DOI: 10.1002/ejic.200801106

Scandium-Catalyzed Polymerization of $CH_3(CH_2)_nCH{=}CH_2$ (n = 0–4): Remarkable Activity and Tacticity Control

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Keywords: Scandium / Olefins / Polymerization / X-ray diffraction

The C_3-symmetric trisoxazoline-supported scandium complex [Sc(*i*Pr-trisox)(CH_2SiMe_3)$_3$] (**2**) is highly active in the stereospecific polymerization of propene, 1-butene, 1-pentene, 1-hexene and 1-heptene, when activated with two equivalents of [Ph_3C][$B(C_6F_5)_4$]. The polymers thus produced were found to possess narrow molecular weight distributions and high levels of tacticity control (up to 99 % *mmmm*). Some insight into the nature of the active species was obtained by ^1H, ^{13}C and ^{29}Si NMR experiments. In particular, the formation of two equivalents of $Ph_3CCH_2SiMe_3$ at ambient temperature was observed alongside a C_3-symmetric scandium complex tentatively assigned as the dication [Sc(*i*Pr-trisox)(CH_2SiMe_3)]$^{2+}$.

Introduction

In stark contrast to Group 4 metals, effective post-metallocene olefin-polymerization catalysts based on Group 3 and lanthanide metals are still relatively scarce.[1] Well-defined molecular rare earth catalysts, which polymerize both ethylene and longer chain α-alkenes are particularly rare.

Nitrogen-based ligands are the most common ligand sets to be employed in non-Cp based lanthanide polymerization catalysts.[2] Yttrium tris(pyrazolyl)hydroborate complexes [Y(Tp)R_2(thf)$_x$] (R = C_6H_5, CH_2SiMe_3) were found to be poorly active in ethylene polymerization, as were the analogous lanthanide complexes; the explanation offered was that the Tp ligands have a limited stability towards the strongly Lewis acid metal centres.[3] The 1,4,7-trimethyl-1,4,7-triazacyclononane (tacn) ligands appear to give rise to more stable systems, and the scandium complex [Sc(tacn)Me_3] was reported by Bercaw,[4] which was found to oligomerize ethylene after activation with ammonium borate salts. Mountford et al. found that changing the alkyl ligands from methyl to CH_2SiMe_3 led to a significant enhancement in the activity.[5] The tacn ligand was also employed by Teuben and co-workers, who prepared a yttrium complex based on a tetradentate amido-tacn ligand, which is analogous to the amido-Cp ligands used in the constrained-geometry catalysts. Thus highly active catalysts for ethylene polymerization [up to 1800 kg(PE) mol(cat)$^{-1}$ h^{-1} bar^{-1}] were obtained.[6]

Whilst scandium dibenzyl complexes containing simple β-diketiminato (nacnac) ligands were found to be inactive for ethylene polymerization when activated with $B(C_6F_5)_3$,[7] the use a more sterically crowded nacnac ligand to suppress coordination of the counterion led to higher activities, approaching those observed for lanthanidocenes.[8] Bis(benzamidinato)yttrium alkyl and hydrido complexes [{PhC($NSiMe_3$)$_2$}YCH_2Ph(thf)] and [(PhC($NSiMe_3$)$_2$)Y(μ-H)]$_2$ have been reported to be moderately active catalysts for the polymerization of ethylene, whilst they are inactive in propene and 1-hexene polymerization.[9] Notably, the monoamidinate complex [PhC(NAr)$_2$]Y(CH_2SiMe_3)$_2$(thf) reported by Bambirra exhibits living polymerization behaviour for ethylene when activated with [$PhNMe_2$H][$B(C_6F_5)_4$].[10] Very recently, Trifonov et al. reported the polymerization of ethylene by bis(amidinate) hydrido complexes of yttrium, neodymium, samarium, gadolinium and ytterbium, with high activities, in particular, for the samarium and yttrium complexes.[11]

Oxygen-based ligands are much less commonly employed for lanthanide olefin polymerization catalysts. Okuda and co-workers reported that lutetium alkyl cations supported by crown ethers are highly active for the polymerization of ethylene.[12] In this case, very mild conditions were required, and BPh_3 was sufficient to activate the neutral complex, thus negating the need for perfluoroaryl boranes or borates. Okuda also reported the use of thf as the only supporting ligand present.[2b] The alkyl complexes Ln(CH_2SiMe_3)$_3$(thf)$_n$ (Ln = Sc, Lu, Yb, Tm, Er, Y, Ho, Dy, Tb) were found to polymerize ethylene, with the best activity being reported for the terbium complex (899 kg(PE) mol(Tb)$^{-1}$ h^{-1} bar^{-1}).

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In this case, Okuda suggested that the active species may very likely be a dicationic monoalkyl complex $[Ln(CH_2SiMe_3)(thf)_n]^{2+}$, since the polymerization reaction was observed to proceed only in the presence of excess activator. Under synthetic conditions in thf, a dicationic complex $[Y(Me)(thf)_6][BPh_4]_2$ was isolated and characterized by X-ray crystallography. Anwander also recently reported the stereospecific polymerization of isoprene using both half-sandwich and homoleptic lanthanide complexes, ligated by tetramethylaluminium, in addition to those containing alkoxide and aryloxide coligands. These complexes have been shown to give an almost quantitative conversion of isoprene, with good stereocontrol and narrow polydispersity indices.[13]

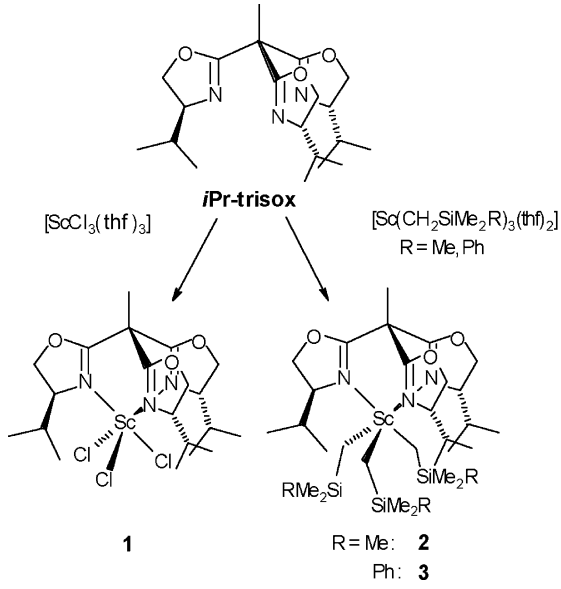
We have shown that C_3-chiral tris(oxazolinyl)ethane (trisox) ligands are versatile supporting ligands for a variety of late transition metals.[14] Since these systems are ideally suited to the trivalent octahedral complexes commonly observed with Group 3 metals and lanthanides, we have also demonstrated the use of these highly symmetric ligands as a successful supporting environment for scandium, thulium, lutetium and other lanthanides that proved to be active in the isospecific polymerization olefins.[15] We herein report the isotactic polymerization of α-olefins for the range from propene to 1-heptene, using the scandium complex [Sc(*i*Pr-trisox)(CH_2SiMe_3)$_3$] (**2**) as precatalyst.

Results and Discussion

Synthesis and Structural Characterization of [Sc(*i*Pr-trisox)R_3]

As part of our development of the 1,1,1-tris(oxazolinyl)-ethane (trisox) ligand as an efficient supporting environment for asymmetric catalysis, we have been investigating the possibility of using this *fac*-N_3 donor ligand for Group 3 and lanthanide metals, with the aim of application in the stereoselective polymerization of α-olefins.[15] We found that the thermal stability of these alkyl complexes decreases with increasing ionic radius of the metal, which renders the scandium precursors the most interesting systems for our purpose.

The preparation of the scandium chloride complex [Sc(*i*Pr-trisox)Cl_3] (**1**) was readily achieved from $ScCl_3(thf)_3$, when stirred with *i*Pr-trisox in thf (Scheme 1). However, this complex was found to be an unsuitable precursor for alkylscandium compounds, since subsequent reaction with a range of alkylating agents gave only complex mixtures, presumably owing to attack at the C=N bond of the oxazoline rings. We therefore chose the preformed scandium trialkyl complexes [Sc(CH_2SiMe_2R)$_3$(thf)$_2$] (R = Me or Ph) as precursor complexes, thus avoiding the unnecessary use of harsh nucleophilic reagents in the presence of the trisox ligand. Reaction of [Sc(CH_2SiMe_2R)$_3$(thf)$_2$] with *i*Pr-trisox gave the six-coordinate complexes [Sc(*i*Pr-trisox)(CH_2SiMe_2R)$_3$] (R = Me **2** or Ph **3**) (Scheme 1). All complexes **1**–**3** have been characterized by X-ray crystallography, of which the structures for **1** and **2** have been communicated previously.[14d,15a] The molecular structure of **3** is shown in Figure 1, and selected bond lengths and angles for all three complexes are provided in Table 1 for comparative purposes.



Scheme 1. Preparation of [Sc(*i*Pr-trisox)Cl_3] (**1**) and [Sc(*i*Pr-trisox)(CH_2SiMe_2R)$_3$] {R = Me (**2**) or Ph (**3**)}.

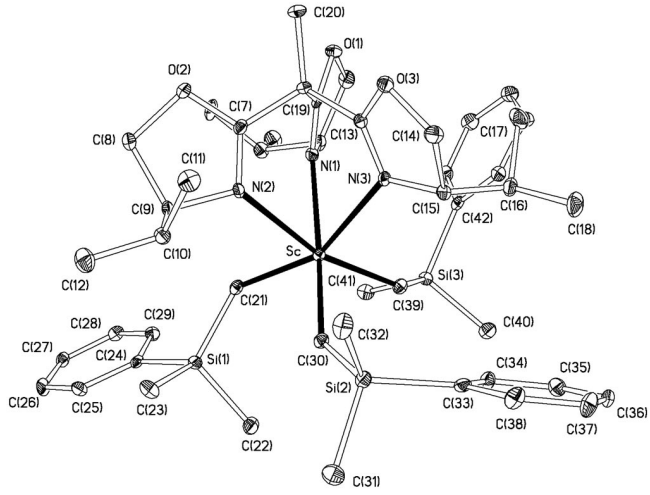


Figure 1. Molecular structure of [Sc(*i*Pr-trisox)(CH_2SiMe_2Ph)$_3$] (**3**). Ellipsoids drawn at 25% probability, and H atoms omitted for clarity.

The scandium centre in all three complexes adopts a *pseudo*-octahedral coordination geometry; the bond angles subtended at Sc deviate significantly from the ideal 90°. The Sc–Cl and Sc–N bond lengths in complex **1** lie within the expected ranges, on comparison with those in the Cambridge Structural Database.[16] It is notable, however, that the Sc–N bond lengths in **2** and **3** are significantly elongated [mean values: 2.288(3) Å for **1**, 2.455(2) Å for **2** and 2.425(3) Å for **3**], presumably due to the more sterically demanding nature of the coligands in **2** and **3** relative to **1**. The Sc–C bond lengths in **2** and **3** are unremarkable in

Table 1. Principal bond lengths [Å] and angles [°] for **1**–**3**.

	1	2	3
Sc–N	2.246(3)	2.456(2)	2.424(3)
	2.324(3)	2.446(1)	2.419(3)
	2.295(2)	2.464(2)	2.420(3)
Sc–Cl	2.403(1)		
	2.413(1)		
	2.398(1)		
Sc–C		2.270(2)	2.270(4)
		2.272(2)	2.263(4)
		2.275(2)	2.274(4)
N–Sc–N	75.62(9)	74.90(5)	75.28(12)
	77.88(9)	73.95(5)	76.06(12)
	78.19(9)	73.81(5)	73.80(11)
Cl–Sc–Cl	98.40(3)		
	102.90(4)		
	99.17(4)		
C–Sc–C		106.69(7)	98.54(16)
		104.38(7)	100.90(16)
		105.51(8)	98.14(16)

comparison to previously reported scandium alkyl complexes.[16] In each complex, the N–Sc–N angles are significantly more acute than the X–Sc–X (X = Cl or alkyl) angles. This phenomenon is thought to be primarily due to geometry constraints of the trisox ligand, since this is a feature common to all octahedral trisox complexes.[14d] It is noteworthy that the mean N–Sc–N angles lie in the order **1** > **3** > **2**, the inverse order of the mean Sc–N bond lengths. Thus, the closer trisox gets to the metal, the larger are the corresponding angles subtended at scandium. The ^{1}H and ^{13}C{^{1}H} NMR spectra of all three compounds support the C_3-symmetry implied from the crystallographic studies, which suggests that the solid-state structure pertains in solution.

Catalytic Polymerization of α-Olefins

In our preliminary communication, we reported that 1-hexene was successfully polymerized by activation of [Sc(*i*Pr-trisox)(CH_2SiMe_3)$_3$] (**2**), performed by adding an equimolar amount of trityl tetrakis(pentafluorophenyl)-borate, [Ph_3C][$B(C_6F_5)_4$].[15a] Under these conditions, only low, variable activities [≈30 kg mol(Sc)$^{-1}$ h^{-1}] and bimodal molecular weight distributions were observed. In contrast, activation with 2 equiv. [Ph_3C][$B(C_6F_5)_4$] gave a remarkably high polymerization performance, with an activity of over 36000 kg mol[Sc]$^{-1}$ h^{-1}; even when the reaction was performed at –30 °C, the activity remained at over 2000 kg mol[Sc]$^{-1}$ h^{-1}, which is high for post-metallocene olefin polymerization catalysts.[1a–1b] Moreover, the resulting poly(1-hexene) was obtained with a molecular weight of 750000, a polydispersity index of 1.09 and 90% isotacticity (reaction conditions: 10 μmol **2** in 0.5 mL chlorobenzene and 5 mL 1-hexene).

As part of our continued interest in this catalyst, we probed the wider applicability of the catalyst, particularly with respect to other α-olefins. Since the polymerization under the aforementioned conditions was somewhat too exothermic to allow reliable control of the reaction temperature for the duration of the polymerization, we chose to dilute the system with a halogenated solvent. The polymerization reactions were therefore performed by using 10 μmol scandium precatalyst in 5 mL chlorobenzene and 2 mL monomer. Under these standard conditions, the isospecific polymerization of α-olefins from propene to 1-heptene was investigated; the results are presented in Table 2.

Table 2. Polymerization data for [Sc(trisox)(CH_2SiMe_3)$_3$] (**2**) (+ 2 equiv. [Ph_3C][$B(C_6F_5)_4$]).

Entry	Monomer	*T* [°C]	Activity[a]	M_w/M_n	M_w	Isotacticity[b]
1	propene	20	560[c]	1.52	134000	50
2	propene	–40	11268[c]	1.80	600000	71
3	1-butene	20	trace[c]	–	–	–
4	1-butene	–40	1780	1.26	582000	99
5	1-pentene	20	60	1.61	183000	83
6	1-pentene	–40	10	1.44	121000	99
7	1-hexene	20	3015	1.94	309000	60
8	1-hexene	–30	1938	1.20	281000	99
9	1-heptene	20	1340	1.88	262000	70
10	1-heptene	–30	47	1.78	316000	99

[a] kg(polymer) mol(Sc)$^{-1}$ h^{-1}; reaction conditions: 5 mL chlorobenzene, 10 μmol **1**, 20 μmol [Ph_3C][$B(C_6F_5)_4$], 2 mL monomer, 15 min. [b] % *mmmm* pentad on the basis of integration of the C^3 resonance in the ^{13}C{^{1}H} NMR spectra. [c] kg(polymer) mol(Sc)$^{-1}$ h^{-1} bar^{-1}; 1 bar monomer pressure.

Interesting observations were made with respect to the polymerization activity in this system. In the case of propene and 1-butene, the activities at ambient temperature were somewhat lower than expected (560 kg mol^{-1} h^{-1} for propene and only trace amounts for 1-butene, Entries 1 and 3) when compared to 1-hexene and 1-heptene (3015 and 1340 kg mol^{-1} h^{-1}, respectively), which is possibly due to the instability of the catalyst resting state with these smaller monomers. The activities at lower temperature were significantly higher for propene, 1-butene and 1-hexene. For propene, the activity was found to be ca. 11300 kg mol^{-1} h^{-1} bar^{-1} (at –40 °C!); at this level of activity, the catalyst is regarded as highly active in post-metallocene olefin polymerization catalysis.[1a] Catalytic activities that are higher at lower temperatures have previously been reported by us for the analogous lanthanide-based catalysts [Ln(*i*Pr-trisox)(CH_2SiMe_3)$_3$] and is most likely attributable to an increase in the stability of the catalyst resting state at lower temperatures.[15b,15c] 1-Heptene was polymerized relatively slowly at low temperature, and 1-octene was not polymerized at all under these conditions – a phenomenon that might well have its roots in the small size of scandium relative to the large monomers. 1-Pentene was found to polymerize with poor levels of activity (albeit with excellent tacticity control at low temperature). We attribute this to low levels of internal C_5 olefin detected in all samples of 1-pentene, which act as a poison for the catalytically active species and thus causes partial suppression of the catalytic process.

The polymerization experiments carried out at ambient temperature show a moderate level of stereocontrol (60–70% isotactic polymer, on the basis of integration of the *mmmm* pentad in the C^3 carbon resonance in the ^{13}C{^{1}H}

NMR spectra). However, despite the addition of the chlorinated solvent, the reaction temperature was observed to increase rapidly during polymerization in these experiments. Conversely, for the low temperature experiments, the evolution of heat was well controlled. In addition, the tacticity of the polymers thus formed was consistently 99% isotactic for all monomers from 1-butene to 1-heptene. The lower control in the tacticity of propene (71%) is possibly due to the fact that the smaller monomer side chain does not provide sufficient steric bulk for the trisox ligand to invoke good stereocontrol or it may be correlated with the high activity of the system, which leads to a local elevation of the temperature.

Since the polymerization only proceeds with a reasonable activity upon addition of 2 equiv. of the trityl activator, it is possible that the catalytically active species is the dicationic complex $[Sc(i\text{Pr-trisox})(CH_2SiMe_3)]^{2+}$, which results from a second alkyl abstraction. Bochmann et al. have previously reported such a "trityl effect"[17] and interpreted it as being a cation–anion contact and solvation effect that would account for the observed increase in activity by a factor of 2–5. However, in our case, the second equivalent of trityl salt leads to increases in activity of up to 10^3 which can only be accounted for by invoking a transformation of the monocation into another cationic active species. ^{1}H-, ^{13}C- and ^{29}Si- NMR tube-scale experiments performed in CD_2Cl_2 indicated that in this case 2 equiv. $Ph_3CCH_2SiMe_3$ were formed at ambient temperature alongside a C_3-symmetric scandium-containing species. This would be consistent with a monoalkyl dication, however, the species detected in solution has defied further characterization. All attempts to isolate it or to stabilize it by the addition of donor ligands have led to its nonspecific degradation. With the aim of stabilizing the mono- or dicationic active species, the phenyldimethylsilyl derivative $[Sc(i\text{Pr-trisox})(CH_2SiMe_2Ph)_3]$ (**3**) was treated with 1 and 2 equiv. $[Ph_3C][B(C_6F_5)_4]$. In this case, however, no well-defined species could be detected, and furthermore, no polymerization activity was observed under a variety of reaction conditions.

Conclusions

We have shown that the 1,1,1-tris(oxazolinyl)ethane (trisox) ligand is a remarkably efficient supporting environment for stereospecific catalysis, particularly in the context of the stereospecific polymerization of α-olefins by scandium alkyl complexes. The activation of the C_3-symmetric neutral scandium alkyl complexes has been shown to yield efficient catalysts for the polymerization of propene through to 1-heptene, in some cases with very high activity and in most cases with excellent stereocontrol. The precise nature of a potentially active dicationic species has thus far eluded us and warrants further investigation in order to build on this knowledge base in the pursuance of the next generation of "post-metallocene" polymerization catalysts.

Experimental Section

General Experimental: All manipulations of air- and moisture-sensitive complexes were performed under an atmosphere of argon by using standard Schlenk line or glove box techniques. Solvents were predried with 4 Å molecular sieves, refluxed over potassium (hexanes, tetrahydrofuran), sodium (toluene), sodium/potassium alloy (pentane) or calcium hydride (chlorobenzene) under dinitrogen and collected by distillation. 1-Pentene, 1-hexene, 1-heptene and 1-octene were dried with calcium hydride, distilled under reduced pressure, and stored in Teflon valve ampoules under argon. Deuterated solvents were dried with potassium (C_6D_6) or calcium hydride (CD_2Cl_2, C_6D_5Cl), distilled under reduced pressure, and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP NMR tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on Varian Unity plus 400, Bruker Avance 200, Bruker Avance II 400 and Avance III 600 spectrometers. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of DEPT-90, DEPT-135, and two dimensional ^{1}H–^{1}H and ^{1}H–^{13}C NMR experiments. ^{1}H and ^{13}C spectra were referenced internally to residual protio-solvent (^{1}H) and solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{29}Si NMR spectra were referenced externally to tetramethylsilane. Elemental analyses were recorded by the Microanalysis service of the University of Heidelberg. The literature compounds 1,1,1-tris(oxazolinyl)-ethane (iPr-trisox),[14b] $[Sc(i\text{Pr-trisox})Cl_3]$ (**1**),[14d] $[Sc(CH_2SiMe_3)_3(thf)_2]$[18a] and $[Sc(CH_2SiMe_2Ph)_3(thf)_2]$[18b] were prepared according to published procedures. $[Sc(i\text{Pr-trisox})(CH_2SiMe_3)_3]$ (**2**) was prepared according to a modified procedure.[15a] All other reagents were purchased from commercial suppliers and used as received unless explicitly stated.

$[Sc(i\text{Pr-trisox})(CH_2SiMe_3)_3]$ (2): $[Sc(CH_2SiMe_3)_3(thf)_2]$ (124 mg, 0.275 mmol) was dissolved in pentane and cooled to 0 °C, and a pentane solution of iPr-trisox (100 mg, 0.275 mmol) was added dropwise with stirring. The reaction was warmed to room temperature and stirred for a further 30 min, after which a large quantity of white precipitate had formed. The precipitate was isolated by filtration and dried in vacuo to afford $[Sc(i\text{Pr-trisox})(CH_2SiMe_3)_3]$ as a white solid (113 mg, 72%). $C_{32}H_{66}N_3O_3ScSi_3$ (670.10): calcd. C 57.4, H 9.9, N 6.3; found C 56.9, H 9.8, N 5.9. ^{1}H NMR (CD_2Cl_2, 399.9 MHz, 293 K): δ = 4.52 (m, 3 H, C*H*iPr), 4.43 (dd, ^2J = 9.0, ^3J = 5.3 Hz, 3 H, C*H*HO), 4.30 (app. t, J = 9.6 Hz, 3 H, CH*H*O), 2.40 (d sept, ^3J = 6.9 Hz, ^3J = 3.5 Hz, 3 H, C*H*Me$_2$), 1.72 (s, 3 H, Me$_{apical}$), 0.88 (d, ^3J = 7.1 Hz, 9 H, CH*Me*$_2$), 0.65 (d, ^3J = 6.8 Hz, 9 H, CH*Me*$_2$), –0.04 (s, 27 H, SiMe$_3$), –0.39 (overlapping d, ^2J = 10.9 Hz, 6 H, C*H*$_2$SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz, 293 K): δ = 166.8 (C=N), 71.2 (CH_2O), 71.1 (*C*HiPr), 43.6 (*C*Me$_{apical}$), 29.3 (*C*HMe$_2$), 18.7 (CH*Me*$_2$), 14.8 (Me$_{apical}$), 14.3 (CH*Me*$_2$), 4.2 (SiMe$_3$), not observed (*C*H$_2$SiMe$_3$) ppm. ^{29}Si{^{1}H} NMR (CD_2Cl_2, 39.7 MHz, 293 K): δ = –4.9 (SiMe$_3$) ppm.

$[Sc(i\text{Pr-trisox})(CH_2SiMe_2Ph)_3]$ (3): A solution of $Sc(CH_2SiMe_2Ph)_3(thf)_2$ (175 mg, 0.275 mmol) in toluene (10 mL) was cooled to –78 °C, and iPr-trisox (100 mg, 0.275 mmol) in toluene (10 mL) was added dropwise. The reaction mixture was stirred for 5 h at –78 °C, then for 30 min at room temperature, after which the solvent was removed under reduced pressure. To this yellow oil, hexane was added (15 mL), and a white–yellow precipitate was formed, which was isolated by filtration and dried in vacuo. Yield: 0.15 mmol (60%). $C_{47}H_{72}N_3O_3ScSi_3$ (856.31): calcd. C 65.9, H 8.5, N 4.9; found C 65.3, H 8.2, N 4.6. ^{1}H NMR (C_6D_6, 399.9 MHz, 293 K): δ = 7.90 (dd, ^3J = 7.9, ^4J = 1.5 Hz, 6 H, o-C_6H_5), 7.32 (t, ^3J = 7.2 Hz, 6 H, m-C_6H_5), 7.19 (t, ^3J = 7.3 Hz, 3 H), 4.29 (m, 3

Table 3. Details of the crystal structure determinations of the complexes **1**, **2** and **3**.

	2	**3**
Formula	$C_{32}H_{66}N_3O_3ScSi_3$	$C_{47}H_{72}N_3O_3ScSi_3$
Formula weight	670.12	856.31
Crystal system	monoclinic	orthorhombic
Space group	$P\ 2_1$	$P\ 2_12_12_1$
a [Å]	10.1985(2)	11.086(1)
b [Å]	19.0942(3)	20.346(2)
c [Å]	10.4478(5)	22.424(2)
β [°]	102.390(5)	90
V [Å^3]	1987.14(6)	5058.1(9)
Z	2	4
d_c [Mg m^{-3}]	1.120	1.124
μ(Mo-K_α) [mm^{-1}]	0.308	0.256
Max., min. transmission factors	0.999, 0.940	0.659, 0.589
Index ranges (indep. set) h, k, l	–14 to 14, –25 to 26, 0 to 14	–13 to 13, 0 to 24, 0 to 26
θ range [°]	2.5–30.1	1.8–25.1
T [K]	173(2)	173(2)
F(000)	732	1848
Reflections collected	11123	85122
Reflections unique, R_{int}	8316, 0.040	8994, 0.1364
Data/restraints/parameters	8316/0/378	8994/0/527
GooF on F or F^2	1.05	1.12
R Indices (obs. data) $R(F)$, $wR(F^2)$	0.035, 0.040 [$F>3\sigma(F)$]	0.0498, 0.0944 [$F>4\sigma(F)$]
R Indices (all data) $R(F)$, $wR(F^2)$	0.059, 0.216	0.0971, 0.1207
Absolute structure parameter	–0.03(2)	–0.07(4)
Largest residual peaks [e Å^{-3}]	0.407 and –0.343	0.331 and –0.324

H, C*H*iPr), 3.68 (dd, ^2J = 9.1, ^3J = 5.0 Hz, 3 H, C*H*HO), 3.38 (app. t, J = 9.5 Hz, 3 H, CH*H*O), 2.48 (d sept, ^3J = 3.8, ^3J = 6.8 Hz, 3 H, C*H*Me$_2$), 1.55 (s, 3 H, Me$_{apical}$), 0.92 (d, ^2J = 6.7 Hz, 3 H, ScC*H*H), 0.81 (d, ^2J = 6.8 Hz, 3 H, ScCH*H*), 0.77 (s, 9 H, SiMe), 0.73 (s, 9 H, SiMe), 0.47 (d, ^3J = 6.7 Hz, 9 H, CH*Me*$_2$), 0.46 (d, ^3J = 6.7 Hz, 9 H, CH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 293 K): δ = 167.0 (C=N), 148.1 (C_6H_5), 134.1 (C_6H_5), 128.3 (C_6H_5), 70.9 (CH_2O), 70.7 (*C*H*i*Pr), 43.5 (*C*Me$_{apical}$), 29.2 (*C*HMe$_2$), 18.3 (CH*Me*$_2$), 15.0 (Me$_{apical}$), 14.1 (CH*Me*$_2$), 4.0 (SiMe), 2.9 (SiMe) ppm. ^{29}Si NMR: δ = –6.89 ppm.

In Situ Reaction of 2 with Two Equivalents of [Ph$_3$C][B(C$_6$F$_5$)$_4$]: [Ph$_3$C][B(C$_6$F$_5$)$_4$] (18.4 mg, 20 μmol) was dissolved in CD_2Cl_2 (0.5 mL), and the resulting yellow solution was added to solid [Sc(*i*Pr-trisox)(CH$_2$SiMe$_3$)$_3$] (6.7 mg, 10 μmol). The white solid immediately dissolved to afford a red solution, which was placed in an NMR tube, sealed, and analyzed in situ by NMR spectroscopy. ^{1}H NMR (CD_2Cl_2, 300.1 MHz, 293 K): δ = 4.72–4.42 (m, 9 H, OCH$_2$, C*H*iPr), 2.35 (sept d, ^3J = 6.8, ^3J = 3.1 Hz, 3 H, C*H*Me$_2$), 1.78 (s, 3 H, Me$_{apical}$), 0.99 (d, ^3J = 8.9 Hz, 9 H, CH*Me*$_2$), 0.73 (d, ^3J = 8.9 Hz, 9 H, CH*Me*$_2$), 0.19 (s, 9 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, 293 K): δ = 168.8 (C=N), 148.7 [^1J(CF) = 247.4 Hz, C_6F_5], 138.6 [^1J(CF) = 233.4 Hz, C_6F_5], 136.2 [^1J(CF) = 241.2 Hz, C_6F_5], 73.8 (OCH$_2$), 71.2 (*C*H*i*Pr), 57.2 (*C*Me$_{apical}$), 30.4 (*C*HMe$_2$), 18.4 (CH*Me*$_2$), 14.7 (Me$_{apical}$), 14.2 (CH*Me*$_2$), 0.3 (SiMe$_3$) ppm. ^{19}F NMR (CD_2Cl_2, 282.4 MHz, 293 K): δ = –133.5 (s, 8 F, *o*-C_6F_5), –164.1 (t, ^3J = 20.3 Hz, 4 F, *p*-C_6F_5), –168.0 (s, 8 F, *m*-C_6F_5) ppm. ^{29}Si NMR (CD_2Cl_2, 79.5 MHz, 300 K): δ = 8.2 ppm.

Polymerization of Olefins: A solution of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (18.4 mg, 20 μmol) in chlorobenzene (0.5 mL) was added to solid **2** (6.7 mg, 10 μmol) to afford a red solution, which was further diluted to 5 mL with chlorobenzene and cooled to the desired temperature. The monomer was then added by syringe (2 mL, 1-pentene through to 1-heptene), by applying a pressure of the gaseous monomer to the reaction vessel (1 bar, propene, butene at ambient temperature) or by adding the red solution to a vessel containing the condensed monomer (butene at –40 °C). The reaction mixtures were stirred for 15 min before quenching with methanol (1 mL) and subsequently concentrated under reduced pressure to afford highly viscous liquids from which the polymers were precipitated by adding methanol (50 mL). GPC analyses of the polymers were carried out on a PSS MCS2031 Compact System equipped with three PSS SDV columns working with thf as the mobile phase at 23 °C. The flow rate was generally set at 1.00 mL min^{-1}. All measurements are relative to polystyrene standards from PSS (Polymer Standards Service, Mainz, Germany).

X-ray Crystallographic Studies: Crystal data and details of the structure determinations are listed in Table 3. Intensity data were collected at low temperature with Enraf–Nonius Kappa CCD (**2**) and Bruker AXS Smart 1000 CCD diffractometers (**3**) (Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å). Data were corrected for Lorentz, polarization and absorption effects. The structures were solved by conventional direct methods (**2**)[19] or by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors (**3**)[20] and refined by full-matrix least-squares methods based on F against all reflections with $I>3\sigma(I)$ or F^2 against all reflections.[19b] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined with a riding model.[21] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. CCDC-257336 (**2**) and -692206 (**3**) 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.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 623 and Post-Doctoral Fellowship to L. L.), the European

Union (RTN and Marie-Curie EIF fellowships to B. D. W.) and the DAAD (L. L.). We thank BASF AG, the state of Baden-Württemberg and the University of Heidelberg (postdoctoral fellowship to B. D. W. within CaRLa) for financial support.

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Received: November 12, 2008
Published Online: January 28, 2009

