}$), 3.70 (br, 4H; α-CH_2, THF), 5.59 (d, 1H, ^3J(H,H) = 8.4 Hz; H^3), 5.81 (d, 1H, ^3J(H,H) = 6.6 Hz; H^5), 6.79 (dd, 1H, ^3J(H,H) = 8.4, ^3J(H,H) = 6.6 Hz; H^4), 7.08 (m, 2H; $H^{17,19}$), 7.15 (m, 2H; $H^{10,18}$), 7.18 ppm (m, 2H; $H^{9,11}$); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.2 (s; C^{SiMe3}), 20.7 (s; $C^{13,14}$), 24.3 (s; $C^{22,23,25,26}$), 24.8 (s; $C^{22,23,25,26}$), 25.3 (s; β-CH_2, THF), 28.7 (s; $C^{21,24}$), 39.2 (d, ^1J(Y,C) = 39.2 Hz; C^{YCH2}), 69.4 (s; α-CH_2, THF), 106.1 (s; C^3), 108.3 (s; C^5), 121.1 (s; $C^{17,19}$), 124.9 (s; C^{18}), 128.1 (s; $C^{9,11}$), 128.7 (s; C^{10}), 135.8 (s; C^7), 140.6 (s; C^4), 144.0 (s; $C^{16,20}$), 144.2 (s; C^{15}), 156.0 (s; C^6), 169.6 ppm (s; C^2).



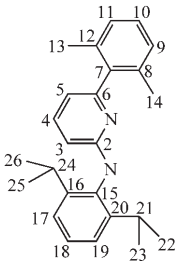
2c: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = −0.41 (d, 4H, ^2J(Y,H) = 3.1 Hz; H^{YCH2}), 0.22 (s, 18H; H^{SiMe3}), 1.18 (d, 6H, ^3J(H,H) = 7.0 Hz; $H^{14,15,17,18}$), 1.24 (br, 4H; β-CH_2, THF), 1.32 (d, 6H, ^3J(H,H) = 7.0 Hz; $H^{14,15,17,18}$), 1.55 (d, 6H, ^3J(H,H) = 6.6 Hz; $H^{20,21}$), 2.22 (s, 3H; H^{30}), 2.25 (s, 6H; $H^{28,29}$), 2.89 (sept, 1H, ^3J(H,H) = 6.6 Hz; H^{19}), 3.12 (sept, 2H, ^3J(H,H) = 7.0 Hz; $H^{13,16}$), 3.61 (br, 4H; α-CH_2, THF), 5.70 (d, 1H, ^3J(H,H) = 8.4 Hz; H^3), 6.12 (d, 1H, ^3J(H,H) = 6.9 Hz; H^5), 6.84 (dd, 1H, ^3J(H,H) = 8.4, ^3J(H,H) = 6.9 Hz; H^4), 6.88 (s, 2H; $H^{24,26}$), 7.25 ppm (s, 2H; $H^{9,11}$); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.2 (s; C^{SiMe3}), 19.1 (s; $C^{28,29}$), 20.9 (s; C^{30}), 23.6 (s; $C^{14,15,17,18}$), 24.4 (s; $C^{14,15,17,18}$), 25.2 (s; β-CH_2, THF), 26.7 (s; $C^{20,21}$), 30.9 (s; $C^{13,16}$), 35.0 (s; C^{19}), 39.8 (d, ^1J(Y,C) = 39.1 Hz; C^{YCH2}), 69.2 (s; α-CH_2, THF), 105.1 (s; C^3), 111.0 (s; C^5), 121.2 (s; $C^{9,11}$), 129.6 (s; $C^{24,26}$), 132.6 (s; C^{25}), 133.0 (s; $C^{23,27}$), 136.0 (s; C^7), 139.8 (s; C^4), 144.0 (s; C^{22}), 146.7 (s; $C^{8,12}$), 149.6 (s; C^{10}), 156.1 (d; C^6), 169.7 ppm (s; C^2).

Synthesis of 3a: $[Y(CH_2SiMe_3)_3(thf)_2]$ (150 mg, 0.30 mmol) was dissolved in toluene (1 mL), before a solution of **1a** (1 mL, 0.3 M in toluene, 0.30 mmol) was added. After stirring the mixture for 5 min it was combined with a suspension of $[C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$ (134 mg, 0.30 mmol) in toluene/THF (1.5 mL, 60/40 mol %), and repeatedly shaken until a clear solution was observed. The slightly yellow oil was layered with hexane (3.5 mL) and kept at room temperature overnight. After 12 h colorless crystals were obtained, which were decanted from the mother liquor and dried, yielding 247 mg (68 %) of **3a**·$(C_6H_{14})_{0.5}$. ^{1}H NMR (400 MHz, [D$_8$]THF, 298 K): δ = −0.61 (d, 2H, ^2J(Y,H) = 3.0 Hz; H^{YCH2}), −0.18 (s, 9H; H^{SiMe3}), 1.03 (d, 12H, ^3J(H,H) = 7.0 Hz; $H^{28,29,30,31,32,33}$), 1.20 (d, 6H, ^3J(H,H) = 7.0 Hz; $H^{24,25,26,27}$), 1.27 (d, 6H, ^3J(H,H) = 7.0 Hz; $H^{24,25,26,27}$), 1.30 (d, 6H, ^3J(H,H) = 7.0 Hz; $H^{28,29,32,33}$), 1.73 (m, 12H; β-CH_2, THF), 2.82 (sept, 2H, ^3J(H,H) = 7.0 Hz; $H^{13,14}$), 2.93 (sept, 2H, ^3J(H,H) = 7.0 Hz; H^{15}), 3.22 (sept, 2H, ^3J(H,H) = 7.0 Hz; $H^{22,23}$), 3.57 (m, 12H; α-CH_2, THF), 5.74 (dd, 1H, ^3J(H,H) = 8.8, ^4J(H,H) = 0.7 Hz; H^3), 6.22 (dd, 1H, ^3J(H,H) = 7.0, ^4J(H,H) = 0.7 Hz; H^5), 6.66 (tt, 4H, ^3J(H,H) = 7.0, ^4J(H,H) = 1.4 Hz; H^{BC6H5}), 6.80 (m, 8H, ^3J(H,H) = 7.0 Hz; H^{BC6H5}), 7.12–7.22 (m, 13H; $H^{9,11,18,19,20}$/BC6H5), 7.25 ppm (dd, 1H, ^3J(H,H) = 8.8, ^3J(H,H) = 7.0 Hz; H^4); ^{13}C NMR (100 MHz, [D$_8$]THF, 298 K): δ = 5.1 (s; C^{SiMe3}), 24.7 (s; $C^{28,29,32,33}$), 25.5 (s; $C^{24,25,26,27}$), 25.6 (s; $C^{30,31}$), 26.6 (s; $C^{24,25,26,27}$), 27.3 (br; β-CH_2, THF), 27.6 (s; $C^{28,29,32,33}$), 29.8 (s; $C^{22,23}$), 32.3 (s; $C^{13,14}$), 36.4 (s; C^{15}), 41.0 (d, ^2J(Y,C) = 42.9 Hz; C^{YCH2}), 69.2 (s; α-CH_2, THF), 110.1 (s; C^3), 114.6 (s; C^5), 122.9 (s; $C^{9,11}$), 123.1 (s; C^{BC6H5}), 126.3 (s; $C^{18,20}$), 126.7 (m; C^{BC6H5}), 127.2 (s; C^{19}), 137.2 (s; C^7), 138.1 (m; C^{BC6H5}), 141.4 (s; C^4), 144.8 (s; C^{16}), 145.5 (s; $C^{17,21}$), 148.7 (s; $C^{8,12}$), 152.3 (s; C^{10}), 156.4 (s; C^6), 166.2 (q, ^1J(C,B) = 49.0 Hz; C^{BC6H5}), 172.5 ppm (s; C^2); elemental analysis calcd (%) for $[C_{48}H_{78}N_2O_3SiY][C_{24}H_{20}B](C_6H_{14})_{0.5}$ (1210.47): C 74.42, H 8.74, N 2.31, Y 7.34; found: C 75.11, H 8.53, N 2.09, Y 7.10.



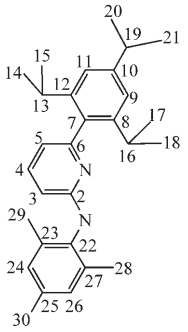
Synthesis of 3b and 3c: $[Y(CH_2SiMe_3)_3(thf)_2]$ (55 mg, 0.11 mmol) was dissolved in benzene/THF (0.5 mL, 80:20 vol %), before a solution of **1b** or **1c** (0.5 mL, 0.22 M in benzene, 0.11 mmol) was added. After stirring the mixture for 5 min, it was combined with a suspension of $[C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$ (49 mg, 0.11 mmol) in benzene/THF (0.5 mL, 80:20 vol %), and repeatedly shaken until a clear solution was observed. The slightly yellow oil was layered with hexane (3.5 mL) and kept at room temperature. After three days pale yellow crystals were observed, which were decanted from the mother liquor and dried, yielding 75 mg (61 %) of **3b** or 95 mg (73 %) of **3c**.

3b: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = −0.61 (d, 2H, ^2J(Y,H) = 3.1 Hz; H^{YCH2}), 0.06 (s, 9H; H^{SiMe3}), 1.04 (d, 6H, ^3J(H,H) = 7.0 Hz; $H^{22,23,25,26}$), 1.19 (d, 6H, ^3J(H,H) = 6.6 Hz; $H^{22,23,25,26}$), 1.41 (br; β-CH_2, THF), 2.00 (s, 6H; $H^{13,14}$), 3.14 (sept, 2H, ^3J(H,H) = 6.6 Hz; $H^{21,24}$), 3.49 (br; α-CH_2, THF), 5.54 (d, 1H, ^3J(H,H) = 8.4 Hz; H^3), 5.67 (d, 1H, ^3J(H,H) = 7.0 Hz; H^5), 6.70 (dd, 1H, ^3J(H,H) = 8.4, ^3J(H,H) = 7.0 Hz; H^4), 6.90 (d, 2H, ^3J(H,H) = 7.7 Hz; $H^{9,11,17,19}$), 7.02 (t, 1H, ^3J(H,H) = 7.7 Hz; $H^{10,18}$), 7.12–7.25 (m, 15H; $H^{9,11,17-20}$, BC_6H_5), 7.89 ppm (br, 8H; $H^{o\text{-}BC6H5}$); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.1 (s, C^{SiMe3}), 20.5 (s, $C^{13,14}$), 24.5 (s; $C^{22,23,25,26}$), 25.3 (s; $C^{22,23,25,26}$), 25.6 (s; β-CH_2, THF), 28.1 (s; $C^{21,24}$), 39.6 (d, ^1J(Y,C) = 43.7 Hz; C^{YCH2}), 68.8 (s; α-CH_2, THF), 107.9 (s; C^3), 110.1 (s; C^5), 122.2 (s; C^{BC6H5}), 124.1 (s; C^{18}), 124.8 (s; $C^{17,19}$), 126.0 (m; C^{BC6H5}), 129.2 (s; $C^{9,11}$), 136.0 (s; C^7), 137.1 (m; C^{BC6H5}), 139.6 (s; C), 140.3 (s; C), 140.6 (s; C^4), 142.5 (s; $C^{16,20}$), 143.8 (s; C^{15}), 154.7 (s;



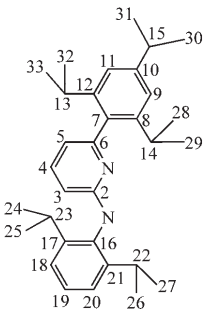
C^{6}), 165.0 (q, ^{1}J(C,B) = 49.9 Hz; C^{BC6H5}), 170.3 ppm (s; C^{2}); elemental analysis calcd (%) for $[C_{41}H_{64}N_2O_3SiY][C_{24}H_{20}B]$ (1069.18): C 73.02, H 7.92, N 2.61; found: C 72.92, H 7.75, N 2.35.

3c: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = −0.61 (d, 2H, ^{2}J(Y,H) = 3.0 Hz; H^{YCH2}), 0.08 (s, 9H; H^{SiMe3}), 1.04 (d, 6H, ^{3}J(H,H) = 6.6 Hz; $H^{14,15,17,18}$), 1.21 (d, 6H, ^{3}J(H,H) = 6.6 Hz; $H^{14,15,17,18}$), 1.22 (d, 6H, ^{3}J(H,H) = 6.6 Hz; $H^{20,21}$), 1.37 (br; β-CH_2, THF), 2.08 (s, 6H; $H^{28,29}$), 2.25 (s, 3H; H^{30}), 2.74 (sept, 1H, ^{3}J(H,H) = 6.6 Hz; H^{19}), 2.78 (sept, 2H, ^{3}J(H,H) = 6.6 Hz; $H^{13,16}$), 3.44 (br; α-CH_2, THF), 5.67 (d, 1H, ^{3}J(H,H) = 8.8 Hz; H^{3}), 6.00 (d, 1H, ^{3}J-(H,H) = 6.9 Hz; H^{5}), 6.71 (dd, 1H, ^{3}J(H,H) = 8.8, ^{3}J(H,H) = 6.9 Hz; H^{4}), 6.90 (s, 2H; $H^{9,11,24.26}$), 7.06 (s, 2H; $H^{9,11,24.26}$), 7.12–7.28 (m, 12H; H^{BC6H5}), 7.91 ppm (br, 8H; $H^{o\text{-}BC6H5}$); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.2 (s; C^{SiMe3}), 19.4 (s; $C^{28,29}$), 20.9 (s; C^{30}), 23.6 (s; $C^{14,15,17,18}$), 24.3 (s; $C^{14,15,17,18}$), 25.6 (s; β-CH_2, THF), 26.6 (s; $C^{20,21}$), 30.7 (s; $C^{13,16}$), 34.7 (s; C^{19}), 39.0 (d, ^{1}J(Y,C) = 43.7 Hz; C^{YCH2}), 69.1 (s; α-CH_2, THF), 106.7 (s; C^{3}), 112.2 (s; C^{5}), 121.3 (s; $C^{9,11}$), 122.3 (s; C^{BC6H5}), 126.1 (m; C^{BC6H5}), 130.2 (s; $C^{24,26}$), 132.6 (s; C^{25}), 134.0 (s; $C^{23,27}$), 135.4 (s; C^{7}), 137.1 (m; C^{BC6H5}), 140.1 (s; C^{4}), 142.1 (s; C^{22}), 147.2 (s; $C^{8,12}$), 150.7 (s; C^{10}), 154.7 (s; C^{6}), 165.0 (q, ^{1}J(C,B) = 49.1 Hz; C^{BC6H5}), 168.6 ppm (d, ^{2}J(Y,C) = 2.3 Hz; C^{2}); elemental analysis calcd (%) for $[C_{45}H_{72}N_2O_3SiY][C_{24}H_{20}B]$ (1125.28): C 73.65, H 8.24, N 2.49; found: C 73.89, H 8.26, N 2.27.

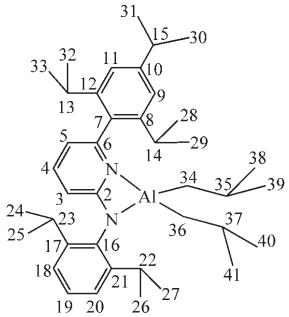


NMR tube reactions of 2a with $[PhNMe_2H][B(C_6F_5)_4]$, formation of 3a′: An NMR tube was charged with **2a** (16 mg, 20 μmol), THF (20 μL) and deuterobenzene (0.5 mL) together with $[PhNMe_2H][B(C_6F_5)_4]$ (16 mg, 20 μmol). Afterwards the tube was sealed and shaken for 5 min to form a clear solution before measurement.

3a′: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = −0.51 (d, ^{2}J(Y,H) = 3.1 Hz, 2H; H^{YCH2}), 0.0 (br, 18H; $H^{SiMe3,SiMe4}$), 1.01 (d, 6H, ^{3}J(H,H) = 6.2 Hz; $H^{28,29,30,31,32,33}$), 1.03 (d, 6H, ^{3}J(H,H) = 6.2 Hz; $H^{28,29,30,31,32,33}$), 1.20 (d, 6H, ^{3}J(H,H) = 7.0 Hz; $H^{28,29,32,33}$), 1.22 (d, 12H, ^{3}J(H,H) = 7.0 Hz; $H^{24,25,26,27}$), 1.42 (br; β-CH_2, THF), 2.52 (s, 6H; H^{NMe2}), 2.77 (sept, 3H, ^{3}J(H,H) = 7.0 Hz; $H^{13,14,15}$), 3.15 (sept, 2H, ^{3}J(H,H) = 7.0 Hz; $H^{22,23}$), 3.54 (br; α-CH_2, THF), 5.56 (d, 1H, ^{3}J-(H,H) = 8.7 Hz; H^{3}), 5.99 (d, 1H, ^{3}J(H,H) = 7.3 Hz; H^{5}), 6.63 (d, 1H, ^{3}J(H,H) = 7.7 Hz; $H^{o\text{-}C6H5N}$), 6.64 (dd, 1H, ^{3}J(H,H) = 8.7, ^{3}J-(H,H) = 7.3 Hz; H^{4}), 6.79 (m, 1H; $H^{p\text{-}C6H5N}$), 7.08 (s, 2H; $H^{9,11}$), 7.12–7.25 ppm (m, 5H; $H^{18,19,20,C6H5N}$); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 0.0 (s; C^{SiMe4}), 3.9 (s; C^{SiMe3}), 23.2 (s; $C^{28,29,32,33}$), 24.1 (s; $C^{24,25,26,27}$), 24.3 (s; $C^{30,31}$), 25.3 (s; $C^{24,25,26,27}$), 25.6 (br; β-CH_2, THF), 26.3 (s; $C^{28,29,32,33}$), 28.2 (s; $C^{22,23}$), 30.7 (s; $C^{13,14}$), 34.7 (s; C^{15}), 40.2 (s; C^{NMe2}), 41.2 (d, ^{2}J(Y,C) = 42.9 Hz; C^{YCH2}), 68.8 (s; α-CH_2, THF), 108.5 (s; C^{3}), 112.7 (s; C^{5}), 113.0 (s; C^{NC6H5}), 117.0 (s; C^{NC6H5}), 121.4 (s; $C^{9,11}$), 124.9 (s; $C^{18,20}$), 126.2 (s) 129.3 (s; C^{NC6H5}), 135.1 (s; C^{19}), 135.8 (br; C^{BC6F5}), 137.7 (s; C^{7}), 138.2 (br; C^{BC6F5}), 139.8 (s; C^{4}), 142.5 (s; C^{16}), 143.7 (s; $C^{17,21}$), 147.1 (s; $C^{8,12}$), 147.9 (br; C^{BC6F5}), 150.2 (br; C^{BC6F5}), 151.1 (s; C^{10}), 154.5 (s; C^{6}), 170.5 ppm (s; C^{2}); ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ = −167.1 (t, ^{3}J(F,F) = 18.3 Hz; *m*-F), −163.1 (t, ^{3}J(F,F) = 21.8 Hz; *p*-F), −132.5 ppm (br; *o*-F).



Synthesis of bis(alkyl)aminopyridinatoaluminum complex 4: A Schlenk vessel was charged with **1a** (45.6 mg, 0.1 mmol) and toluene (2 mL) before triisobutylaluminum (TIBA, 25 wt% in toluene, 1 mL, 0.1 mmol) was added. After the mixture had been stirred for 30 min, all volatiles was removed, to yield the corresponding, spectroscopic pure **4** as a colorless oil in almost quantitative yield. For X-ray analysis of **4** the residue was dissolved in hexane (3 mL). Slow evaporation of the solvent over a period of five days left colorless crystals. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.47 (dd, 2H, ^{2}J(H,H) = 14.0, ^{3}J(H,H) = 7.9 Hz; H^{AlCH2}), 0.54 (dd, 2H, ^{2}J(H,H) = 14.0, ^{3}J(H,H) = 7.3 Hz; H^{AlCH2}), 0.91 (d, 6H, ^{3}J-(H,H) = 6.6 Hz; H^{38-41}), 1.05 (d, 6H, ^{3}J(H,H) = 6.6 Hz; $H^{24-33,38-41}$), 1.06 (d, 6H, ^{3}J(H,H) = 6.6 Hz; $H^{24-33,38-41}$), 1.15 (d, 6H, ^{3}J(H,H) = 6.6 Hz; $H^{24-33,38-41}$), 1.21 (d, 6H, ^{3}J(H,H) = 7.0 Hz; $H^{24-33,38-41}$), 1.31 (d, 6H, ^{3}J-(H,H) = 7.0 Hz; $H^{24-33,38-41}$), 1.41 (d, 6H, ^{3}J(H,H) = 7.0 Hz; $H^{24-33,38-41}$), 2.04 (m, 2H, ^{3}J(H,H) = 6.6 Hz; $H^{35,37}$), 2.80 (sept, 1H, ^{3}J(H,H) = 6.6 Hz; H^{15}), 2.90 (sept, 2H, ^{3}J(H,H) = 6.6 Hz; $H^{13,14}$), 3.55 (sept, 2H, ^{3}J-(H,H) = 7.0 Hz; $H^{22,23}$), 5.62 (dd, 1H, ^{3}J(H,H) = 8.4, ^{4}J(H,H) = 0.9 Hz; H^{3}), 6.08 (dd, 1H, ^{3}J(H,H) = 7.3, ^{4}J(H,H) = 0.9 Hz; H^{5}), 6.80 (dd, 1H, ^{3}J(H,H) = 8.4, ^{3}J(H,H) = 7.3 Hz; H^{4}), 7.13 (br, 2H; $H^{18,20}$), 7.19 ppm (br, 3H; $H^{9,11,19}$); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 22.2 (br; C^{AlCH2}), 22.8 ($C^{28,29,32,33}$), 24.2 ($C^{24,25,26,27}$), 24.6 ($C^{28,29,32,33}$), 24.9 ($C^{24,25,26,27}$), 26.4 ($C^{38,39,40,41}$), 26.5 ($C^{38,39,40,41}$), 27.8 ($C^{30,31}$), 28.4 ($C^{35,37}$), 28.7 ($C^{22,23}$), 30.8 ($C^{13,14}$), 34.9 (C^{15}), 104.9 (C^{3}), 111.5 (C^{5}), 121.0 ($C^{9,11}$), 124.4 ($C^{18,20}$), 126.3 (C^{19}), 138.3 (C^{7}), 139.4 (C^{4}), 141.0 ($C^{17,21}$), 145.7 (C^{16}), 146.8 ($C^{8,12}$), 150.2 (C^{10}), 154.7 (C^{6}), 167.3 ppm (C^{2}); elemental analysis calcd (%) for $C_{40}H_{61}AlN_2$ (596.92): C 80.49, H 10.30, N 4.69; found: C 80.53, H 10.41, N 4.53.



Polymerization studies:

General description of polymerization experiments: The catalytic ethylene polymerization reactions were performed in a stainless steel 1 L autoclave (Medimex) in semibatch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature- and pressure-controlled and equipped with separated toluene, catalyst, and cocatalyst injection systems, and a sample outlet for continuous reaction monitoring. Multiple injection of the catalyst with a pneumatically operated catalyst injection system was used at an ethylene pressure of 5 bar. During a polymerization run, the pressure, ethylene flow, inner and outer reactor temperature, and stirrer speed were monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 h at 125 °C prior to use. The reactor was then brought to the desired temperature, stirred at 600 rpm, and charged with toluene (230 mL) together with trialkylammonium (tetrapentafluorophenyl)borate (11 μmol, 0.12 g) and the required amount of aluminum scavenger (1 mL of a 0.1 M stock). After pressurizing with ethylene to reach a total pressure of 5 bar, the autoclave was equilibrated for 5 min. Subsequently aminopyridinatoyttrium dialkyl complex (1 mL, 0.01 M stock solution in toluene) together with toluene (30 mL) was injected to start the reaction. During the run the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing flow. After the desired reaction time the reactor was vented and the residual aluminum alkyls were destroyed by addition of ethanol (100 mL). In the case of subsequent oxidation, the reactor was vented and stirred for 1 h at 80 °C under an atmosphere of dry air before ethanol (100 mL) was added. Polymeric product was collected, stirred for 30 min in acidified ethanol, and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and subsequently in vacuum at 80 °C.

Synthesis of the catalyst stock solutions: The complexes **2a**–**2c** were prepared as described above. For catalytic ethylene conversion the pale yellow residues were dissolved in toluene (10 mL) and used without further purification.

X-ray crystal structure analysis: Data collection was accomplished by using either a Bruker SMART APEX CCD or a Stoe IPDSII diffractom-

eter equipped with a low-temperature unit (λ(MoK) = 0.71073 Å). Details of the X-ray crystal structure analyses are listed in Table 1. CCDC-285279 (**3a**), CCDC-605499 (**3c**), CCDC-294801 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Acknowledgements

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[12] The mean Y−C bond length of 35 structurally characterized Y-CH_2-$Si(CH_3)_3$ moieties (CCDC) is 2.401 Å.

[13] The mean Y-C-Si angle of 35 structurally characterized Y-CH_2-Si-$(CH_3)_3$ moieties (CCDC) is 134.3°.

[14] The definition highly active is taken from: G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447.

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