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Synthesis of Titanatranes Containing Bis(aryloxo)-(alkoxo)amines and their Use in Catalysis for Ethylene Polymerization

*Sudhakar Padmanabhan, Wei Wang, Shohei Katao, Kotohiro Nomura**

Summary: Syntheses of titanatranes containing $[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2\text{-}\{O(CH_2)_n\text{-}CH_2\}]N^{3-}$ (n = 1,2) have been explored. Catalytic activity for ethylene polymerization by $Ti_2(O^iPr)_2\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2\text{-}CH_2)]N\}_2$ (**1a**) - MAO catalyst increased at high temperature; the activity also increased upon addition of $AlMe_3$. $Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(OCH_2CH_2)]N\}$ (**1c**) showed higher activity than **1a** under the same conditions. $Ti\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(HOCH_2CH_2CH_2)]N\}_2$ was isolated from the reaction of $Ti(O^iPr)_4$ with bis(2-hydroxy-3,5-dimethylbenzyl)-propanolamine; the structure was determined by X-ray crystallography.

Keywords: aluminum; ethylene; polymerization; titanium; titanium complex

Introduction

Chemistry of transition metal complexes containing chelate trianionic ligands such as tris(amido)amine, tris(alkoxo)amine, and tris(aryloxo)amine has been the subject of considerable attention, because these ligands are capable of providing a range of stable steric and electronic environments for catalytically active metal centers.[1–6] Since examples applied to catalysis for certain organic synthesis and polymerizations have been known,[6] also since design and synthesis for efficient (non-metallocene type) transition metal complex catalyst for precise olefin polymerization attracts considerable attention recently in the field of organometallic chemistry, and polymer chemistry,[7] we thus had an interest to explore the possibility with titanatranes as the new candidates.

We reported that titanium complexes containing tris(aryloxo)amine ligand, $TiX[(O\text{-}2,4\text{-}R_2C_6H_2\text{-}6\text{-}CH_2)_3N]$ [R = Me, ^tBu; X = O^iPr, $O\text{-}2,6\text{-}{}^iPr_2C_6H_3$], were effective as catalyst precursors for ethylene polymerization in the presence of MAO, and remarkable increase in the activity was observed at higher temperature (100–120 °C); the activity further increased by addition of small amount of $AlMe_3$.[8] Titanium complexes containing C_3 and C_s symmetric $[OCH(Ph)CH_2]_3N^{3-}$ had also been introduced later as the related example.[9] More recently, reaction of dimeric titanatranes, $Ti_2(OR')_2\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)]N\}_2$ [R′ = ^iPr (**1a**), ^tBu (**1b**)] with $AlMe_3$ afforded heterobimetallic complex, $\{TiMe[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)N]\}[Me_2Al(\mu_2\text{-}O\text{-}R')]$ (**2a**,**b**); **2b** exhibited moderate catalytic activity for ethylene polymerization in octane without additional cocatalyst at 120 °C, affording high molecular weight polyethylene with unimodal distribution (Scheme 1).[10] The result suggests that the cationic species formed by a cleavage of the Ti–O bonds plays a key role for the polymerization.

In this paper, we thus present results for syntheses of titanium complexes containing $[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2\{O(CH_2)_nCH_2\}]\text{-}N^{3-}$ (n = 1,2), some reactions and their use in catalysis for ethylene polymerization.

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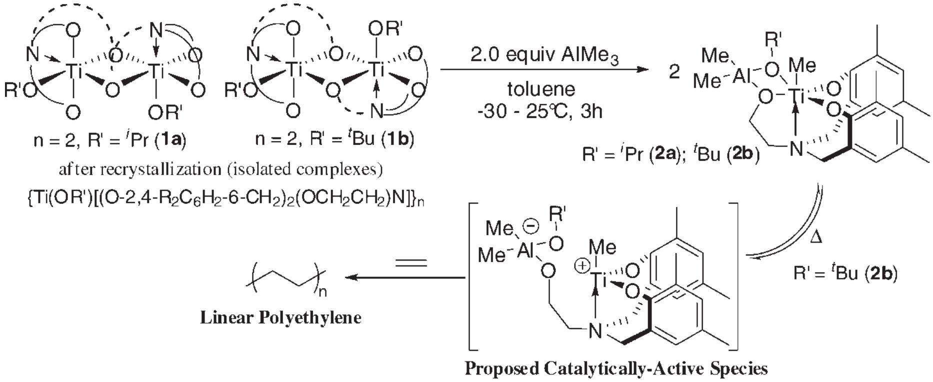


Scheme 1.

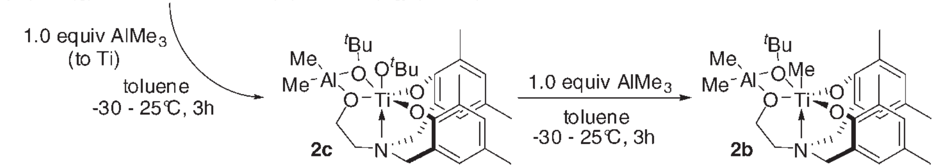
Results and Discussion

$Ti_2(OR')_2\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)]N\}_2$ [$R' = {}^iPr$ (**1a**), ^tBu (**1b**)] were prepared by reaction of $Ti(OR')_4$ with $[(HO\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(HOCH_2CH_2)]\text{-}N$ in toluene,[10] and the complexes after recrystallization were identified by ^1H-, ^{13}C-NMR spectra, elemental analyses; their structures were determined by X-ray crystallography.[10] In contrast, monomeric $Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)]N\}$ (**1c**) was prepared according to the reported procedure.[11]

In contrast, the resultant solids (crude material washed with *n*-hexane before recrystallization) obtained from the reaction of $Ti(O^tBu)_4$ with $[(HO\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(HOCH_2CH_2)]N$ in toluene contained ^tBuOH (ca. 1 equiv.) observed by the ^1H NMR spectrum, and the reaction with $AlMe_3$ (1.0 equiv. to Ti) in toluene afforded $\{Ti(O^tBu)[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)N]\}\text{-}[Me_2Al(\mu_2\text{-}O^tBu)]$ (**2c**) identified by ^1H-, ^{13}C-NMR spectra, elemental analysis and the structure was determined by X-ray crystallography (Scheme 2).[12] The reaction of **2c** with $AlMe_3$ (1.0 equiv.) afforded **2b** in high yield confirmed by ^1H-, ^{13}C-NMR spectra.

The crystallographic analysis reveals that **2c** has a rather distorted octahedral geometry around Ti, consisting of $O(^tBu)$-Ti-N axis [N(1)-Ti(1)-O(1) = 177.17(8)°] and a distorted plane of two aryloxo and two alkoxo ligands (Figure 1). Ti–N bond distance [2.3554(19) Å] is somewhat longer than those in **2a,b** [2.328(3) Å], probably due to the influence by ligand positioned to *trans* position (O^tBu vs Me). **2c** was stable and could be stored for long period in the dry box without partial decomposition, as seen in **2a**,**b**.

The dimeric and the monomeric titanatranes (**1a**,**c**) exhibited moderate catalytic activities for ethylene polymerization in the presence of MAO (Table 1), and the activities increased at high temperature (100–120 °C); the activities in octane were higher than those in toluene. The activities by **1a** further increased upon addition of small amount of $AlMe_3$.[8] Note that the



Scheme 2.

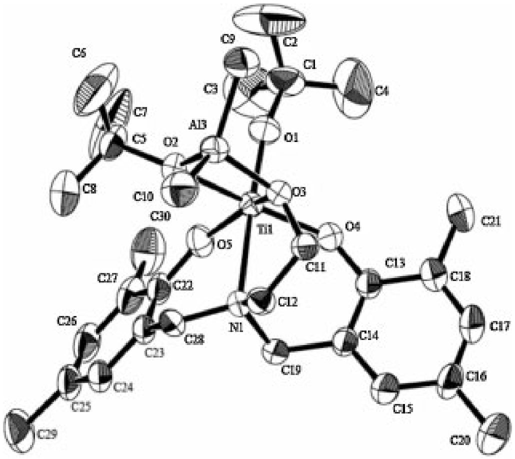


Figure 1.
ORTEP Drawings for {Ti(O^{t}Bu)[(O-2,4-Me$_2$C$_6$H$_2$-6-CH$_2$)$_2$(μ_2-OCH$_2$CH$_2$)N]}-[Me$_2$Al(μ_2-O^{t}Bu)] (**2c**). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond distances (Å): Ti(1)-O(1) 1.7677(19), Ti(1)-O(2) 2.1603(19), Ti(1)-O(3) 2.0522(17), Ti(1)-O(4) 1.8727(18), Ti(1)-O(5) 1.8585(18), Ti(1)-N(1) 2.3554(19). Selected bond angles (°): O(1)-Ti(1)-O(2) 90.54(8), O(1)-Ti(1)-N(1) 177.17(8), O(2)-Ti(1)-O(3) 71.15(6), O(2)-Ti(1)-O(4) 162.67(7), O(4)-Ti(1)-O(5) 101.46(8), O(2)-Ti(1)-N(1) 91.35(7), O(2)-Al(1)-O(3) 84.04(8).

activity by **1c** was higher than that by **1a** under the same conditions, and this might be due to that the use of aryloxo ligand would be favored in terms of a proposed equilibrium between dormant (octahedral hetero-bimetallic) and the catalytically-active (cationic alkyl) species (Scheme 1). The resultant polymers prepared by **1a,c** – MAO catalysts were linear polyethylene (PE) confirmed by ^{13}C NMR spectra, and possessed relatively high molecular weights with unimodal molecular weight distributions in most cases. In contrast, the distributions for resultant Pes prepared in the co-presence of AlMe$_3$ were bimodal.

2a exhibited moderate catalytic activities for ethylene polymerization in the presence of MAO, and both the activity and the M_w value were similar to those by **1a** in the presence of AlMe$_3$/MAO (runs 14,16,24,25). The results suggest that **2a** would be first formed in the reaction mixture in the presence of both MAO and AlMe$_3$ (small amount), and the efficient formation of **2a** should be responsible for generating the proposed catalytically-active species, leading to the higher catalytic activity.

Note that **2b** exhibited moderate catalytic activity for ethylene polymerization in octane without MAO, affording high molecular weight PE with uniform molecular weight distribution (run 27).[10] However, **2a** showed the negligible activity under the same conditions. Although the effect of alkoxide ligand on Al toward the activity is critical, the results clearly suggest that the ethylene polymerization took place by cleavage of Ti–O bonds and the cationic species formed plays an important key role as the plausible catalytically active species for the ethylene polymerization.

The reaction of bis(2-hydroxy-3,5-dimethylbenzyl)propanolamine with Ti(O^{i}Pr)$_4$ in toluene gave pale yellow solids after removal of volatile compounds from the mixture *in vacuo*. Formation of the analogous titanium complex having one chelate donor ligand might be assumed from both the ^{1}H- and ^{13}C NMR spectra.[14] However, the resultant solids collected from the chilled solution (−30 °C) consisting of toluene/dichloromethane/hexane were another red microcrystals suggested by the NMR spectra. The complex was identified by ^{1}H, ^{13}C-NMR spectra and elemental analysis as Ti[(O-2,4-Me$_2$C$_6$H$_2$-6-CH$_2$)$_2$(HOCH$_2$CH$_2$-CH$_2$)N]$_2$ (**3**), and the structure was determined by X-ray crystallography

Table 1.
Polymerization of ethylene by **1a**,**c**,**2a**,**b** – MAO catalyst systems.[a)]

run	complex (μ mol)	MAO/$AlMe_3$ (Al/Ti)[b)]	solvent	temp./°C	time/min	yield/mg	activity[c)]	M_w[d)] $\times 10^{-4}$	M_w/M_n[d)]
1[e)]	**1a** (1.0)	3000/–	toluene	60	60	22	22	67.0	bimodal
2	**1a** (1.0)	3000/10	toluene	60	60	48	48		
3[e)]	**1a** (1.0)	3000/–	toluene	80	60	42	42	42.8	bimodal
4	**1a** (1.0)	3000/10	toluene	80	60	85	85		
5[e)]	**1a** (1.0)	3000/–	toluene	100	60	83	83	24.5	2.45
6[e)]	**1a** (1.0)	3000/10	toluene	100	60	172	172	19.0	bimodal
7[e)]	**1a** (1.0)	3000/–	toluene	100	10	21	126	26.0	2.01
8[e)]	**1a** (1.0)	3000/10	toluene	100	10	45	270	16.7	bimodal
9[e)]	**1a**(10.0)	500/–	toluene	100	60	540	54	4.09	4.01
10[e)]	**1a** (1.0)	3000/–	octane	80	60	150	150	27.2	2.50
11[e)]	**1a** (1.0)	3000/–	octane	100	60	149	149	52.9	2.89
12	**1a** (1.0)	3000/10	octane	100	60	405	405		
13[e)]	**1a** (1.0)	3000/–	octane	120	60	165	165	25.5	2.52
14[e)]	**1a** (1.0)	3000/10	octane	120	60	355	355	14.1	bimodal
15[e)]	**1a** (1.0)	3000/–	octane	120	10	24	144	18.8	2.45
16[e)]	**1a** (1.0)	3000/10	octane	120	10	60	360	19.0	3.18
17	**1c** (0.01)	10000/–	octane	60	60	5	50		
18	**1c** (0.01)	10000/–	octane	100	60	85	850		
19	**1c** (0.01)	5000/–	octane	120	60	127	1270		
20	**1c** (0.01)	10000/–	octane	120	20	57	1710		
21	**1c** (0.01)	10000/–	octane	120	60	147	1470	32.0	2.05
22	**1c** (0.01)	20000/–	octane	120	60	99	990		
23	**1c** (0.01)	40000/–	octane	120	60	60	600		
24[e)]	**2a** (1.0)	3000/–	octane	120	10	80	480	16.7	2.48
25[e)]	**2a** (1.0)	3000/–	octane	120	60	351	351		
26[e)]	**2a** (1.0)	–	octane	120	60	trace[f)]	–		
27[e)]	**2b** (1.0)	–	octane	120	60	94	94	100.2	2.58

[a)] Reaction conditions: solvent (30 mL), ethylene 8 atm, 100 mL scale autoclave, d-MAO (prepared by removing AlMe3 and toluene from commercially available MAO).
[b)] Molar ratio of Al/Ti.
[c)] Activity = kg-PE/mol-Ti.h.
[d)] GPC data in *o*-dichlorobenzene versus polystyrene standards.
[e)] Cited from ref. [10].
[f)] Negligible amount of polymer was formed.

(Figure 2).[15] Two titanium molecules were seen, although both bond lengths and bond angles were the same. As shown in Figure 2 (center, right), complete overlapping of the Ph group on one side was seen when we rotated the solid state structures, however, overlapping of the Ph rings in the other side was not observed (which probably makes the CH_2 and other signals to appear separately for each ligand moieties in the ^1H NMR spectrum). The observation is somewhat related to a recent report by Kobayashi et al.[16] in the formation of BINOLate zirconium complexes containing two ligand moieties during attempted crystallization of the $(BINOLate)_2Zr$(*N*-benzylimidazole)$_2$. Although we could not isolate the desired complex, the fact observed here should be important for designing the efficient catalyst with this approach.

We have shown that monomeric $Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)]N\}$ (**1c**) showed higher catalytic activity than the dimeric $Ti_2(O^iPr)_2\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)]N\}_2$ (**1a**); the anionic donor ligand (aryloxo/alkoxo) thus plays an important role for the high activity. $Ti[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(HOCH_2CH_2\text{-}CH_2)N]_2$ (**3**) was formed from the reaction of bis(2-hydroxy-3,5-dimethylbenzyl)-propanolamine with $Ti(O^iPr)_4$, and the desired complex having one chelate donor ligand could not be isolated. We believe that these facts should be important for designing

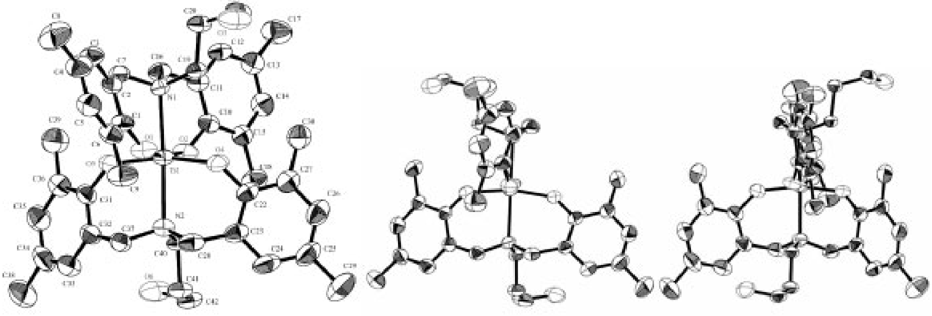


Figure 2.
ORTEP drawings for Ti[(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$($HOCH_2CH_2CH_2$)N]$_2$ (**3**). The drawings for two different molecules (center and right): one side of the molecule overlaps the phenyl groups and other side does not. Selected bond angles (°): O(1)-Ti(1)-O(2) 167.03(15), O(1)-Ti(1)-O(4) 89.48(16), O(1)-Ti(1)-O(5) 92.91(16), O(1)-Ti(1)-N(1) 82.84(15), O(4)-Ti(1)-O(5) 167.39(15), O(4)-Ti(1)-N(2) 83.69(14), N(1)-Ti(1)-N(2) 177.49(13), Ti(1)-N(1)-C(19) 108.2(2). Selected bond distances (Å): Ti(1)-O(1) 1.877(4), Ti(1)-O(2) 1.890(3), Ti(1)-O(4) 1.884(3), Ti(1)-O(5) 1.874(3), Ti(1)-N(1) 2.270(3), Ti(1)-N(2) 2.274(3). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

more effective complex catalysts for precise olefin polymerization.

Experimental Part

General Procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Toluene (anhydrous grade, Kanto Kagaku Co., Ltd.) and *n*-octane (anhydrous grade, Aldrich) for polymerization were stored in a bottle in the drybox in the presence of molecular sieves. Ethylene was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd) and was used as received. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure upon heating in the drybox to give white solids. Bis(2-hydroxy-3,5-dimethylbenzyl)-ethanolamine and bis(2-hydroxy-3,5-dimethylbenzyl)propanolamine were prepared according to the previous report.[17] Molecular weights and molecular weight distributions for polyethylene were measured by GPC (Tosoh HLC- 8121GPC/HT) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mmϕ ID), ranging from $<10^2$ to $<2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*- butyl-*p*-cresol as eluent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrenes. All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA 400 spectrometer (399.65 MHz, ^{1}H; 100.40 MHz, ^{13}C). Deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere in the dry box, and all chemical shifts are given in ppm and are referenced to Me_4Si. ^{13}C NMR spectra for polyethylene were measured with proton decoupling, and the analysis samples were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 wt), and these spectra were measured at 110 °C.

Synthesis of Ti[(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$($HOCH_2CH_2$)N]$_2$ (3)

Bis(2-hydroxy-3,5-dimethylbenzyl)propanolamine (0.343 g, 1.00 mmol) in toluene (10 mL) was added dropwise into a toluene solution (10 mL) containing Ti(O^{i}Pr)$_4$ (0.284 g, 1.00 mmol) at −30 °C. The mixture was then stirred at room temperature for 6 h, and the volatiles were then evaporated under vacuum, leaving pale yellow microcrystals. The resultant solids were dissolved in a mixed solution of toluene/dichloromethane/*n*-hexane (3/3/1, total 10 mL), and the chilled solution gave **3** as the orange microcrystals. Yield: 0.265 g (36.3% based on Ti). ^{1}H NMR ($CDCl_3$, 25 °C): 1.48 (s, 3H), 1.72 (m, 1H), 1.82 (m, 1H), 2.06 (s, 3H), 2.19 (s, 3H), 2.23 (s, 3H), 2.85 (m, 2H), 3.28 (m, 2H), 3.67 (m, 2H), 4.57 (d, $J = 12$ Hz, 1H), 4.78 (d, $J = 12$ Hz, 1H), 6.82 (m, 6H). ^{13}C NMR ($CDCl_3$, 25 °C): 16.39 (Ar-CH_3), 17.02 (Ar-CH_3), 20.52 (Ar-CH_3), 20.61 (Ar-CH_3), 23.00 (C-CH_2-C), 45.94 (N-CH_2), 58.24 (Ar-CH_2), 59.09 (Ar-CH_2), 60.84 (O-CH_2), 121.95, 121.97, 122.87, 123.10, 127.03, 131.04, 131.54, 159.49, 160.33. Anal. Calcd. for $C_{42}H_{54}N_2O_6Ti$: C, 69.03; H, 7.45; N, 3.83, Found: C, 68.87; H, 7.22; N, 3.82.

Polymerization of Ethylene

Solvent (29.0 mL) and MAO (3.0 mmol) were charged into the autoclave (100 mL scale) in the drybox, and the apparatus was placed under ethylene atmosphere (1 atm). After the addition of toluene or *n*-octane solution (1.0 mL) containing **1a** via a syringe, the reaction apparatus was immediately pressurized to 7 atm (total 8 atm), and the mixture was stirred magnetically for 10 or 60 min. After the above procedure, ethylene was purged, and the mixture was then poured into EtOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with EtOH, and was then dried *in vacuo*.

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[12] The synthetic procedure for $\{Ti(O^tBu)[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)N]\}[Me_2Al(\mu_2\text{-}O^tBu)]$ (**2c**) was the same as those for **2a**,**b**[10] except that $Ti_2(OR')_2\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2C\text{-}OCH_2CH_2)]N\}_2(^tBuOH)_2$ was used in place of **1b**. Yield 87.1%. ^{1}H NMR ($CDCl_3$, 25 °C): δ −0.72 (s, 6H), 1.43 (s, 3H), 1.50 (s, 9H), 2. 19 (s, 6H), 2.31 (s, 6H), 2.53 (t, 5.6 Hz, 2H), 3.36 (d, 12.8 Hz, 2H), 3.42 (d, 13.2 Hz, 2H), 3.78 (t, 5.52 Hz, 2H), 6.58 (s, 2H), 6.87 (s, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): δ −8.30 (Al-CH_3), 16.52 (Ar-CH_3), 20.52 (Ar-CH_3), 31.64 ($C(CH_3)_3$), 32.14 ($C(CH_3)_3$), 57.79 (N-CH_2), 60.50 (Ar-CH_2), 60.83 (Ar-CH_2), 62.92 (Al-O-$C(CH_3)_3$), 64.92 (O-CH_2), 86.98 (Ti-O-$C(CH_3)_3$), 122.06, 124.18, 124.52, 126.94, 127.46, 130.80, 131.51, 159.93. Anal. Calcd. for $C_{27}H_{42}AlNO_4Ti$: C, 62.39; H, 8.38; N, 2.43. Found: C, 62.09; H, 8.34; N, 2.42.

[13] Crystallographic analysis: all measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by direct method and expanded using Fourier techniques, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Calculation was performed using the Crystal Structure crystallographic software package. The selected crystal collection parameters: crystal color, habit = yellow, block; formula = $C_{30}H_{48}NO_5TiAl$; crystal system, space group = monoclinic, $P2_1/n$ (#14); $a = 17.5435(6)$ Å; $b = 9.4428(3)$ Å; $c = 19.4061(6)$ Å; $\beta = 90.0796(12)°$; $V = 3214.81(18)$ Å^3; $Z = 4$; $D_{calcd} = 1.193$ g/cm^3; $F_{000} = 1240.00$; no. of reflections measured = 29437; no. of observations ($I > 2.00\sigma(I)$) = 4879; $R_1 = 0.0474$; $wR_2 = 0.1424$; goodness of fit = 1.009. The crystallographic data were deposited in Cambridge Crystallographic Data Centre as CCDC648342, and the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or e-mail deposit@ccdc.cam.ac.uk.

[14] ^{1}H NMR ($CDCl_3$, 25 °C): 1.08 (br s, 6H), 1.78 (br s, 2H), 2.20 (br s, 12H), 2.80 (br s, 2H), 3.47 (br s, 2H), 4.42 (br s, 4H), 5.28 (br s, 2H), 6.65 (s, 2H), 6.85 (s, 2H). ^{1}H NMR ($CDCl_3$, 55 °C): 1.20 (br s, 3H), 1.85 (t, 2H), 2.20 (s, 6H), 2.78 (t, 2H), 3.46 (d, 2H), 3.74 (d, 2H), 4.36, (d, 2H), 5.27 (septet, 1H), 6.65 (S. 2H), 6.85 (S, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): 16.88 ($CH(CH_3)_2$, 20.51 (Ar-CH_3), 27.10 (br,

C-CH_2-C), 31.39 (Ar-CH_3), 56.74 (br, N-CH_2), 60.10 (br, Ar-CH_2), 73.95 (br, O-CH_2), 83.92 (br, CH), 123.93, 124.40, 127.13, 130.53, 158.92.

[15] The selected crystal collection parameters: crystal color, habit = red, block; formula = $C_{42}H_{54}N_2O_6Ti$; crystal system, space group = triclinic, P-1 (#2); $a = 13.2119(7)$Å; $b = 13.2975(8)$Å; $c = 26.8000(14)$Å; $\alpha = 76.2033(16)^\circ$; $\beta = 85.8076(15)^\circ$; $\gamma = 89.4258(16)^\circ$; $V = 4560.2(4)$Å^3; $Z = 4$; $D_{calcd} = 1.064$ g/cm^3; $F_{000} = 1560.00$; no. of reflections measured = 35823; no. of observations ($I > 3.00\sigma(I)$) = 8601; $R_1 = 0.0634$; $wR_2 = 0.1049$; goodness of fit = 1.004. The crystallographic data were deposited in Cambridge Crystallographic Data Centre as CCDC648185.

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