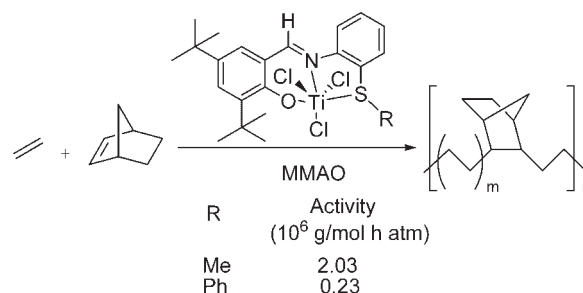


Ethylene-Norbornene Copolymerization by New Titanium Complexes Bearing Tridentate Ligands. Sidearm Effects on Catalytic Activity^a

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The Ti complexes containing tridentate $[O^-NS^R]$ ($R = \text{Me}, ^i\text{Pr}$) ligands with alkylthio sidearms were prepared. The methylthio ether complex ($R = \text{Me}$ shown in the Scheme) exhibits an excellent activity for copolymerization of ethylene with norbornene upon activation with MMAO, which is 10 times more active than the corresponding phenylthio one ($R = \text{Ph}$).



Introduction

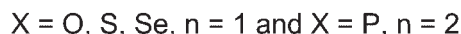
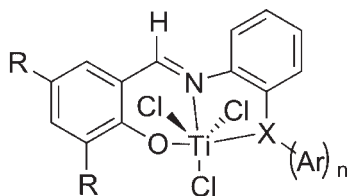
Development of effective catalysts for olefin polymerization/copolymerization is of fundamental importance both in basic research and industrial applications. In this connection, a series of single-site catalysts, including metallocenes^[1] and non-metallocenes,^[1d,2–9] have been prepared over the decades for the production of new polyolefin materials with well-defined architecture. In recent years, non-metallocene molecular catalysts have attracted considerably attention.^[2–9] Group 4 metal

complexes containing phenoxy-imine ligands are among the typical examples.^[4–9] These bis-ligated species of the type $[O^-N]_2MCl_2$ are excellent pre-catalysts for olefin polymerization including ethylene living polymerization,^[5,6] highly syndiospecific propene living polymerization,^[7] living copolymerization of ethylene with α -olefin,^[8] and for the synthesis of functional block copolymers.^[9]

In view of the advantages of phenoxy-imine backbone^[4–9] and the role of pendant heteroatom groups in catalysis,^[10–12] we have designed a number of tridentate $[O^-NX^R]$ ligands where $X = O, S, Se,$ and P (Figure 1),^[13] and investigated the effects of aryl substituents on the performance of the resultant Ti complexes $[O^-NX^R]TiCl_3$ in olefin polymerization/copolymerization. These complexes prove to be highly active catalysts for ethylene polymerization and copolymerization with α -olefin upon activation with MMAO (modified methylaluminoxane). However, they show only a moderate activity for ethylene-norbornene copolymerization^[13b,13c] which leads to one of the most important high performance polymer materials with many unique properties.^[14,15] We wondered whether the appended sidearm plays a role in the catalytic activity. Considering the steric/electronic nature of alkyl versus aryl substituents on the thio-sidearm, we synthesized new alkylthio sidearmed complexes $[O^-NX^R]TiCl_3$ and

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^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.



■ Figure 1. Structure of $[O^-NX^A]TiCl_3$ complexes.

investigated their catalytic activity. It is found that the methylthio complex **4a** is an excellent catalyst for ethylene-norbornene copolymerization with an activity of 2.03×10^6 g Polymer (mol Ti) $^{-1}$ h $^{-1}$ atm $^{-1}$ which is about 10 times more active than the corresponding arylthio counterparts. These findings are reported in this communication.

Experimental Part

Materials

All manipulations of air- and moisture-sensitive compounds were carried out under N₂ atmosphere using standard Schlenk or cannula techniques, or in a glovebox. ¹H and ¹³C NMR spectra were recorded on a Bruker AM300 spectrometer at 300.1 and 75.5 MHz, respectively. All chemical shifts were reported in δ units with reference to internal TMS (0.00 ppm). Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 983 spectrometer. Elemental analyses were performed on a Vario EL III instrument. Methylene chloride was distilled over CaH₂ prior to use. All other

organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Modified methylaluminumoxane was purchased from Akzo Chemical as a 10 wt.-% solution in toluene. Polymerization-grade ethylene was purified before used. Deuterated solvents were dried using standard procedures and stored in the glovebox. Compounds **1b**,^[16] **2a–b**,^[13c] and **4c**^[13b,13c] (Scheme 1) were prepared according to literature methods. Other chemicals were used as received unless otherwise noted. X-ray crystallographic data was collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo K α radiation. The structure of **4b** showed a half dichloromethane of solvation. Further details were included in the Supporting Information.

Synthesis of Titanium Complexes **4a** and **4b**

Compounds **1a–b** were prepared from *o*-chloride nitrobenzene with sodium mercaptide in dimethyl sulfoxide (DMSO) or in ethanol. Ligands **3a** and **3b** were synthesized by condensation of 3,5-*tert*-butylsalicylaldehyde with appropriate 2-alkylsulfanyl-aniline **2a–b**, as shown in Scheme 1.

4a: To a suspension of potassium hydride (KH) (0.079 g, 2.0 mmol) in tetrahydrofuran (THF) (10 mL) was added a solution of **3a** (0.711 g, 2.0 mmol) in THF (10 mL) at -78°C . The resulting suspension was warmed to room temperature and stirred for 2 h. After removal of the solvent under vacuum, toluene (40 mL) was added to the residue to give a yellow solution. It was then added dropwise to a solution of TiCl₄ (0.379 g, 2.0 mmol) in toluene (10 mL) at room temperature, and the mixture was stirred overnight. The solid was filtered off and washed with toluene (20 mL \times 2). The combined organic solutions were concentrated under vacuum to about 25 mL and then kept at -30°C overnight to afford **4a** as reddish crystals (0.467 g, 46%).

¹H NMR (300 MHz, CDCl₃): δ = 8.76 (s, 1H, CHN), 7.74 (d, J = 2.4 Hz, 1H, Ar-H), 7.66–7.62 (m, 1H, Ar-H), 7.52–7.43 (m, 4H, Ar-H), 3.06 (s, 3H, SCH₃), 1.54 (s, 9H, C(CH₃)₃), 1.34 (s, 9H, C(CH₃)₃).

¹³C NMR (75.5 MHz, CDCl₃): δ = 163.7 (CH=N), 160.6, 150.4, 147.6, 136.4, 133.2, 133.0, 131.1(2), 131.0(9), 130.4, 129.9, 127.5, 119.2 (Ar-C), 35.4, 34.8, 31.2, 29.8, 27.5.

IR (KBr, cm⁻¹): ν : 2964 (s), 1605 (m), 1590 (m), 1544 (vs), 1485 (s), 1247 (s), 1128 (m), 762 (m).

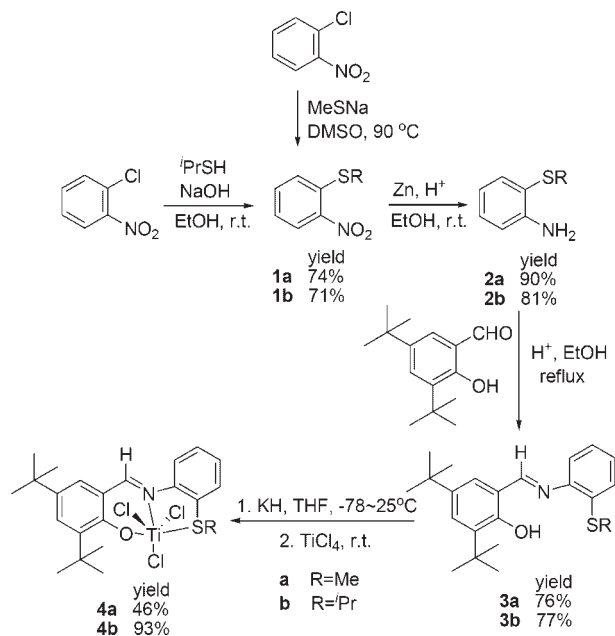
C₂₂H₂₈Cl₃NOSTi: Calcd. C, 51.94; H, 5.55; N, 2.75. Found: C, 50.64; H, 5.51; N, 2.53.

4b was prepared using the same procedure as that reported for **4a**. Reagents: KH (0.099 g, 2.5 mmol), ligand **3b** (0.947 g, 2.5 mmol), and TiCl₄ (0.570 g, 3.0 mmol). After the reaction was complete, the red solid was collected and extracted with CH₂Cl₂ (60 mL). Concentration of the clear CH₂Cl₂ solution gave **4b** as a red solid (1.230 g, 93%). X-ray-quality crystals were obtained by recrystallization from a CH₂Cl₂/hexane solution.

¹H NMR (300 MHz, CDCl₃): δ = 8.82 (s, 1H, CHN), 7.76 (s, 1H, Ar-H), 7.63 (d, J = 8.1 Hz, 1H, Ar-H), 7.60–7.50 (m, 2H, Ar-H), 7.48–7.35 (m, 2H, Ar-H), 4.06 (sept, J = 6.6 Hz, 1H, CH(CH₃)₂), 1.54 (s, 15H, C(CH₃)₃, CH(CH₃)₂), 1.37 (s, 9H, C(CH₃)₃).

¹³C NMR (75.5 MHz, CDCl₃): δ = 163.5 (CH=N), 161.7, 152.0, 147.4, 136.8, 136.2, 133.2, 132.0, 131.0, 129.1, 127.5, 126.0, 119.6 (Ar-C), 47.2, 35.4, 34.8, 31.2, 30.0, 22.1.

IR (KBr, cm⁻¹): ν : 2961 (s), 2908 (w), 2866 (w), 1587 (m), 1543 (s), 1471 (m), 1243 (s), 858 (s), 759 (s).



■ Scheme 1.

$C_{24}H_{32}Cl_3NOSTi$: Calcd. C, 53.70; H, 6.01; N, 2.61. Found: C, 53.16; H, 6.14; N, 2.23.

General Procedure of Ethylene-Norbornene Copolymerization

A flame-dried Schlenk flask was charged with ethylene and placed in an oil bath at a desired temperature. A desired amount of freshly distilled toluene was transferred into the flask, and saturated with ethylene. Norbornene and MMAO were injected into the flask in sequence via a syringe, and the mixture was stirred for 5 min. When a toluene solution of the catalyst precursor was added through a syringe, the copolymerization started. After a desired time, the copolymerization was quenched with acidified ethanol, and poured into a large amount of acidified ethanol (300 mL, 10 vol.-% HCl in ethanol). The precipitated copolymer was collected, washed with ethanol, and then dried at 50 °C under vacuum till a constant weight.

Copolymer Characterization

The ^{13}C NMR data of the copolymers were recorded by dissolving the samples in (D_4)-*o*-dichlorobenzene at 110 °C. Molecular weights (\bar{M}_w , and \bar{M}_n) and polydispersities were determined on a Waters alliance GPC 2000 series at 135 °C using a polystyrene calibration. 1,2,4-trichlorobenzene was employed as a solvent at a flow rate of 1.0 mL·min $^{-1}$. The DSC measurements were performed on a Perkin-Elmer Pyris 1 Differential Scanning Calorimetry at a heating rate of 10 °C·min $^{-1}$ from -20 °C to 200 °C. The reported values originated from the second heating scan.

Results and Discussion

Synthesis and Characterization of Ti Complexes

The synthetic routes to ligands **3a–b** and complexes **4a–b** are shown in Scheme 1. Treatment of 2-chloronitrobenzene with 1.0 equiv of sodium thiomethoxide in DMSO at 90 °C afforded 2-methylthionitrobenzene **1a**. Reaction of 2-chloronitrobenzene with 1.1 equiv of 2-propanethiol and NaOH in EtOH at room temperature afforded 2-isopropylthionitrobenzene **1b**,^[16] followed by reduction of zinc dust in the presence of glacial acetic acid to generate the corresponding anilines **2**.^[13c] The phenoxy-imine [O $^-$ NS R] tridentate ligands **3a–b** were readily synthesized by condensation reaction of 3,5-di-*tert*-butylsalicylaldehyde with 1 equiv of 2-alkylthiolaniline **2a–b** in acetic acid in good yields. Imines **3a–b** were prepared as pure products by directly cooling the reaction mixture to low temperature. After deprotonation of **3** by 1 equiv of KH in THF, the resultant [**3**] $^-K^+$ reacted with 1.2 equiv of TiCl $_4$ at room temperature in toluene to give the desired trichloride titanium complexes **4a–b** in 46% and 93% yields, re-

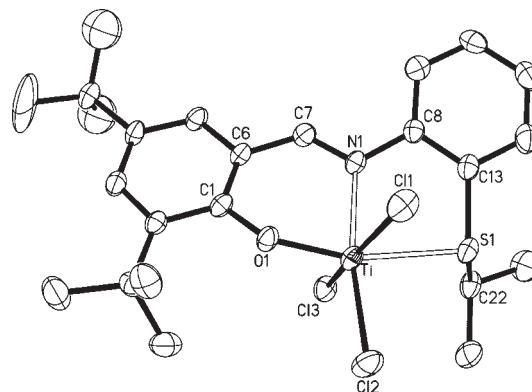


Figure 2. Molecular structure of **4b** (the solvated CH $_2$ Cl $_2$ molecule is not shown). Selected bond lengths (Å) and angles (deg.): Ti–O(1), 1.791(4); Ti–N(1), 2.187(5); Ti–S(1), 2.586(2); Ti–Cl(1), 2.329(2); Ti–Cl(2), 2.248(2); Ti–Cl(3), 2.294(2), O(1)–C(1), 1.354(6); C(1)–C(6), 1.382(7); C(6)–C(7), 1.442(7); C(7)–N(1), 1.308(6); N(1)–C(8), 1.438(7); C(8)–C(13), 1.388(7); C(13)–S(1), 1.778(6); S(1)–C(22), 1.838(6); O(1)–Ti–Cl(2), 105.6(1); N(1)–Ti–Cl(2), 169.5(1); Cl(1)–Ti–Cl(3), 165.7(1); O(1)–Ti–S(1), 162.2(1).

spectively. Complex **4b** was directly extracted with CH $_2$ Cl $_2$ as a pure product from the reaction mixture in an excellent yield. Complex **4a** was further purified by recrystallization from toluene upon cooling to -30 °C.

All compounds were fully characterized by 1H and ^{13}C NMR, IR and elemental analyses. The unique imine proton chemical shift $\delta_{CH=N}$ was observed at ca 8.6 ppm in **3a–b**, which was downfield shifted to ca 8.8 ppm upon complexation with the Ti(IV) ion in complexes **4a–b**. The characteristic CH=N carbon chemical shift at $\delta_c \approx 163$ ppm was found in the ^{13}C NMR spectra of both ligands and complexes.

The molecular structure of complex **4b** was further confirmed by single-crystal X-ray analyses.^[17] The Ti atom is bonded to three chlorine atoms, one sulfur, one nitrogen and one oxygen atom in a distorted-octahedral geometry with the chlorine atoms in a *mer* disposition, as shown in Figure 2. This structure is similar to that of complex **4c** (Figure 3).^[13] Such configuration is probably favorable for the insertion of olefin, thus facilitating polymerization. The Ti–S distance of 2.586(2) Å, the Ti–N distance of 2.187(5)

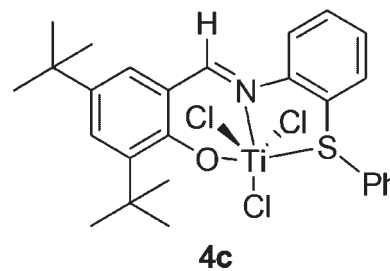


Figure 3. Structure of complex **4c**.

Table 1. Results of Ethylene-Norbornene Copolymerization^{a)}

Entry	4	NBE	Al/Ti	T_p	Yield	Activity ^{b)}	NBE content ^{c)}	\overline{M}_w ^{d)}	$\overline{M}_w/\overline{M}_n$ ^{d)}	T_g
		mmol		°C				g	°C ^{e)}	
1	4a	10	500	50	1.801	1.80	21.7	7.59	1.54	n.o. ^{f)}
2	4a	20	500	50	2.033	2.03	43.9	25.63	1.54	109.3
3	4a	30	500	50	1.342	1.34	47.1	32.35	1.71	117.7
4	4a	40	500	50	1.163	1.16	48.8	39.16	1.53	125.9
5	4a	20	250	50	1.760	1.76	41.8	30.34	1.54	107.8
6	4a	20	1 000	50	2.380	2.38	37.5	23.34	1.26	84.2
7	4a	20	2 500	50	2.745	2.75	36.0	15.30	1.37	n.o.
8	4a	20	500	0	0.088	0.09	13.7	44.27	1.55	-7.7 ^{g)}
9	4a	20	500	30	1.010	1.01	28.2	35.24	1.63	46.4
10	4a	20	500	70	2.014	2.01	40.8	18.24	1.57	110.0
11	4b	20	500	50	0.231	0.23	31.3	13.72	1.80	58.1
12	4c	20	500	50	0.229	0.23	30.9	6.79	1.49	66.6

^{a)}Copolymerization Condition: ethylene, 0.1 MPa; V_{total} , 45 mL; catalyst, 4 μmol (0.003 M in toluene); reaction time, 15 min; NBE, 5.95 M in toluene; ^{b)}Activity: 10^6 g Polymer (mol Ti)⁻¹ h⁻¹ atm⁻¹; ^{c)}mol-%, determined by ¹³C NMR spectroscopy; ^{d)}Determined by GPC relative to polystyrene standards, $\times 10^{-4}$ g · mol; ^{e)}Determined by DSC; ^{f)}n.o. = not observed. $T_m = 111.6$ °C; ^{g)} $T_m = 51.3$ °C.

Å, and the average Ti-Cl distance of 2.290(2) Å in **4b** are close to the corresponding values observed in **4c**.^[13]

Ethylene-Norbornene Copolymerization

In comparison with phenylthio complex **4c**, methylthio complex **4a** is a much better catalyst for ethylene-norbornene copolymerization in the presence of MMAO. As shown in Table 1, the reaction conditions influenced strongly the copolymerization behaviors and the structures of the copolymers. For example, the copolymerization activity was slightly decreased with an increasing feed of norbornene from 10 to 40 mmol at 1 atmosphere of ethylene (entries 1–4). Accordingly, norbornene incorporation and molecular weight (\overline{M}_w) of the copolymer increased (entries 1–4). When 40 mmol of norbornene was fed, the molar incorporation ratio of norbornene was up to 48.8 mol-%. Under the optimal condition, the highest activity (2.03×10^6 g Polymer (mol Ti)⁻¹ h⁻¹ atm⁻¹; entry 2) was observed for **4a**, which was 10 times higher than the phenylthio complex **4c** (entry 2 versus 12). When Al/Ti ratio was varied from 250 to 2 500, the activity increased but both norbornene incorporation and molecular weight were decreased (entries 2, 5–7). The decrease of \overline{M}_w was probably ascribed to the chain-transfer to aluminum center. It was interesting to note that when Al/Ti was as low as 250, the catalyst **4a** still gave a very

good copolymerization activity of 1.76×10^6 g Polymer (mol Ti)⁻¹ h⁻¹ atm⁻¹ (entry 5). The glass transition temperature (T_g) of the copolymer was increased with an increase of the norbornene incorporation (entries 1–4). As the copolymerization temperature was raised from 0 to 70 °C, the catalytic activity was firstly increased and then decreased (entries 2, 8–10). The highest activity was achieved at 50 °C. Steric factors played a governing role. For instance, replacement of methyl group in **4a** with an isopropyl group (**4b**) resulted in a big decrease in both catalytic activity and norbornene incorporation (entries 2 versus 11). The molecular weight distribution of the copolymers generated from **4a–c** was relatively narrow, among 1.3 to 1.8, similar to those produced by single-site catalysts.^[18]

Conclusion

The Ti complexes [O⁻NS^R]₂TiCl₃ (R = Me (**4a**), ^{*i*}Pr (**4b**)) containing tridentate phenoximine ligands with alkylthio sidearms were prepared. In the presence of MMAO, complex **4a** has proven to be an excellent catalyst for ethylene-norbornene copolymerization. Its activity was about one magnitude higher than the corresponding phenylthio complex **4c**, indicating that the steric hindrance of the substituents on sulfur atom in the pre-catalyst strongly influenced the copolymerization behavior. The increase in

the steric hindrance led to an obvious decrease in both catalytic activity and comonomer incorporation ratio. Further study aiming at the mechanism of copolymerization is currently in progress.

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