Polymerization

C_3 Chirality in Polymerization Catalysis: A Highly Active Dicationic Scandium(III) Catalyst for the Isoselective Polymerization of 1-Hexene**

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The possibility of controlling the tacticity and molecular-weight distribution in polymers by ligand design provides the basis for the success of Group 4 metallocene catalysis of α-olefins.[1] Isotacticity of a poly(α-olefin) requires chirality at the active site, and the molecular shape of bent metallocenes lends itself particularly to the construction of C_2- or C_1-chiral molecular catalysts.[2] There is no report of the use of C_3-chiral stereodirecting ligands in polymerization catalysis, although they confer an element of molecular helicity to a complex which is thought to be beneficial for face selectivity in the key migratory insertion step.[3]

In recent years there has been a considerable effort to investigate "post-metallocene" catalysts[4,5] with non-Cp ligand systems which has led to alternative catalyst structures. Some of these non-metallocene Group 4 catalysts were found to be highly active in the polymerization of 1-hexene and other α-olefins; several of these catalysts exhibit living behavior.[6–13] In particular, the amine bis(phenolate) based catalysts reported by Kol and co-workers have shown remarkably high activity and may be modified to give isospecific poly(1-hexene).[6,10,12] The ubiquitous Group 4 metal catalysts aside, the focus has very recently shifted to

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[**] This work was supported by the CNRS and the EU (RTN Network "AC3S"). BASF as well as Degussa AG provided valuable chemicals. We thank Dr. André De Cian for collecting the X-ray crystallographic data.

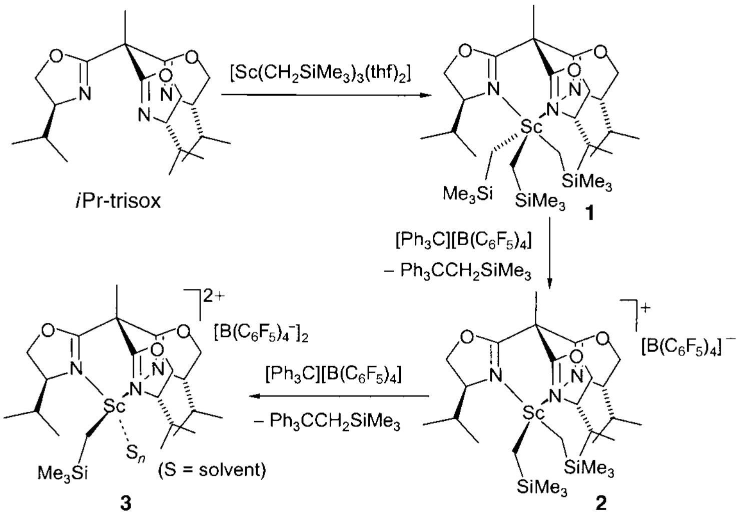
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200462804

the use of Group 3 and lanthanide metals for olefin polymerization catalysis.[14] Important contributions to the field were made by the groups of Hessen[15] and Okuda,[16] who found that the ionic radius of the metal cation plays a crucial role in determining the polymerization activity. Okuda and co-workers also noted that in the case of simple trialkyl complexes of these metals, it is most likely the monoalkyl dicationic species $[M(CH_2SiMe_3)(solvent)_n]^{2+}$ that is the catalytically active species.

The trivalent metal centers of the Group 3 elements are ideally suited for the development of C_3-symmetric polymerization precatalysts if combined with a chiral neutral tripod spectator ligand. We recently developed a new class of chiral trisoxazoline ligands, which are capable of binding facially to d-block metals and which provide the type of C_3-chiral complex geometry referred to above.[17] Based on this concept, herein we report a highly active isoselective Sc catalyst. We note that, in general, scandium-based catalysts have been studied much less than those of the other Group 3 and lanthanide metals.[18] The polymerization of ethylene with scandium complexes supported by (achiral) triazacyclononane derivatives was reported by the groups of Bercaw[19] and Mountford.[20]

The trialkyl complex [Sc(*i*Pr-trisox)$(CH_2SiMe_3)_3$] (**1**) was prepared by the reaction of the trialkyl precursor [Sc$(CH_2SiMe_3)_3(thf)_2$] with an equimolar amount of *i*Pr-trisox (Scheme 1). Complex **1** is insoluble in all common hydrocarbon solvents and is unstable in halogenated and coordinating solvents, such that characterization by NMR spectroscopy was not possible.



Scheme 1. Synthesis of the Sc complex [Sc(*i*Pr-trisox)$(CH_2SiMe_3)_3$] (**1**) and its conversion into the mono- and dicationic catalysts **2** and **3** by alkyl abstraction.

Single crystals of **1** suitable for X-ray diffraction were obtained directly from the reaction mixture, and the molecular structure is shown in Figure 1. The trisoxazoline ligand is facially coordinated, with all three oxazoline moieties bound to the metal center. We are only aware of two previous examples of crystallographically characterized scandium–oxazoline complexes: the bis(oxazolinyl)pyridine–scandium triflate complexes reported by Evans et al.[21,22] The Sc–$N_{oxaz.}$ bonds in complex **1** are significantly longer than expected (Sc–N 2.446(1)–2.464(2) Å)[23,24] which suggests that the trisoxazoline ligand is less strongly bound to the metal center in this case, presumably as a result of the steric constraints imposed by the bulky trimethylsilylmethyl groups. As a whole, this strong distortion from an octahedral coordination geometry renders the N-Sc-N′ angles more acute than expected for a facially coordinating tripod (N-Sc-N′ 73.81(5)–74.90(5)°), whereas the C-Sc-C′ angles between the sterically crowded alkyl ligands are opened up significantly (C-Sc-C′ 104.38(7)–106.69(7)°). The weakly bound nature of the trisoxazoline ligand in **1** could provide an explanation for the observed instability in halogenated and coordinating solvents, in which ligand displacement may occur.

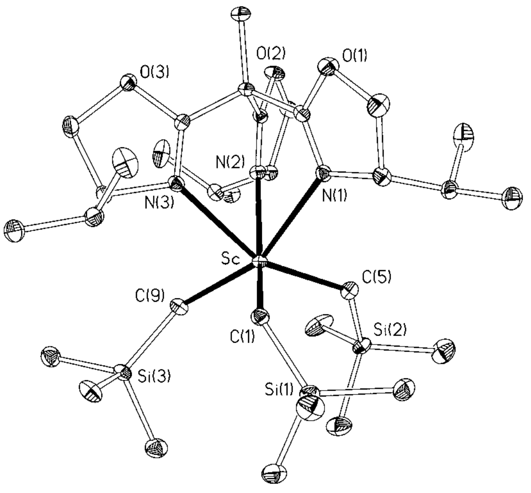


Figure 1. Structure of **1** at the 25% probability level. H atoms omitted for clarity. Principal bond lengths [Å] and angles [°]: Sc–C(1) 2.270(2), Sc–C(5) 2.272(2), Sc–C(9) 2.275(2), Sc–N(1) 2.456(2), Sc–N(2) 2.446(1), Sc–N(3) 2.464(2), C(1)-Sc-C(5) 106.69(7), C(1)-Sc-C(9) 104.38(7), C(5)-Sc-C(9) 105.51(8), N(1)-Sc-N(2) 74.90(5), N(1)-Sc-N(3) 73.95(5), N(2)-Sc-N(3) 73.81(5).

The addition of a solution of 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 or C_6D_5Br to solid **1** resulted in the formation of a new species, which we tentatively assigned as [Sc(*i*Pr-trisox)$(CH_2SiMe_3)_2$]-$[B(C_6F_5)_4]$ (**2**) based on the ^1H and ^{13}C NMR spectroscopic data and the observation of 1 equivalent of $Ph_3CCH_2SiMe_3$ (Scheme 1). Solutions of **2** (prepared in situ) in chlorobenzene are active in the catalytic polymerization of 1-hexene, albeit with rather low activity ($\approx 30\,kg\,mol^{-1}\,h^{-1}$) and somewhat variable reproducibility with respect to tacticity control.[25] Moreover, GPC analysis of the polymers obtained revealed bimodal molecular-mass distributions, thus indicating the presence of at least two catalytically active species.

It has been suggested by Okuda and co-workers that a dicationic species may, in fact, be the catalytically active species in certain rare-earth polymerization catalysts.[16] We therefore investigated the reaction of **1** with 2 equivalents of

$[Ph_3C][B(C_6F_5)_4]$. ^1H, ^{13}C, and ^{29}Si NMR tube-scale experiments indicated that in this case 2 equivalents of $Ph_3CCH_2SiMe_3$ were formed alongside a C_3-symmetric scandium-containing species, which we propose to be the dicationic complex [Sc(*i*Pr-trisox)(CH_2SiMe_3)]$[B(C_6F_5)_4]_2$ (**3**). In contrast to the monocation **2**, the complex **3** generated in situ is highly active in the polymerization of 1-hexene and displayed good tacticity control. Polymerization studies were carried out at various temperatures, and the activities and polymer characteristics are provided in Table 1.

Table 1: 1-Hexene polymerization data for **3**.[a]

T [°C]	t [min]	Yield [g]	Activity kg mol^{-1} h^{-1}	M_w	M_w/M_n
−30	3	1.01	2030	750000	1.18
−20	1.5	1.90	7600	552000	1.87
0	1	2.18	13080	354000	2.36
21	0.5	3.02	36230	227000	2.22

Yields based on 3.4 g of hexene.

Polymerization starting out at 21 °C was highly exothermic, which caused the reaction mixture to boil within 20 seconds, thus preventing control of the reaction temperature. The activity of 36200 kg mol^{-1} h^{-1} observed for **3** (Table 1) is greater by three orders of magnitude than that of the monocation **2** and comparable to the extremely high activities reported by Kol and co-workers for zirconium amine bis(phenoxide) complexes.[26] However, under these conditions the tacticity of the poly(1-hexene) produced was relatively low and GPC analysis of the polymer indicated a bimodal mass distribution ($M_W/M_n = 2.22$), which is consistent with a partial thermal degradation of the molecular catalyst. Upon decreasing the polymerization temperature to −30 °C, the activity dropped to 2030 kg mol^{-1} h^{-1}, which is still very high in absolute terms for hexene and related α-olefins.[4] At this temperature however, the poly(1-hexene) produced was highly isotactic (*mmmm* = 90 % by $^{13}C\{^1H\}$ NMR spectroscopy) (Figure 2).[27,28] GPC analysis of the polymer obtained under these conditions established a very narrow monomodal molecular-mass distribution with $M_W = 750000$ and PDI = 1.18, thus indicating that the isoselective catalytic polymerization carried out at low temperature shows living-type behavior.

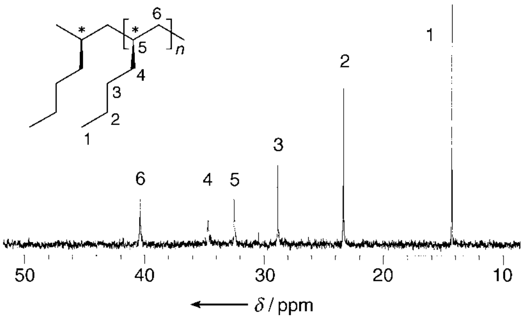


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of poly(1-hexene) obtained with catalyst **3** at −30 °C (recorded in $CDCl_3$).

The ^1H NMR spectra of all the poly(1-hexene) samples established the complete absence of olefinic end groups at all temperatures studied, indicating that chain termination by β-hydride elimination does not occur to a significant extent in this system.[29]

In conclusion we have shown that the C_3-chiral trisoxazoline is a suitable supporting ligand for scandium-catalyzed olefin polymerization whilst invoking sufficient stereocontrol over the substrate to induce a high level of tacticity in the polymer microstructure.[30] Studies into the mechanistic details of this system, the polymerization of other α-olefins, and the use of alternative Group 3 metals are currently underway.

Experimental Section

1: $[Sc(CH_2SiMe_3)_3(thf)_2]$[31] (124 mg, 0.275 mmol) was dissolved in toluene and cooled to −78 °C for the dropwise addition of a toluene solution of *i*Pr-trisox (100 mg, 0.275 mmol) with stirring. The reaction was allowed to warm 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*Pr-trisox)$(CH_2SiMe_3)_3$] as a white solid (113 mg, 72 %). When the reaction was not stirred, slow warming to ambient temperature afforded white crystals that were suitable for X-ray diffraction studies. The compound was insoluble in all hydrocarbon solvents and decomposed in halogenated solvents and $[D_8]$THF; thus no NMR data could be recorded.

2: $[Ph_3C][B(C_6F_5)_4]$ (30 mg, 0.328 mmol) was dissolved in C_6D_5Br (0.5 mL) and the resulting yellow solution was added to solid [Sc(*i*Pr-trisox)$(CH_2SiMe_3)_3$] (22 mg, 0.328 mmol). The white solid immediately dissolved to afford a red solution, which was added to an NMR tube, sealed, and analyzed in situ by NMR spectroscopy. The formation of $Ph_3CCH_2SiMe_3$ was confirmed by the ^1H and $^{13}C\{^1H\}$ NMR spectra of a sample prepared from Ph_3CCl and $LiCH_2SiMe_3$. ^1H NMR (C_6D_5Br, 300.1 MHz, 293 K): $\delta = 4.50$ (6H, m; OCH_2), 4.21(3H, t, $^3J = 9.6$ Hz; C*H**i*Pr), 2.28 (3H, sept d, $^3J = 6.6$ Hz, $^3J = 3.4$ Hz; C*H*Me_2), 1.72 (3H, s; Me_{apical}), 0.82 (9H, d, $^3J = 6.9$ Hz; CHMe_2), 0.66 (9H, d, $^3J = 6.9$ Hz; CHMe_2), 0.33 ppm (9H, s; $SiMe_3$), 0.16 (9H, s; $SiMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 75.5 MHz, 293 K): $\delta =$ 171.1 (C=N), 148.7 (C_6F_5; ^1J(CF) = 247.4 Hz), 138.6 (C_6F_5; ^1J(CF) = 233.4 Hz), 136.2 (C_6F_5; ^1J(CF) = 241.2 Hz), 72.6 (OCH_2), 71.0 (*C*H*i*Pr), 57.2 (*C*Me_{apical}), 30.0 (*C*HMe_2), 18.2 (CHMe_2), 14.5 (Me_{apical}), 14.0 (CHMe_2), 3.8 ($SiMe_3$), 0.9 ppm ($SiMe_3$); ^{19}F NMR (CD_2Cl_2, 282.4 MHz, 293 K): $\delta = -133.5$ (8F, br s; *o*-C_6F_5), −164.1 (4F, t, $^3J = 20.3$ Hz; *p*-C_6F_5), −168.0 ppm (8F, br s; *m*-C_6F_5); ^{29}Si NMR (CD_2Cl_2, 79.5 MHz, 300 K): $\delta = -21.8$ ppm.

3: $[Ph_3C][B(C_6F_5)_4]$ (20 mg, 0.02 mmol) was dissolved in CD_2Cl_2 (0.5 mL) and the resulting yellow solution was added to solid [Sc(*i*Pr-trisox)$(CH_2SiMe_3)_3$] (7 mg, 0.01 mmol). The white solid immediately dissolved to afford a red solution, which was added to an NMR tube, sealed, and analyzed in situ by NMR spectroscopy. ^1H NMR (CD_2Cl_2, 300.1 MHz, 293 K): $\delta = 4.72$–4.42 (9H, m; OCH_2, C*H**i*Pr), 2.35 (3H, sept d, $^3J = 6.8$ Hz, $^3J = 3.1$ Hz; C*H*Me_2), 1.78 (3H, s; Me_{apical}), 0.99 (9H, d, $^3J = 8.9$ Hz; CHMe_2), 0.73 (9H, d, $^3J = 8.9$ Hz; CHMe_2), 0.19 ppm (9H, s; $SiMe_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 293 K): $\delta = 168.8$ (C=N), 148.7 (C_6F_5; ^1J(CF) = 247.4 Hz), 138.6 (C_6F_5; ^1J(CF) = 233.4 Hz), 136.2 (C_6F_5; ^1J(CF) = 241.2 Hz), 73.8 (OCH_2), 71.2 (*C*H*i*Pr), 57.2 (*C*Me_{apical}), 30.4 (*C*HMe_2), 18.4 (CHMe_2), 14.7 (Me_{apical}), 14.2 (CHMe_2), 0.3 ppm ($SiMe_3$); ^{19}F NMR (CD_2Cl_2, 282.4 MHz, 293 K): $\delta = -133.5$ (8F, s; *o*-C_6F_5), −164.1 (4F, t, $^3J = 20.3$ Hz; *p*-C_6F_5), −168.0 ppm (8F, s; *m*-C_6F_5); ^{29}Si NMR (CD_2Cl_2, 79.5 MHz, 300 K): $\delta = 8.2$ ppm.

Polymerization of 1-hexene: $[Ph_3C][B(C_6F_5)_4]$ (20 mg, 22 μmol) was dissolved in C_6H_5Cl (0.5 mL) and the resulting yellow solution was added to solid [Sc(*i*Pr-trisox)(CH_2SiMe_3)$_3$] (7 mg, 10 μmol). The white solid immediately dissolved to afford a red solution. The red solution was added to a Schlenk tube containing 1-hexene (5 mL), which had been precooled to the desired temperature for at least 10 min prior to the addition. The reaction was judged complete when the reaction could no longer be stirred owing to the high viscosity of the poly(1-hexene). The volatile components were removed under reduced pressure and the residue dissolved in THF. The solution was transferred into a preweighed flask, and the THF was removed under reduced pressure to yield poly(1-hexene) as a waxy solid.

Crystal data for **1**: $C_{32}H_{66}N_3O_3ScSi_3$, yellow blocks, crystal dimensions $0.20 \times 0.20 \times 0.02\ mm^3$, $M = 670.12$, monoclinic, space group $P2_1$, $a = 10.1985(2)$, $b = 19.0942(3)$, $c = 10.4478(2)$ Å, $\beta = 102.390(5)°$, $U = 1987.14(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.12\ g\,cm^{-3}$, $F(000) = 732$, $\mu = 0.308\ mm^{-1}$, trans. (min/max): 0.940/0.999, $T = 173$ K, $Mo_{K\alpha}$, $-14 < h < 14$, $-25 < k < 26$, $-14 < l < 14$, 11123 reflections collected ($2.5 < \theta < 30.05°$) on a Nonius Kappa CCD diffractometer, 8316 ($I > 3\sigma(I)$) used in the structure refinement (378 parameters refined); $R = 0.035$, $R_w = 0.040$, GOF = 1.050; largest peak 0.407 e Å^{-3}. CCDC-257336 contains 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.

Received: December 3, 2004

Keywords: homogeneous catalysis · polymerization · polymers · scandium · stereocontrol

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[25] The highest tacticity control is observed at +40 °C while the tacticity is lower at ambient temperature and below, which is probably in part due to aggregation of the catalyst (and manifest in the bimodal GPC traces). This observation is only consistent with enantiomorphic tacticity control.

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[29] The catalyst displays living-type behavior at low temperatures with negligible chain termination. However, chain termination and catalyst decomposition occur concurrently at elevated temperatures at which the reaction cannot be controlled owing to the high exothermicity. This seems to entail homolytic M–C cleavage under these conditions, and there is much literature precedent for the thermal instability of scandium alkyl complexes.[18] It is thus not surprising that we observe decomposition under the highly exothermic conditions employed in this study. However, the exact nature of this process remains unknown. In the ^{1}H NMR spectra of all the polymer samples produced by the dicationic species, no signals attributable to olefinic end groups were observed to within the detection limits of the instrument. Therefore, although we cannot rule out β-hydride elimination altogether, it is certainly not a significant contributor.

[30] An additional control experiment to distinguish enantiomorphic from chain-end tacticity control would entail the use of an achiral trisox ligand. We previously reported such a ligand that is dimethyl-substituted in the 4-position of the oxazolines: S. Bellemin-Laponnaz, L. H. Gade, *Chem. Commun.* **2002**, 1286; however, we found that for steric reasons, this substitution pattern normally precludes the coordination of this ligand as a tripod to a single metal center, and this also seems to be the case for the scandium complexes. Since the unsubstituted oxazoline derivatives were unstable und thus inaccessible, we are unable to perform this experiment.

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