LIGAND MIGRATION IN THE REACTION OF TITANIUM COMPLEXES WITH $AlMe_3$

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contribution to the area of titanium chemistry.

Five different titanium compounds *cis*-$[Ti(\eta^2\text{-hbo})_2(OEt)_2]\cdot 0.5$toluene (**1**), *cis*-$[TiCl_2(\eta^2\text{-thp})_2]$ (**2**), $[TiCl_2(edbp)_2]$ (**3**), $[Ti_2(\mu\text{-OMe})_2(edbp)_2(Me)_2]$ (**6**), $[Ti_2(\mu\text{-OMe})_2(edbp)_2(OMe)_2]$ (**7**) (Hhbo = 2-(2-hydroxyfenyl)benzoxazole, Hthp = tetrahydropyran-2-methanol, H_2edbp = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)), have been prepared and tested in combination with MAO as catalysts for propene polymerization and ethene and oct-1-ene copolymerization with the aim of gaining insight into the structure of the active species. Investigation of the **1**/$AlMe_3$ or **2**/$AlMe_3$ systems resulted in isolation of $[Al(\eta^2\text{-hbo})_2(Me)]$ (**4**) and $[Al_2(\mu_2\text{-}\eta^2\text{-thp})_2(Me)_4]$ (**5**) in high yields. This indicates that the trimethylaluminum contained in MAO abstracts ligands from **1** or **2**, affecting thus the catalytic performance of the **1**,**2**/MAO catalysts. In contrast, compound **3** reacted with MAO affording methylated product **6**. Accordingly, the **3**/MAO catalyst differed from the above ones, furnishing at 70 °C e.g., narrow molecular weight polypropylene (M_n = 454 000; M_w/M_n = 2.49; T_m = 158.2 °C).

Keywords: Polymerizations; Polymerization catalysts; Titanium complexes; Aluminum complexes; Lewis acids; Ligand migration; Chelates; X-ray diffraction.

Within the last decade, we have witnessed an increasing and rapid development of high-performance olefin polymerization catalysts based on soluble, well-defined transition metal complexes[1]. Many convenient methods for generating these species are now available; among the most used are the reaction of a metal dihalide L_nMX_2 (L = auxiliary ligand) with olefin MAO or the reaction of a dialkyl species L_nMR_2 with either fluorinated boranes[2–6], borate salts[8–12], or aluminate salts[13]. Recent interest in the development of non-metallocene complexes for the polymerization of α-olefins has created

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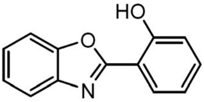
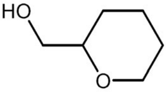
a new range of octahedral titanium chelating complexes with alkoxo[14] and phenoxo-imine[15] ligands. Fujita and co-workers at Mitsui Chemicals developed these ligands further and reported in a series of publications of new highly active Group-4 olefin polymerization catalysts[16]. The fact that the transition metal precursors are coordinatively saturated implies that one of the functions of the aluminum cocatalysts is to trigger a reorganization around the metal. An extensive study shows that the activity, molecular weight distribution (M_w/M_n), isotacticity and melting point of polymers depend on cocatalyst composition[15]. In this paper, we describe the preparation and characterization of new titanium and aluminum compounds and an evaluation of the possible role played by the ligands in catalyst active site formation. First, we wanted to study the ligands hbo and thp and their possible involvement in some of the transformations that may occur during the catalytic cycle. Second, we wished to expand our study to a system containing the chelating H_2edbp resulting in a ligand more strongly bound ligand to the metal center.



Hhbo



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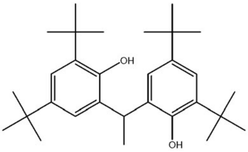


H_2edbp

EXPERIMENTAL

Materials and Methods

All reactions were conducted under N_2 atmosphere. Chemicals were treated as follows: THF, distilled from CuCl, predried over solid NaOH, and then distilled from Na/benzophenone; toluene, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2 and then P_2O_5; hexane, distilled from P_2O_5; methanol, ethanol and CH_3CN distilled from CaH_2; tetrahydropyran-2-methanol (Hthp, Aldrich) distilled prior to use. $Ti(OMe)_4$ (Aldrich), $Ti(OEt)_4$ (Aldrich) and $AlMe_3$ (as 2 M solutions in toluene; Aldrich), 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (H_2edbp; Aldrich), 2-(2-hydroxyphenyl)benzoxazol (Hhbo; Aldrich) and all deuterated solvents (Cambridge Isotope Laboratories) were used as received. The MAO used was of the grade MMAO-12 (commercial MAO made via hydrolysis route) and was used as purchased as a 10 wt.% solution in toluene from Albermarle.

NMR spectra were obtained at room temperature (25 °C) on a Bruker ESP 300E spectrometer, unless otherwise mentioned. Chemical shift data (δ, ppm) are referenced to the residual protons in deuterated solvents. Coupling constants, *J*, are given in Hz. IR spectra (in cm^{-1}) were measured on a Perkin–Elmer 180 instrument in Nujol mulls. Microanalyses were conducted with an ASA-1 (Karl-Zeiss, Jena) instrument.

Polymerization. General Procedures

Propene polymerizations. All feeds were passed through columns of activated alumina and the Q-5™ catalyst prior to introduction to the reactor. A stirred 2-l jacketed Autoclave Engineer's Zipper–Clave™ reactor was charged with about 625 g of Isopar-E solvent and about 150 g of propene. Hydrogen was added as a molecular weight control agent by differential pressure expansion from a 75-ml addition tank (ΔP_m = 350 kPa). The reactor was heated to 70 °C and allowed to equilibrate. The metal complex and MMAO-12 (Ti:Al 1:1000) were mixed as dilute toluene solutions, transferred to a catalyst addition tank and injected into the reactor through a stainless steel transfer line. Heat was continually removed from the reaction with a cooling coil in the jacket.

Ethene/oct-1-ene copolymerizations. All feeds were passed though columns of activated alumina and the Q-5™ catalyst prior to introduction to the reactor. A stirred 2-l Parr reactor was charged with about 740 g of Isopar-E solvent and 118 g of oct-1-ene comonomer. Hydrogen was added as a molecular weight control agent by differential pressure expansion from a 75-ml addition tank at 25 psi (2070 kPa). The reactor contents were then heated to the polymerization temperature 140 °C and saturated with ethene at 500 psi (3.4 MPa). The metal complex and MMAO-12 (Ti:Al 1:1000) were mixed as dilute toluene solutions, transferred to a catalyst addition tank and injected into the reactor through a stainless steel transfer line. The polymerization conditions were maintained for 15 min with ethene added on demand. Heat was continually removed from the reaction with an internal cooling coil.

The resulting polymerization solution was removed from the reactor, quenched with isopropyl alcohol, and stabilized by the addition of 10 ml of a toluene solution of ca. 67 mg of a hindered phenol antioxidant (Irganox™ 1010 from Ciba Geigy Corp.) and ca. 133 mg of a phosphorous stabilizer (Irgafos™ 168 from Ciba Geigy Corp.). Between polymerization runs a wash cycle was conducted in which 850 g of mixed alkanes was added to the reactor, then heated to 150 °C and then the solvent drained immediately prior to a new polymerization run.

Polymers were recovered by drying at 140 °C in a vacuum oven set for about 20 h. High-temperature gel permeation chromatography (GPC) analyses of polymer samples carried out in 1,2,4-trichlorobenzene at 135 °C on a Waters 150C high-temperature instrument. A polystyrene/polyethylene or polystyrene/polypropylene universal calibration was carried out using narrow-molecular-weight-distribution polystyrene standards from Polymer Laboratories.

X-ray Crystallographic Study

Crystal data collection and refinement for compounds **1**–**4** are summarized in Table I. The poor quality and the week diffracting power of compounds **5** and **6** allowed any partial structure determination in these case and unit cell parameters and selected bond lengths are given in captions to Figs 5 and 6. Preliminary examination and collection of intensity data were carried out on a KUMA CCD KM-4 κ-axis diffractometer with graphite-monochromatized MoKα. All data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Kuma Diffraction programs. The structures were solved by direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL software[17a]. Carbon-bonded hydrogen atoms were included in calculated positions and refined in the riding mode. A high degree of anisotropy observed form some carbon atoms of ethoxy group in **1** and toluene in **1** and **3** molecules

TABLE I
X-ray data for compounds **1**, **2**, **3** and **4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{67}H_{60}N_4O_{12}Ti_2$	$C_{12}H_{22}Cl_2O_4Ti$	$C_{30}H_{44}Cl_2O_2Ti$	$C_{27}H_{19}AlN_2O_4$
Formula weight	1208.99	349.10	555.42	462.42
T, K	100(1)	100(1)	100(1)	100(1)
Space group	P-1	$P2_12_12$	$Cmc2_1$	$P2_1/c$
Crystal system	triclinic	orthorhombic	orthorhombic	monoclinic
Unit cell dimensions				
a, Å	13.061(3)	8.970(2)	16.050(4)	12.096(2)
b, Å	13.385(3)	9.862(3)	12.687(5)	21.255(2)
c, Å	16.889(3)	8.780(2)	17.873(4)	10.668(2)
α, °	102.64(3)	90	90	90
β, °	92.25(3)	90	90	92.99(2)
γ, °	93.95(3)	90	90	90
V, Å^3	2869.7(10)	776.7(3)	3639.4(19)	2739.0(7)
Z	2	2	4	4
D_c, Mg/m^3	1.399	1.493	1.014	1.121
F(000)	1260	364	1384	960
Habit	plate	plate	block	prism
Crystal size, mm	0.5×0.4×0.08	0.6×0.4×0.1	0.4×0.3×0.3	0.4×0.2×0.2
μ, mm^{-1}	0.348	0.901	0.402	0.105
θ range, °	2.05 to 25.06	3.85 to 28.49	3.41 to 28.44	3.37 to 28.56
Number of reflections measured	10397	5423	10440	17839
Number of unique reflections	10025	1835	3438	6417
R_{int}	0.0251	0.0402	0.0652	0.0473
Number of observed reflections	6562 [$I > 2\sigma(I)$]	1655 [$I > 2\sigma(I)$]	2888 [$I > 2\sigma(I)$]	3804 [$I > 2\sigma(I)$]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0427, wR_2 = 0.1161	R_1 = 0.0310, wR_2 = 0.0546	R_1 = 0.0540, wR_2 = 0.1230	R_1 = 0.0654, wR_2 = 0.1880
S	1.045	1.057	1.042	1.088

indicated possible disorder which could not be resolved. The disordered lattice toluene molecules in **3** were eliminated from the refinement using PLATON/SQUEEZE[17b]. All non-hydrogen atoms were refined with anisotropic displacement parameters.

CCDC 225500–225503 (for compounds **1**–**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Syntheses

cis-[Ti(η-hbo)$_2$(OEt)$_2$]·0.5toluene (**1**). 2-(2-Hydroxyfenyl)benzoxazol (Hhbo) (2.01 g, 9.52 mmol) was dissolved in ethanol (60 ml) and Ti(OEt)$_4$ (1.09 g, 4.78 mmol) was added. The yellow solution was stirred for 2 h. The light yellow precipitate was filtered off, washed with hexane (2 × 10 ml) and dried to give crude product. Crystals suitable for the structure determination were obtained from solution after 48 h. Total yield 2.63 g (91%). For $C_{30}H_{26}N_2O_6Ti$ (558.5) calculatad: 64.52% C, 4.69% H, 5.02% N, 8.58% Ti; found: 64.49% C, 4.73% H, 4.99% N, 8.59% Ti. ^{1}H NMR (300 MHz, CD$_3$CN): 1.17 (t, 6 H, OCH$_2$C**H**$_3$, $J_{\text{H-H}}$ = 7.0); 3.59 (q, 4 H, OC**H**$_2$CH$_3$, $J_{\text{H-H}}$ = 7.0); 7.14 (m, 4 H, 4,6-**H**C$_6$H$_4$OCONC$_6$H$_4$); 7.53 (m, 8 H, 3′,4′,5′,6′-**H**C$_6$H$_4$OCONC$_6$H$_4$); 7.78 (m, 1 H, 5-**H**C$_6$H$_4$OCONC$_6$H$_4$); 7.84 (m, 1 H, 3-**H**C$_6$H$_4$OCONC$_6$H$_4$). IR: 392 (w), 430 (w), 518 (w), 588 (m), 632 (m), 672 (w), 696 (m), 746 (s), 820 (w), 856 (m), 876 (m), 904 (m), 1052 (s), 1104 (m), 1136 (m), 1124 (m), 1136 (m), 1248 (m), 1266 (m), 1320 (m), 1354 (s), 1498 (m), 1538 (s), 1576 (m) 1610 (s), 1618 (m).

cis-[TiCl$_2$(η^2-thp)$_2$] (**2**). TiCl$_4$ (3.45 g, 18.20 mmol) was dissolved in toluene (50 ml) and tetrahydropyran-2-methanol (Hthp) (4.23 g, 36.41 mmol) was added. Evolution of HCl started immediately and the gas was removed under vacuum. The mixture was next stirred at room temperature under applied vacuum for 12 h until an oil was formed. Then hexane (100 ml) was added and the resulting suspension was stirred. The white precipitate was filtered off, washed with hexane (3 × 10 ml), and dried under vacuum. Crystals suitable for X-ray diffraction analysis were obtained after one week at room temperature when the white solid was dissolved in toluene (10 ml) and hexane (30 ml) was added. Total yield 5.58 g (88%). For $C_{12}H_{22}Cl_2O_4Ti$ (349.1) calculated: 41.29% C, 6.35% H, 20.31% Cl, 13.72% Ti; found: 41.21% C, 6.40% H, 20.38% Cl, 13.69% Ti. ^{1}H NMR (300 MHz, CD$_3$CN): 1.21 (m, 4 H, 4-HC$_5$H$_9$O); 1.88 (m, 8 H, 2,3-HC$_5$H$_9$O); 3.70 (m, 4 H, 1-HC$_5$H$_9$O); 4.05 (m, 4 H, CH$_2$); 4.37 (m, 2 H, 5-HC$_5$H$_9$O). IR: 284 (w), 362 (vs), 380 (vs), 422 (s), 480 (s), 530 (w), 560 (m), 596 (s), 618 (vs), 726 (w), 784 (s), 832 (w), 856 (m), 880 (s), 930 (s), 952 (s), 996 (s), 1020 (s), 1034 (vs), 1054 (vs), 1074 (vs), 1098 (vs), 1182 (w), 1202 (w), 1272 (w).

*[TiCl$_2$(edbp)] (**3**·toluene)*. To a rapidly stirred hexane solution (75 ml) of H$_2$edbp (10.0 g, 22.8 mmol), TiCl$_4$ (4.32 g, 22.8 mmol) was slowly and carefully added. The solution became immediately dark red and evolution of gaseous HCl started. Stirring was maintained at room temperature for 12 h. A red crystalline solid precipitated, which was filtered off and washed with cold hexane (50 ml). Crystals suitable for X-ray analysis were obtained from a mixture of hexane toluene (1:1) at 248 K as **3**·toluene. Total yield 9.53 g (75%). For $C_{30}H_{44}Cl_2O_2Ti$ (555.5) calculated: 64.87% C, 7.98% H, 12.76% Cl; found: 64.60% C, 7.98% H, 12.68% Cl. ^{1}H NMR (major conformer, 300 MHz, CD$_2$Cl$_2$): 1.29 (s, 18 H, C(CH$_3$)$_3$); 1.36 (s, 18 H, C(CH$_3$)$_3$); 1.66 (d, 3 H, CH(CH$_3$), $J_{\text{H-H}}$ = 7.2); 4.49 (q, 1 H, CH(CH$_3$), $J_{\text{H-H}}$ = 7.2); 7.19 (d, 2 H,

Ph, $J_{H\text{-}H}$ = 2.3); 7.26 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3). ^{1}H NMR (minor conformer, 300 MHz, CD_2Cl_2): 1.31 (s, 18 H, $C(CH_3)_3$); 1.45 (s, 18 H, $C(CH_3)_3$); 1.72 (d, 3 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 6.3); 4.59 (q, 1 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 6.3); 7.18 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.1); 7.26 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.1). IR: 368 (m), 418 (s), 462 (vs), 540 (w), 592 (s), 638 (s), 652 (w), 744 (s), 772 (s), 804 (w), 886 (vs), 908 (s), 930 (s), 1100 (s), 1136 (m), 1158 (s), 1200 (s), 1224 (s), 1264 (m), 1288 (m), 1364 (vs), 1412 (m), 1596 (m).

[Al(η^2-hbo)$_2$(Me)] (**4**). To a solution of **1** (1.00 g, 1.79 mmol) in toluene (60 ml), $AlMe_3$ (0.89 ml, 2 M solution in toluene) was added dropwise at room temperature. After 24 h of stirring, the dark-blue solution was reduced in volume under vacuum to 20 ml and left to crystallize at room temperature. After one week, colorless crystals of **4** were obtained. Total yield 0.72 g (87%). For $C_{27}H_{19}AlN_2O_4$ (462.4) calculated: 70.13% C, 4.14% H, 6.06% N; found: 70.10% C, 4.12% H, 6.02% N. ^{1}H NMR (300 MHz, $CDCl_3$): –0.77 (s, 3 H, CH_3); 6.89 (m, 2 H, 6-$\mathbf{H}C_6H_4OCONC_6H_4$); 7.24 (m, 2 H, 4-$\mathbf{H}C_6H_4OCONC_6H_4$); 7.47 (m, 8 H, 3′,4′,5′,6′-$\mathbf{H}C_6H_4OCONC_6H_4$); 7.67 (m, 2 H, 5-$\mathbf{H}C_6H_4OCONC_6H_4$); 8.10 (m, 2 H, 3-$\mathbf{H}C_6H_4OCONC_6H_4$). ^{27}Al NMR (400 MHz, C_6D_6): 37.2. IR: 228 (w), 272 (w), 316 (s), 340 (m), 352 (w), 376 (m), 424 (s), 468 (s), 500 (w), 536 (w), 564 (w), 588 (m), 604 (m), 638 (m), 662 (s), 680 (vs), 694 (vs), 708 (m), 740 (vs), 744 (vs), 748 (vs), 772 (s), 812 (s), 860 (m), 888 (vs), 936 (w), 972 (w), 1004 (m), 1032 (m), 1060 (m), 1068 (m), 1108 (m), 1132 (m), 1152 (s), 1188 (m), 1254 (s), 1270 (vs), 1288 (w), 1300 (w), 1336 (s).

[Al$_2$(μ$_2$-η^2-thp)$_2$(Me)$_4$] (**5**). To a solution of **2** (1.50 g, 4.29 mmol) in THF (60 ml), $AlMe_3$ (4.29 ml, 2 M solution in toluene) was added dropwise at room temperature. After 12 h of stirring, the solution volume was reduced under vacuum to 30 ml and left to crystallize at room temperature. After four weeks, colorless crystals of **4** were taken directly from the solution. Total yield 1.32 g (89%). For $C_{16}H_{34}Al_2O_4$ (344.4) calculated: 55.80% C, 9.95% H; found: 55.82% C, 9.91% H. ^{1}H NMR (300 MHz, CD_3CN): –1.06 (s, 12 H, CH_3); 1.23–1.65 (m, 12 H, 2,3,4-$\mathbf{H}C_5H_9O$); 3.41–4.15 (m, 10 H, 1,5-$\mathbf{H}C_5H_9O$, $C\mathbf{H}_2$). ^{27}Al NMR (400 MHz, C_6D_6): 60.3. IR: 226 (m), 300 (m), 320 (m), 348 (w), 408 (m), 436 (w), 456 (m), 492 (s), 532 (m), 586 (s), 672 (vs, br), 792 (s), 828 (m), 860 (s), 876 (s), 936 (s), 954 (s), 994 (w), 1036 (vs), 1062 (vs), 1084 (vs), 1108 (vs), 1164 (w), 1180 (vs), 1264 (m), 1280 (m), 1296 (w), 1332 (w). When the volume of the solution was reduced to 10 ml, blue crystals of $[TiCl_3(thf)_3]$ were obtained based on X-ray measurements of unit cell parameters[18].

*[Ti$_2$(μ-OMe)$_2$(edbp)$_2$(Me)$_2$] (**6**·3CH$_2$Cl$_2$). A*) To a rapidly stirred THF solution (50 ml) of **3** (1.2 g, 2.2 mmol), $AlMe_3$ (0.32 ml, 2 M solution in toluene) was slowly added at room temperature. The color of the reaction mixture gradually changed from dark to light red. The solution was stirred for 2 h and then the solvent was removed under vacuum and CH_2Cl_2 (30 ml) was added. After prolonged standing at 248 K, orange crystals suitable for X-ray analysis were obtained as **6**·3CH_2Cl_2. Total yield 0.58 g (48%). Analysis was made for a solid precipitated from THF solution. For $C_{64}H_{100}O_6Ti_2$ (1061.3) calculated: 72.43% C, 9.50% H; found: 72.02% C, 9.38% H. ^{1}H NMR (300 MHz, CD_2Cl_2): 1.25 (s, 18 H, $C(CH_3)_3$); 1.26 (s, 18 H, $C(CH_3)_3$); 1.31 (s, 6 H, CH_3); 1.37 (s, 18 H, $C(CH_3)_3$); 1.40 (s, 18 H, $C(CH_3)_3$); 1.67 (d, 3 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 7.3); 1.81 (d, 3 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 7.3); 3.42 (s, 6 H, OCH_3); 4.50 (q, 1 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 7.3); 4.77 (q, 1 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 7.3); 7.18 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3); 7.26 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3); 7.38 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3); 7.48 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3). IR: 528 (m), 594 (m), 638 (w), 760 (m), 808 (w), 856(s), 904 (w), 924 (m), 1112 (s), 1164 (m), 1200 (w), 1234 (s), 1254 (s), 1298 (m), 1360 (m), 1398 (s), 1412 (m), 1596 (w), 1652 (w).

B) To a rapidly stirred toluene solution (40 ml) of **7** (1.0 g, 0.91 mmol), $AlMe_3$ (0.91 ml, 2 M solution in toluene) was slowly added at room temperature. The solution immediately became dark red and was stirred for 12 h. Then the solvent was removed under vacuum and CH_2Cl_2 (25 ml) was added. Orange crystals of **6** were obtained after standing in solution at 248 K for 2 days. Total yield 0.82 g (85%). Spectroscopic data and elemental analyses were identical to these described above.

*$[Ti_2(\mu\text{-}OMe)_2(edbp)_2(OMe)_2]$ (**7**). A*) To a rapidly stirred hexane solution (80 ml) of **3** (2.49 g, 4.5 mmol), NaOMe (0.49 g, 9.0 mmol) was added. The mixture was stirred at room temperature for 24 h. The solution was then filtered to remove NaCl, next reduced under vacuum to 30 ml and filtered again. Red crystals then precipitated from the CH_2Cl_2 solution. Total yield 1.96 g (78%). For $C_{64}H_{100}O_8Ti_2$ (1093.3) calculated: 70.31% C, 9.22% H; found: 70.21% C, 9.05% H. ^1H NMR (300 MHz, CD_2Cl_2): 1.29 (s, 18 H, $C(CH_3)_3$); 1.30 (s, 18 H, $C(CH_3)_3$); 1.35 (s, 18 H, $C(CH_3)_3$); 1.36 (s, 18 H, $C(CH_3)_3$); 1.67 (d, 3 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 7.3); 1.81 (d, 3 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 7.3); 2.34 (s, 6 H, OCH_3); 3.42 (s, 6 H, OCH_3); 4.50 (q, 1 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 7.3); 4.77 (q, 1 H, $CH(CH_3)$, $J_{H\text{-}H}$ = 7.3); 7.18 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3); 7.26 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3); 7.38 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3); 7.48 (d, 2 H, Ph, $J_{H\text{-}H}$ = 2.3). IR: 416 (vw), 468 (w), 482 (m), 542 (s), 574 (s), 626 (vs), 800 (w), 808 (w), 864 (vs), 866 (vs), 904 (w), 924 (m), 1036 (s), 1112 (vs), 1200 (m), 1236 (vs), 1258 (s), 1296 (m), 1360 (m), 1412 (m), 1596 (w).

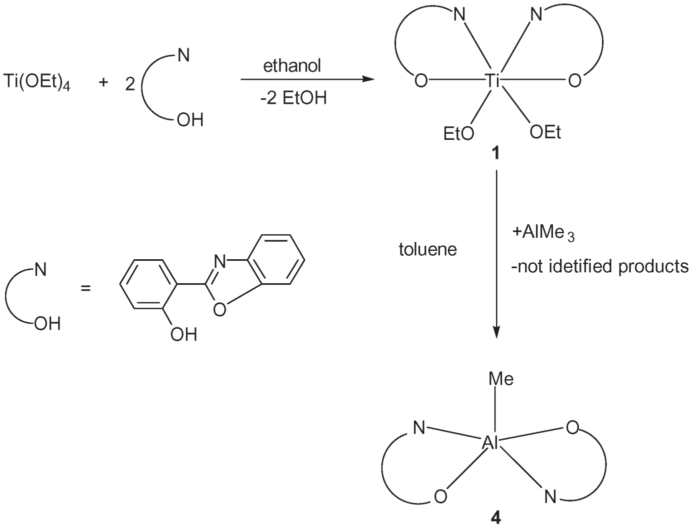
B) To a rapidly stirred hexane solution (70 ml) of H_2edbp (2.13 g, 4.9 mmol), $Ti(OMe)_4$ (0.84 g, 4.9 mmol) was added. The color of the reaction mixture gradually changed from light yellow to dark red. The mixture was stirred at room temperature for 48 h, filtered and washed with hexane. Red crystals then precipitated from the CH_2Cl_2 solution. Total yield 2.67 g (91%). Spectroscopic data and elemental analyses were identical to those described above.

RESULTS AND DISCUSSION

*Synthesis of Complexes **1**–**7***

Reaction of $Ti(OEt)_4$ or $TiCl_4$ with 2-(2-hydroxyfenyl)benzoxazole (Hhbo) or tetrahydropyran-2-methanol (Hthp) in a 1:2 ratio gave air-sensitive, but stable under nitrogen, light yellow *cis*-$[Ti(\eta^2\text{-hbo})_2(OEt)_2]\cdot 0.5$toluene (**1**; 91%) and colorless *cis*-$[TiCl_2(\eta^2\text{-thp})]$ (**2**; 88%), respectively. The reaction of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (H_2edbp), containing two acidic protons with $TiCl_4$ in a 1:1 molar ratio in hexane proceeded with spontaneous evolution of HCl resulting in red crystals of $[TiCl_2(edbp)_2]$ (**3**; 75%). The similar compound $[TiCl_2(mbp)]$ (**3a**) (mbp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato) was previously obtained when $TiCl_4$ was treated with H_2mbp [19].

Attempts to substitute ethoxide and chlorine ligands in **1** and **2**, respectively, by methyl groups using $AlMe_3$ as alkylating agent failed. However, when **1** was allowed to react with $AlMe_3$ in a 1:1 molar ratio in toluene at room temperature $[Al(\eta^2\text{-hbo})_2(Me)]$ (**4**) was isolated in 87% yield. Similar reaction of **2** with $AlMe_3$ in 1:2 ratio in tetrahydrofuran produced the dinuclear aluminum complex [$Al_2(\mu_2\text{-}\eta^2\text{-thp})_2(Me)_4$] (**5**; 89%) (Schemes 1 and 2). The ^{27}Al NMR spectrum for **4** and **5** shows resonances at 37.2 and 60.3 ppm, respectively, consistent in both compounds with the five-coordinated aluminum atoms. When the volume of the filtered solution was reduced, blue crystals of [$TiCl_3(thf)_3$] were obtained, based on X-ray measurements of unit cells parameters[18]. These findings clearly indicate that the $AlMe_3$ plays the dual role: (i) reducing Ti(IV) to its trivalent state[19], and (ii) completely abstract the hbo and thp ligands from the titanium center constituting the main obstacle for the development of a competitive single-site catalysts[20].

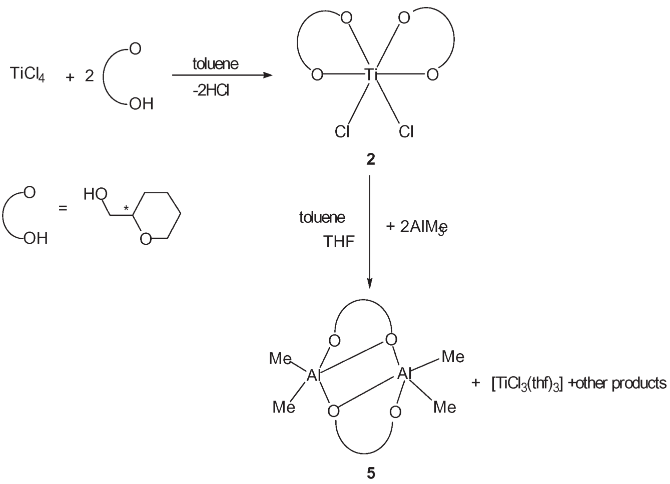


SCHEME 1

Ligand migration from titanium metal site of compound **1** to aluminum atom of compound **4**

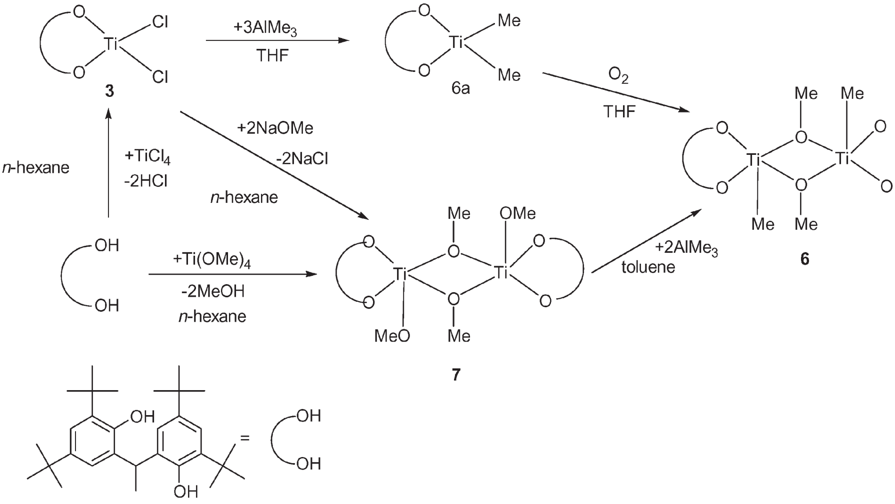
To extend this chemistry we have carried out related reactions of other species obtained earlier such as *cis*-[$TiX_2(\eta^2\text{-maltolato})_2$], *cis*-[$TiX_2(\eta^2\text{-guaiacolato})_2$] [14] (X = Cl, OEt; maltolato = (*O*,*O*)-3-oxido-2-methylpyran-4-one; guaiacolato = (*O*,*O*)-2-methoxyphenoxido) and other relevant compounds with $AlMe_3$. The reactions proceeded similarly to that in the formation of **5**, as evidenced by elemental analysis and ^1H and ^{27}Al NMR.

The lability of the hbo, thp, maltolato and guaiacolato ligands to liberation from the titanium centers after addition of $AlMe_3$ forced us to use the 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (H_2edbp) ligand. By selecting the this ligand, which contains phenol moieties with *tert*-butyl "tails", we ex-



SCHEME 2
Ligand migration from titanium metal site of compound **2** to aluminum atom of compound **5**

pected to obtain titanium compounds with markedly improved solubility in hydrocarbons, and an increased probability of compound stability in the presence of the aluminum cocatalyst[19]. The successful route to substitution of chloride ligands in **3** by use of $AlMe_3$ is shown in Scheme 3. The reaction of **3** with 3 equivalents of $AlMe_3$ in THF afforded an air-sensitive species, which unexpectedly, after recrystallization from CH_2Cl_2, yielded orange crystals of dimeric $[Ti_2(\mu\text{-}OMe)_2(edbp)_2(Me)_2]$ (**6**; 48%). Although the crystallization had been carried out under nitrogen, oxygen had inadvertently entered the vessel because the grease on the stopper had been washed away by solvent. The detailed mechanism of this reaction is not established, but, no doubt, the driving force of the reaction is insertion of O_2 into a Ti–Me bond of the proposed $[Ti(edbp)(Me)_2]$ (**6a**) intermediate. Compound **6a** has not yet been isolated in pure form. We propose that it is formed by substitution of two chlorine atoms in **3** by methyl groups of $AlMe_3$ (see Scheme 3) and is relevant to the earlier obtained species $[Ti(mbp)Me_2]$ [19]. The insertion of dioxygen into a Ti–Me bond similar to the Cossee pathway[22] for the insertion of olefins is well-documented[22]. Compound **6** in 85% yield can also be obtained by straightforward terminal OMe group replacement in $[Ti_2(\mu\text{-}OMe)_2(edbp)_2(OMe)_2]$ (**7**) by the methyl group of $AlMe_3$ in toluene. The complex **6** is new and was identified by elemental analysis and spectroscopic data. The precursor **7** can be obtained by direct reaction of $Ti(OMe)_4$ with 1 equivalent of H_2edbp in hexane at room temperature or by substitution of two chlorine atoms in **3** by OMe groups. In the solid state, **1**–**7** can be stored under nitrogen at room temperature for extended periods without appreciable decomposition. They are soluble in CH_3CN, CH_2Cl_2 and toluene.



SCHEME 3
Syntheses of compounds **3**, **6** and **7**

X-ray Crystal Structures of ***1***–***6***

The molecular structures of **1**–**6** in the solid state are shown in Figs 1–6, respectively. Single-crystal X-ray analysis revealed that **1** has a six-coordinate center in a distorted octahedral geometry with two *trans*-O and two *cis*-N atoms of the two chelating hbo ligands as well as two mutually *cis*-OEt groups; thus it possesses approximate C_2 symmetry. The titanium atom in species **2** is surrounded by four oxygen atoms of two thp ligands and two *cis*-Cl atoms and lies on a twofold axis. The Ti–Cl, Ti–N, Ti–O bond lengths of **1** and **2,** depicted in Figs 1 and 2, are similar to those previously reported for *cis*-$[TiCl_2(\eta^2\text{-maltolato})_2]$, *cis*-$[Ti(\eta^2\text{-maltolato})_2(OEt)_2]$ [14] and $[TiCl_2(L^2)_2]$ [16] (L^2 = *N*-(3,5-di-*tert*-butyl-2-hydroxybenzylidene)-2,3,4,5,6-pentafluoroanilinato). The crystal structure of **3** is shown in Fig 3. In this complex, the titanium atom exhibits tetrahedral coordination and lies on a twofold axis. The tita-

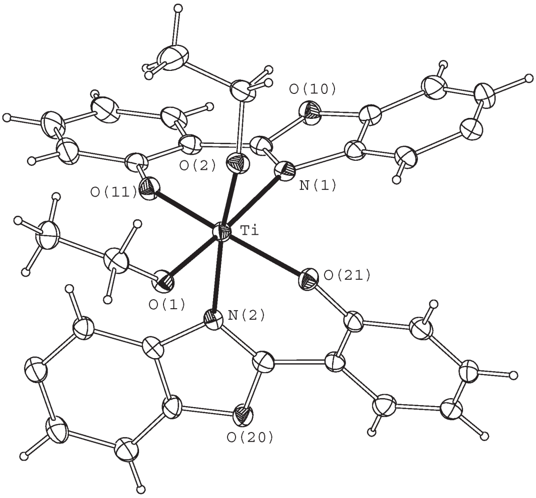


Fig. 1

ORTEP drawing (50% probability) of *cis*-[Ti(OEt)$_2$(η^2-hbo)$_2$]·0.5toluene (**1**). Selected bond lengths (in Å): Ti(1)–O(1) 1.820(2), Ti(1)–O(2) 1.798(2), Ti(1)–O(11) 1.918(2), Ti(1)–O(21) 1.925(2), Ti(1)–N(1) 2.269(3), Ti(1)–N(2) 2.258(3)

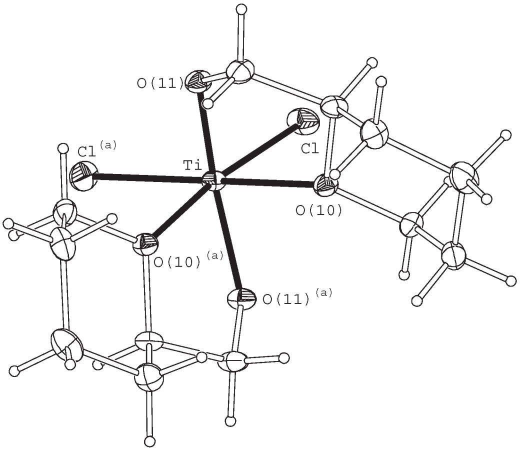


Fig. 2

ORTEP drawing (50% probability) of *cis*-[TiCl$_2$(η^2-thp)$_2$] (**2**). Selected bond lengths (in Å): Ti–Cl 2.299(1), Ti–O(10) 2.169(2), Ti–O(11) 1.845(2). Symmetry transformations used to generate equivalent atoms: $-x + 2$, $-y + 2$, z

nium atom is surrounded by two oxygen atoms of the chelating edbp ligand, which has a boat conformation, and two chlorine atoms. The Ti–O(1) bond distance 1.761(3) Å is exceedingly short and the phenoxo ligands must be considered to be donors of more than two electrons. The Ti–O and Ti–Cl bond lengths and bond angles in **3** are similar to those previously reported for **3a** [19].

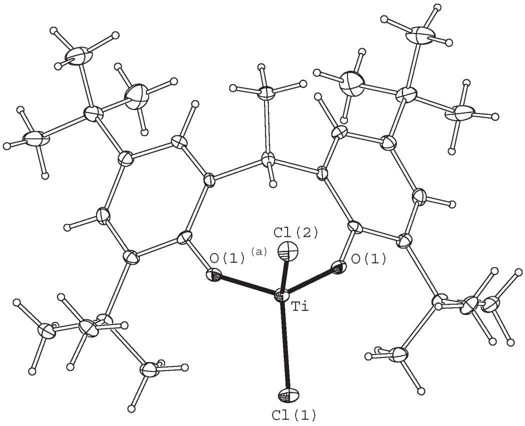


FIG. 3
ORTEP drawing (50% probability) of [$TiCl_2$(edbp)] (**3**). Selected bond lengths (in Å): Ti–O(1) 1.761(3), Ti–Cl(1) 2.236(2), Ti–Cl(2) 2.239(2)

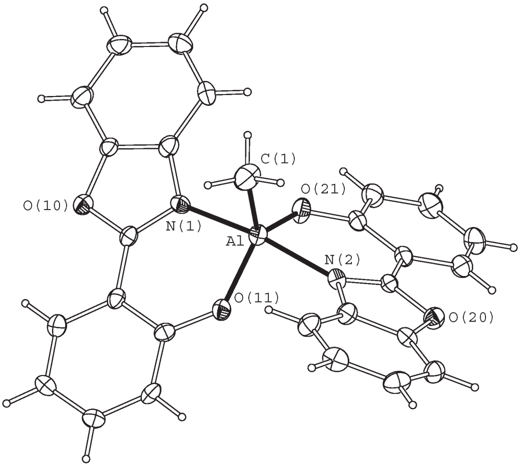


FIG. 4
ORTEP drawing (50% probability) of [Al(η^2-hbo)$_2$(Me)] (**4**). Selected bond lengths (in Å): Al–C(1) 1.952(3), Al–O(11) 1.790(2), Al–O(21) 1.794(2), Al–N(1) 2.067(3), Al–N(2) 2.044(3)

The molecular structure of **4** is shown in Fig. 4. The structure consists of a discrete monomeric unit with a five-coordinated aluminum atom. The coordination geometry around the Al atom can be described as a distorted trigonal bipyramid. The two hbo anions act as didentate chelating ligands, forming two planar six-membered Al–O–C–C–C–N rings. The angle defined by the two apical substituents N(1)–Al–N(2) is 166.40(11)°. The Al–C distance of 1.952(3) Å and phenoxide Al–O bond lengths of 1.789(3) Å are similar to the corresponding distances in $[Al(mesal)_2Me]$[23] (Hmesal = methyl salicylate). The ether Al–O distances 2.054(3) Å are shorter than those observed for the five-coordinated bis(μ_2-methoxyethanolato-*O*,*O*)tetramethyldialuminum complex (2.269(6) Å)[24]. In compound **5**, the tetrahydropyran rings reside on a symmetry plane and are disordered. Unfortunately, their disorder could not be resolved and therefore the structure of **5** was not determined completely. Nonetheless, the structure of **5** is well-defined (see capture to Fig. 5) and can be discussed. The molecule of **5** is a centrosymmetric dimer with two five-coordinate aluminum atoms. The monomeric subunits are bonded by alkoxide oxygen atoms to form a central four-membered $Al_2(\mu\text{-}O)_2$ core. The geometry of each aluminum atom coordination sphere can be described as a distorted trigonal bipyramid. The equatorial plane is defined by methyl carbon atoms and the alkoxide oxygen. The axial positions are occupied by the ether oxygen atom and alkoxide oxygen atom of the second monomeric unit.

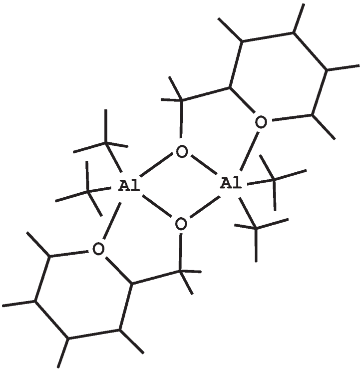


FIG. 5
The drawing of $[Al_2(\mu_2\text{-}\eta^2\text{-thp})_2(Me)_4]$ (**5**). Crystal data: monoclinic, *C*2/*m*, *a* = 15.625(2) Å, *b* = 9.153(2) Å, *c* = 7.300(2) Å, β = 110.05(2)°, *T* = 100(1) K

The centrosymmetric [$Ti_2(\mu\text{-}OMe)_2(edbp)_2(Me)_2$] (**6**) compound has a dimeric structure; an overall view of the molecule is presented in Fig 6. Unfortunately, due to high unit cell parameters and too small crystal size, the structure of **6** was not determined completely and can only be considered as structural model of the complex. Without any doubts, however, each titanium atom is five-coordinated by two oxygen atoms of didentate edbp chelating ligands, two bridging μ-OMe oxygen atoms and terminal carbon atom of the methyl group. The Ti–O bond distances are in accordance with those found in **3** and in [$Ti_2(\mu\text{-}OEt)_2(OEt)_2(\eta^2\text{-}maltolato)_2$] [14]. The Ti–C1A bond length 1.975(13) Å is similar to this previously reported for [$Ti(mbp)Me_2$] [19].

Olefin Polymerization

We examined the catalytic behavior of a series of Ti complexes with functionalized ligands possessing C_2 symmetry using methylalumoxane (MMAO-12) as the cocatalyst. The results for propene polymerization using complexes **1** and **2** and previously studied maltolato and guaiacolato titanium complexes showed similarly moderate activity and the polymer property (Table II). DSC analyses revealed that the obtained polypropylene

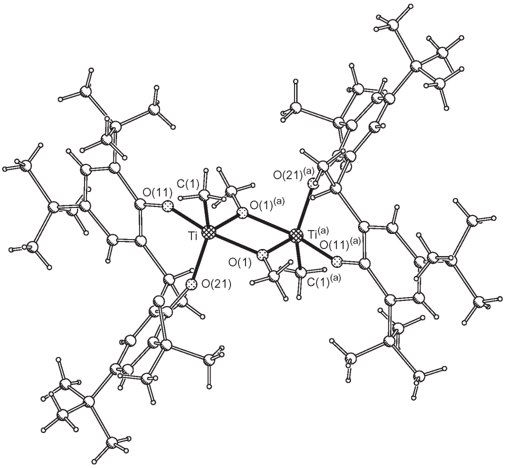


FIG. 6

View of [$Ti_2(\mu\text{-}OMe)_2(edbp)_2(Me)_2$] (**6**) crystallographic model. The atoms are represented by circles of an arbitrary radius. Selected bond lengths (in Å): Ti–C(1A) 1.975(13), Ti–O(1)$^{(a)}$ 1 1.927(9), Ti–O(1) 2.110(10), Ti–O(11) 1.862(10), Ti–O(21) 2.014(11), Ti–Ti$^{(a)}$ 1 3.292(5). Symmetry transformations used to generate equivalent atoms: $-x, -y, -z + 1$

TABLE II
Results of propylene polymerization/MAO[a]

Entry	Complex	Catalyst μmol	Polymer yield, g	Run time, min	Efficiency, g PP/g Ti	M_w[b]	PDI[b]	T_m[c], °C
1	*cis*-$[TiCl_2(\eta^2\text{-maltolato})_2]$ [14]	20	1.3	45	1 360	407 000	8.47	153.5
2	$[TiCl_2(\eta^2\text{-maltolato})_2(OSiPh_3)]$ [25]	20	3.7	45	3 860	452 000	9.96	156.2
3	*cis*-$[TiCl_2(\eta^2\text{-guaiacolato})_2]$ [14]	20	1.1	45	1 150	437 000	3.62	156.7
4	$[Ti_2(\mu\text{-O})Cl_2(\eta^2\text{-guaiacolato})_4]$ [14]	20	6.5	45	3 390	323 000	9.41	156.7
5	*cis*-$[Ti(\eta^2\text{-hbo})_2(OEt)_2]$	10	9.4	30	19 632	224 000	6.01	154.6
6	*cis*-$[TiCl_2(\eta^2\text{-thp})_2]$	10	9.4	30	19 006	206 000	8.37	153.2
7	$[TiCl_2(edbp)]$	20	8.0	75	8 354	454 000	2.49	158.2

[a] Conditions: MMAO-12/complex = 1000 (for entries 1–3 and 5–7) and 2000 for entry 4; tem- perature 70 °C. [b] Determined by GPC using polystyrene/polypropylene universal calibration. [c] Determined by DSC.

TABLE III
Results of ethene/oct-1-ene copolymerization/MAO[a]

Entry	Complex	Catalyst μmol	Polymer yield, g	Run time, min	Efficiency, g PP/g Ti	M_w[b]	PDI[b]
1	[Cp*–SiMe2–N^{t}Bu]$TiCl_2$	2	42.5	17	443 818	90 000	5.54
2	*cis*-[$TiCl_2$(η^2-maltolato)$_2$] [14]	20	24.6	48	25 689	156 000	40.2
3	[$TiCl_2$(η^2-maltolato)$_2$($OSiPh_3$)] [25]	20	25.8	55	26 942	172 000	26.1
4	*cis*-[$TiCl_2$(η^2-guaiacolato)$_2$] [14]	20	24.7	44	25 794	173 000	30.3
5	[Ti_2(μ-O)Cl_2(η^2-guaiacolato)$_4$] [14]	10	20.3	36	42 398	169 000	27.8
6	*cis*-[Ti(η^2-hbo)$_2$(OEt)$_2$]	7.5	8.2	15	22 830	80 000	30.1
7	*cis*-[$TiCl_2$(η^2-thp)$_2$]	11	12.8	15	24 300	68 000	17.2
8	[$TiCl_2$(edbp)]	20	14.6	75	6 000	130 000	6.23

[a] Conditions: MMAO-12/complex = 1000 (for entries 1–2 and 4–8) and 2000 for entry 3; tem- perature 140 °C. [b] Determined by GPC using polystyrene/polyethylene universal calibration.

(Table II, entries 1–6) possesses high melting points (153.5–156.7 °C). GPC analyses revealed that the polypropylene also possesses high M_w (206 000–452 000), and high polydispersities (M_w/M_n values ca. 3.62–9.96 for entries 1–6). Further efforts aimed at developing improved versions of those catalysts led to the discovery of catalyst **3**/MAO (entry 7). This catalyst, which has an edbp ligand strongly bonded to the titanium atom, furnished narrow-molecular-weight polypropylene (70 °C: M_n = 454 000, M_w/M_n = 2.49) and exhibiting a T_m of 158.2 °C. The narrower molecular weight distribution indicates the formation of fewer different active sites due to the more strongly bound ligand in this case.

Ethene/oct-1-ene copolymerization with the complexes presented in Table III using MAO as cocatalyst, were carried out at 140 °C. The activities of these catalytic systems were found to be one order of magnitude lower in comparison with the [Cp*–$SiMe_2$–N–*t*-Bu]$TiCl_2$/MAO catalyst system under identical conditions. It is noteworthy that the copolymer produced with those catalysts (entries 2–7) possess high polydispersity (M_w/M_n values 17–40) and high molecular weight (M_n ca. 68 000–173 000) values, characteristic of a Ziegler–Natta polymerization catalyst. These facts strongly indicate that during the process of catalyst formation the ligands have been abstracted from titanium atom and many active sites formed. In contrast, the catalyst **3**/MAO (entry 8) under similar polymerization conditions is less active (6 kg PP/g Ti) but the molecular weight distribution of this copolymer (M_w/M_n = 6.23) is much lower, than those for entries 2–7. The significantly decreased activity of **3**/MAO catalyst for ethene/oct-1-ene copolymerization may be due to the lower solubility of the catalyst in the presence of the alkane solvent. The polymer densities of the ethene/oct-1-ene copolymers were found to be in excess of 0.93 g/ml indicating that little if any oct-1-ene was incorporated into the propagating polymer. These polymers samples were white powders upon isolation and drying. The exception is for entry 1 of Table III where the polymer was determined to have a density of 0.89 g/ml indicating a significant amount of oct-1-ene incorporation resulting in a clearly elastomeric polymer upon drying.

CONCLUSIONS

It was shown that the trimethylaluminum has sufficient reducing strength to lower the oxidation state of Ti(IV) to Ti(III) and trigger the ligand migration. The results of X-ray crystallography clearly demonstrated that in **1**/$AlMe_3$ and **2**/$AlMe_3$ systems, an important rearrangement of the titanium metal centers took place and that the ligands have been abstracted by

$AlMe_3$ yielding species **4** and **5** and providing in return alkyl functionalities. The presence of $AlMe_3$ in the MAO cocatalyst increases the extent of migration of the ligands from titanium in **1**/MAO and **2**/MAO catalysts, thus decreasing the selectivity. Such catalysts produce polymer with a broad molecular weight distribution. When the remaining trimethylaluminum was evaporated in vacuo from the used MAO, the produced polyethylenes have M_w/M_n values[16b] ca. <2. Further efforts aimed at developing an improved version of these catalysts led to the discovery of **3**/MAO catalyst producing polypropylene at 70 °C with M_n = 454 000, M_w/M_n = 2.49, T_m = 158.2 °C.

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