A New Class of Mono- and Tetra-nuclear Titanatranes: Synthesis, Structure, and Ethylene Polymerization Studies. Role of Single-Sited Active Species?

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Mono- and tetranuclear titanatranes bearing the C_3-symmetric aminotriol ligand $N(CH_2CHPhOH)_3$ were synthesized. The structure of the tetratitanium compound was determined by single-crystal X-ray crystallography. The new titanatrane derivative included four aminotriols ligated to four titanium atoms, forming a tetranuclear unit with μ_2-O and μ_3-O bridges. The mono- and tetranuclear titanatranes were capable of polymerizing ethylene with a turnover frequency of up to 375 kg of PE/((mol of catalyst) h bar). The polymers obtained had $T_m \approx 133$ °C, indicative of linear polyethylene, and were further characterized by NMR. The ethylene polymerization activities of mono- and tetranuclear titanium catalysts were related by a factor of 4, indicating possibly the formation of a common single-site active species.

Introduction

The past decade has witnessed a compelling series of studies employing very efficient nonmetallocene catalysts for olefin polymerization.[1] Organometallic and coordination compounds of early and late transition metals containing noncyclopentadienyl ligands are generally the precatalysts, and their activation to polymerize olefins has been usually effected by addition of aluminum alkyls such as MAO or borate salts.[2] One of the attractive features of these nonmetallocene catalysts is their ability to polymerize α-olefins in a living or pseudo-living manner, and the polymers obtained in general have been highly isotactic.[3] Still, a comprehensive correlation between the symmetry effects of the ligand, and hence that of the precatalysts, with the tacticity of the polyolefins produced is nearly absent. This is even more true when the correlation is evaluated in the context of the superior control over polymer architecture exhibited by the molecular symmetry of the metallocene precatalysts.[4] We recently employed precatalysts based on Ti-containing C_2-symmetric and C_1-symmetric (meso) aminodiolate ligands, for transformation reactions[5a] as well as for polymerization of 1-hexene.[5b] We also reported the production of highly isotactic polyhexenes with the former catalyst, while the latter catalyst yielded atactic polymers. As an extension, we have initiated studies to evaluate the efficiency of titanatranes containing a C_3-symmetric trialkanolamine ligand in olefin polymerization reactions.

Titanatranes containing triethanolamine ligands have been synthesized and studied in detail by Verkade,[6a−g] who has also employed these catalysts for production of heterotactic-biased poly(*rac*-lactic acid). Half-sandwich titanocene compounds possessing trialkanolamine ligands have been used as precatalysts for the syndiospecific polymerization of styrene.[6h,i] Chiral titanatranes of the type $Ti[N(CH_2CHRO)_3]X$, where $R = CH_3$, C_6H_5, C_6H_{11} and $X = O^iPr$, Cl, were first synthesized by Nugent and used in asymmetric catalysis.[7] Here we report the synthesis of a new class of racemic

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[1] Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

[2] (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (b) Chen, E. Y.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

[3] For a review on living polymerization see: (a) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236. For examples of living polymerization of α-olefins with Zr and Hf precatalysts with NON ligand systems see: (b) Liang, L.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797. (c) Mehrkhodavandi, P.; Schrock, R. R.; Bonitatebus, P. J., Jr. *Organometallics* **2002**, *21*, 5785. (d) Mehrkhodavandi, P.; Schrock, R. R.; Pryor, L. L. *Organometallics* **2003**, *22*, 4569. (e) Schrock, R. R., Adamchuk, J.; Ruhland, K.; Lopez, L. P. H. *Organometallics* **2003**, *22*, 5079. For examples of living polymerization of α-olefins with Zr acetamidinates see: (f) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958. (g) Harney, M. B.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 4536. For examples of living polymerization by ligand structure modifications see: (h) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Chem. Commun.* **2001**, *20*, 2120. (i) Tshuva, E. Y.; Groysman, S.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2002**, *21*, 662. (j) Groysman, S.; Goldberg, I.; Kol, M.; Genizi, E.; Goldschmidt, Z. *Organometallics* **2003**, *22*, 3013.

[4] (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (b) Brintzinger, H. H.; Fisher, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

[5] (a) Manivannan, R.; Sundararajan, G., Kaminsky, W. *Macromol. Rapid Commun.* **2000**, *21*, 968. (b) Manivannan, R.; Sundararajan, G. *Macromolecules* **2002**, *35*, 7883.

[6] (a) Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 4628. (b) Naiini, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 5009. (c) Naiini, A. A.; Ringrose, S. L.; Su, Y.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 1290. (d) Kim, Y.; Verkade, J. G. *Organometallics* **2002**, 21, 2395. (e) Kim, Y.; Jnaneshwara, G. K.; Verkade, J. G. *Inorg. Chem.* **2003**, *42*, 1437. (f) Kim, Y.; Hong, E.; Lee, M. H.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 36. (g) Kim, Y.; Do, Y. *J. Organomet. Chem.* **2002**, *655*, 186.

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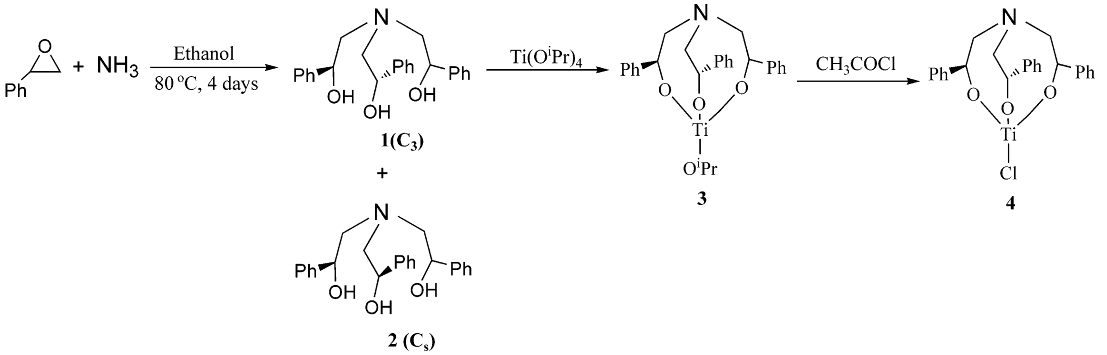
Scheme 1. Synthesis of Ligands 1 and 2 and the Mononuclear Titanatrane 4

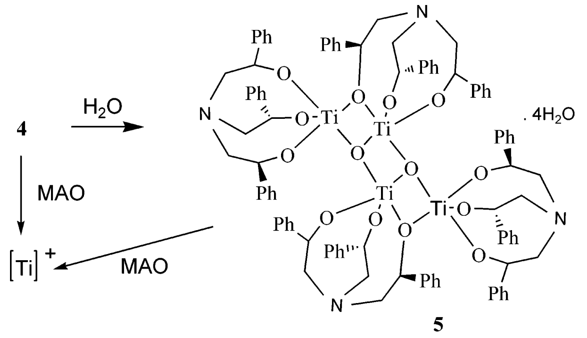


titanatranes containing the tetradentate oxoamine ligands N(CH$_2$CH(Ph)OH)$_3$ (C_3-**1** and C_s-**2**). We have also discovered that partial hydrolysis of the mononuclear ligand **1** containing a Ti−chloro compound (**4**) gives a crystalline tetranuclear titanatrane (**5**). Such formation of multinuclear titanatranes from the controlled hydrolysis of a mononuclear triethanolamine titanium compound has been reported,[8] though formation of a tetranuclear intermediate has not been observed thus far under these conditions. In the present investigation, we wish to report the initial results on the performance of these precatalysts **4** and **5** upon activation with MAO for ethylene polymerization.

Results and Discussion

A diastereomeric mixture containing C_3 (**1**) and C_s (**2**) ligands was obtained by reacting 3 equiv of styrene oxide with 1 equiv of NH$_3$ in methanol. The preparation of an optically pure methyl analogue of **1** was first reported by Morrison[9] and then modified by Nugent.[7] We find that it is convenient to synthesize the required aminotriols in a mixture of both C_3 and C_s forms using racemic styrene oxide and ammonia (Scheme 1). After removal of side products containing unwanted amino alcohols by flash chromatography, the ligand **1** was isolated as colorless crystals from a 50:50 solution of toluene and hexane and was further purified by recrystallization from 2-propanol. The mother liquor was subjected to semipreparative HPLC using 80:20 mixture of methanol and water for separation of the ligands **1** and **2**.

Scheme 2. Synthesis of the Tetranuclear Titanium Precatalyst and Generation of a Common Monotitanate Active Species for Ethylene Polymerization



When **1** was treated with 1 equiv of Ti(O^{i}Pr)$_4$ in toluene, the reaction proceeded with a loss of 3 equiv of 2-propanol. The ^{1}H and ^{13}C NMR spectra indicated the formation of the compound and the accompanying symmetric nature in the solution state. Treatment of this titanium isopropoxide compound **3** with CH$_3$COCl in toluene resulted in the formation of **4** in 65% yield. The crystal structure of the methyl analogue was reported by Nugent in 1994.[7] The ^{1}H NMR spectrum of compound **4** was consistent with the proposed structure indicated in Scheme 1, with the proton signals shifting downfield by approximately 1.00 ppm relative to the free ligand, and a somewhat smaller downfield shift of 0.4−0.8 ppm was observed for the CH$_2$N resonances.

The titanium chloride compound **4**, in the presence of 0.5 equiv of water, underwent partial hydrolysis, as shown in Scheme 2, yielding the new class of titanatrane **5** as colorless crystals. Addition of more than 0.5 equiv of water yielded amorphous materials that exhibit low solubility in common organic solvents, rendering further characterization difficult.

Crystal and Molecular Structure of {Ti$_2$[N(CH$_2$CHPhO)$_3$]$_2$(μ_3-O)}$_2$ (5). The outcome of our X-ray structural analysis revealed that **5** is a tetranuclear Ti compound containing two Ti$_2$[N(CH$_2$CHPhO)$_3$]$_2$ units which are linked by a pair of triply bridging oxo ligands with four solvated water molecules. The ORTEP drawing is depicted in Figure 1. The crystallographic data and selected interatomic distances and angles are provided in Tables 1 and 2, respectively. The geometry around each Ti can be viewed as a distorted octahedron, similar to that found in [Ti$_3$(μ_2-O){OCH(CH$_3$)$_2$}{(OCH$_2$CH$_2$)$_2$(μ_2-OCH$_2$CH$_2$)N}$_2${(OCH$_2$CH$_2$)(μ_2-OCH$_2$CH$_2$)$_2$N}]$_2$.[8]

In Ti(2) and Ti(3) the axial sites are occupied by two oxygen atoms of the tripodal ligand **1** and the equatorial planes are occupied by oxygen, nitrogen atoms of **1**, and the two oxygen atoms which are introduced by hydrolysis. In the case of Ti(1) and Ti(4) the axial sites are occupied by two oxygen atoms of **1**, while the equatorial planes are occupied by oxygen, the nitrogen of **1**, an oxygen atom of the neighbor ligand, and an oxygen atom introduced via hydrolysis. Among the four titanium atoms, Ti(2) and Ti(3) are in similar coordination

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(7) (a) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1994**, *116*, 6142. (b) Bonchio, M.; Calloni, S.; Furia, F. D.; Licini, G.; Modena, G.; Moro, S.; Nugent, W. A. *J. Am. Chem. Soc.* **1997**, *119*, 6935. (c) Bonchio, M.; Licini, G.; Bortolini, O.; Moro, S.; Nugent, W. A. *J. Am. Chem. Soc.* **1999**, *121*, 6258.

(8) Kemmitt, T.; Al-Salim, N. I.; Gainsford, G. J. *Inorg. Chem.* **2000**, *39*, 6067.

(9) Morrison, J. D.; Grandbois, E. R.; Weisman, G. R. In *Asymmetric Reactions and Processes in Chemistry*; Eliel, E. L., Otsuka, S., Eds.; ACS Symposium Series 185; American Chemical Society: Washington, DC, 1982.

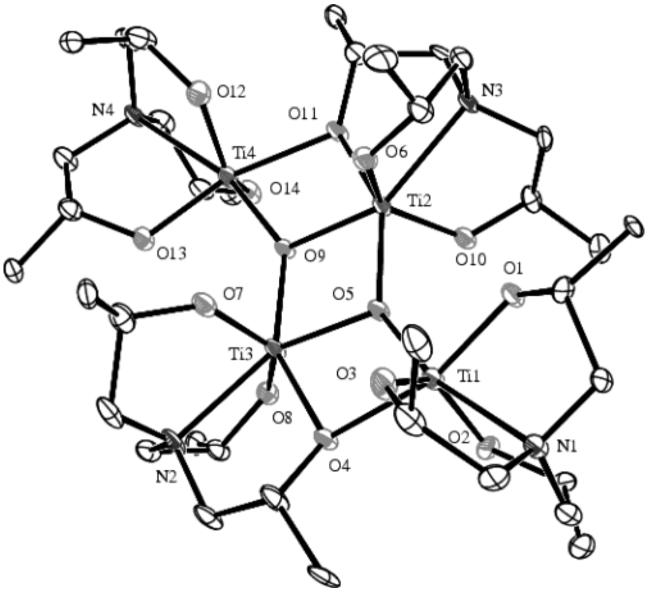

Figure 1. ORTEP drawing of **5**.

Table 1. Crystallographic Data for 5

formula	$C_{96}H_{104}N_4O_{18}Ti_4$
fw	1793.43
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	13.465(5)
b, Å	27.531(1)
c, Å	29.197(1)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	10 823(7)
Z	4
T (K)	293(2)
ρ, Mg m^{-3}	1.101
μ, mm^{-1}	0.343
cryst size, mm	0.3 × 0.3 × 0.25
θ range, deg	2.53−23.33
no. of rflns collected	67 119
no. of unique data	15 619
R_{int}	0.1986
refinement method	full-matrix-block least squares on F^2
no. of params	1098
no. of restraints	0
goodness of fit on F^2	0.972
R1[a]	0.1094
wR2[b]	0.2771
largest diff Fourier peaks and holes, e Å^{-3}	0.976 and −0.400

[a] $R1 = \sum|F_o - F_c|/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

environments, both lending one of their oxo arms for double bridging, and are separated by a Ti(2)···Ti(3) distance of 3.107(3) Å, which is the shortest among the three Ti···Ti distances (Table 2). All four titanium atoms, the four bridging oxygen atoms, and the four nitrogen atoms are almost in a plane. Among the four Ti−N bonds, two are longer (Ti(4)−N(4) = 2.424(8) Å and Ti(1)−N(1) = 2.402 (8) Å) than the other two (Ti(2)−N(3) = 2.331(8) Å and Ti(3)−N(2) = 2.352 (8) Å). However, one of the Ti−N bonds, Ti(4)−N(4), is slightly longer (not within ±3*σ*) than the reported Ti−N bond lengths (range 2.293(3)−2.400(3) Å) for triethanolaminotitanatranes.[8,10] The average Ti−O bond length, excluding Ti−O bridging distances, is 1.876(8) Å. To our knowledge, this is the first example of a tetranuclear titanium network containing a C_3-symmetric ligand.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5[a]

Ti(1)−Ti(3)	3.175(3)	Ti(2)−Ti(4)	3.177(3)
Ti(2)−Ti(3)	3.107(3)		
Ti(1)−N(1)	2.402(8)	Ti(3)−N(2)	2.352(8)
Ti(2)−N(3)	2.331(8)	Ti(4)−N(4)	2.427(8)
Ti(1)−O(5)	1.925(7)	Ti(3)−O(5)	1.934(7)
Ti(2)−O(5)	1.973(6)		
Ti(2)−O(9)	1.936(6)	Ti(4)−O(9)	1.900(6)
Ti(3)−O(9)	2.013(6)		
Ti(1)−O(4)	2.138(7)	Ti(2)−O(11)	2.026(6)
Ti(3)−O(4)	2.014(7)	Ti(4)−O(11)	2.134(7)
Ti(1)−O(1)	1.902(7)	Ti(3)−O(7)	1.829(8)
Ti(1)−O(2)	1.837(9)	Ti(3)−O(8)	1.855(8)
Ti(1)−O(3)	1.853(9)	Ti(4)−O(12)	1.838(9)
Ti(2)−O(6)	1.802(8)	Ti(4)−O(14)	1.845(8)
Ti(2)−O(10)	1.837(8)	Ti(4)−O(13)	1.883(8)
O(2)−Ti(1)−O(3)	136.2(4)	O(12)−Ti(4)−O(14)	134.8(4)
O(2)−Ti(1)−O(1)	102.3(4)	O(12)−Ti(4)−O(13)	100.4(4)
O(3)−Ti(1)−O(1)	98.7(4)	O(14)−Ti(4)−O(13)	101.7(4)
O(2)−Ti(1)−O(5)	103.5(3)	O(12)−Ti(4)−O(9)	112.5(3)
O(3)−Ti(1)−O(5)	114.4(4)	O(14)−Ti(4)−O(9)	107.2(4)
O(1)−Ti(1)−O(5)	90.4(3)	O(13)−Ti(4)−O(9)	88.0(3)
O(2)−Ti(1)−O(4)	87.1(3)	O(12)−Ti(4)−O(11)	83.5(3)
O(3)−Ti(1)−O(4)	84.2(3)	O(14)−Ti(4)−O(11)	88.8(3)
O(1)−Ti(1)−O(4)	162.1(3)	O(13)−Ti(4)−O(11)	159.9(3)
O(5)−Ti(1)−O(4)	72.5(3)	O(9)−Ti(4)−O(11)	72.4(2)
O(2)−Ti(1)−N(1)	75.4(3)	O(12)−Ti(4)−N(4)	73.7(3)
O(3)−Ti(1)−N(1)	73.1(4)	O(14)−Ti(4)−N(4)	73.7(3)
O(1)−Ti(1)−N(1)	76.0(3)	O(13)−Ti(4)−N(4)	76.8(3)
O(5)−Ti(1)−N(1)	165.6(3)	O(9)−Ti(4)−N(4)	164.5(3)
O(4)−Ti(1)−N(1)	121.5(3)	O(11)−Ti(4)−N(4)	123.0(3)
O(6)−Ti(2)−O(10)	135.7(3)	O(7)−Ti(3)−O(8)	135.4(3)
O(6)−Ti(2)−O(9)	105.7(3)	O(7)−Ti(3)−O(5)	106.6(4)
O(10)−Ti(2)−O(9)	116.5(3)	O(8)−Ti(3)−O(5)	115.5(4)
O(6)−Ti(2)−O(5)	89.8(3)	O(7)−Ti(3)−O(9)	89.7(3)
O(10)−Ti(2)−O(5)	88.1(3)	O(8)−Ti(3)−O(9)	87.8(3)
O(9)−Ti(2)−O(5)	75.6(3)	O(5)−Ti(3)−O(9)	74.7(3)
O(6)−Ti(2)−O(11)	103.2(4)	O(7)−Ti(3)−O(4)	103.1(4)
O(10)−Ti(2)−O(11)	100.8(3)	O(8)−Ti(3)−O(4)	101.1(3)
O(9)−Ti(2)−O(11)	74.1(3)	O(5)−Ti(3)−O(4)	75.2(3)
O(5)−Ti(2)−O(11)	149.3(3)	O(9)−Ti(3)−O(4)	149.5(3)
O(6)−Ti(2)−N(3)	76.1(3)	O(7)−Ti(3)−N(2)	74.5(4)
O(10)−Ti(2)−N(3)	74.5(3)	O(8)−Ti(3)−N(2)	76.1(4)
O(9)−Ti(2)−N(3)	149.3(3)	O(5)−Ti(3)−N(2)	150.4(3)
O(5)−Ti(2)−N(3)	135.0(3)	O(9)−Ti(3)−N(2)	134.6(3)
O(11)−Ti(2)−N(3)	75.6(3)	O(4)−Ti(3)−N(2)	75.8(3)
C(9)−N(1)−C(17)	113.2(9)	C(73)−N(4)−C(81)	117.1(6)
C(9)−N(1)−C(8)	114.7(10)	C(73)−N(4)−C(89)	112.0(6)
C(17)−N(1)−C(8)	110.8(10)	C(81)−N(4)−C(89)	111.7(6)
C(65)−N(2)−C(32)	111.0(9)	C(48)−N(3)−C(57)	108.9(8)
C(65)−N(2)−C(33)	114.9(8)	C(48)−N(3)−C(49)	113.4(9)
C(32)−N(2)−C(33)	109.8(10)	C(57)−N(3)−C(49)	115.6(8)
C(25)−O(4)−Ti(3)	119.5(7)	C(58)−O(11)−Ti(2)	118.8(4)
C(25)−O(4)−Ti(1)	128.4(6)	C(58)−O(11)−Ti(4)	125.8(4)
Ti(3)−O(4)−Ti(1)	99.7(3)	Ti(2)−O(11)−Ti(4)	99.5(3)
Ti(1)−O(5)−Ti(3)	110.7(3)	Ti(4)−O(9)−Ti(2)	111.8(3)
Ti(1)−O(5)−Ti(2)	141.7(4)	Ti(4)−O(9)−Ti(3)	142.2(4)
Ti(3)−O(5)−Ti(2)	105.3(3)	Ti(2)−O(9)−Ti(3)	103.7(3)

[a] Symmetry transformations were used to generate equivalent atoms.

Catalytic Activity in the Ethylene Polymerization Process. The catalytic activity in the ethylene polymerization of **4** and **5**, in association with MAO, was studied, and the results are summarized in Table 3. Polymerization reactions were carried out in the temperature range of 0−70 °C and at several Al/Ti molar ratios. While no induction period was observed for any

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(10) Dunn, S. C.; Mountford, P.; Robson, D. A. *J. Chem. Soc., Dalton Trans.* **1997**, 293.

Table 3. Polymerization of Ethylene with 4/MAO and 5/MAO[a]

temp (°C)	pressure (bar)	yield (g)	activity[b]	T_m[c] (°C)	M_η[d] (kg/mol)
		Catalyst **4**/MAO			
30	1	2.5	250	136	625
30	2	3.4	170	138	800
30	3	3.9	130	141	1010
0	1	3.7	375	136	420
10	1	3.0	300	134	550
50	1	3.0	300	133	380
60	1	1.6	160	133	290
70	1	0.5	50	132	210
		Catalyst **5**/MAO			
30	1	0.7	70	135	330
30	2	1.1	55	133	450
30	3	1.2	40	132	620
0	1	0.8	80	136	205
10	1	0.7	74	135	250
50	1	0.8	80	134	370
60	1	0.8	85	130	410
70	1	0.4	40	132	280

[a] Polymerization conditions: [**4**] = 1.09 × 10^{-5} mol; [**5**] = 0.27 × 10^{-5} mol; Al/Ti = 200; solvent toluene. [b] In units of kg of PE/((mol of catalyst) h bar). [c] Determined from differential scanning calorimetry. [d] From intrinsic viscosity using a Ubbelohde viscometer at 135 °C.

of the polymerization reactions, it was also found that the polymerization rate increased for the first 10 min, after which time it remained constant. It can be seen from Table 3 that at a constant Al/Ti ratio, while the temperature was increased to 50 °C, led to an increase in the polymerization rate. At higher temperatures a decrease in activity was observed, and this might be related to the thermal instability of the precatalyst or that of the active species at higher temperatures. The optimal temperature for each system depended on the balance between the propagation rate and the thermal instability. For instance, the polymerization activity of the system based on compound **5** was still increasing at the highest temperature used (i.e., 60 °C).

In all cases, the polymerization activity of compound **4** was 4 times greater than that observed for compound **5** (except at higher temperatures, >50 °C). In other words, the activity *per titanium atom* was the same for both compounds, indicating possibly that the tetranuclear species is cleaved into mononuclear cationic species in the presence of MAO. For example, at 30 °C titanatrane **5** showed an activity of around 70 kg of PE/((mol of titanatrane) h bar) (which corresponds to four titanium atoms) that upon normalization to one titanium atom gives an activity of 280 kg of PE/((mol of catalyst) h bar), which is of the same order of activity observed for the mononuclear titanatrane **4** (~250 kg of PE/((mol of catalyst) h bar)). The actual and normalized activities of the catalysts obtained from **4** and **5** with MAO are compared in Figure 2 as a function of polymerization temperature. The temperature dependence of the activities for the mononuclear catalyst **4** is easily simulated by **5** when its own activity is multiplied by a factor of 4.

Our attempts to examine the structures of the compounds **4** and **5** by solution Ti NMR failed, possibly because of the distorted-octahedral structure of the titanium atoms.[11] Surprisingly, however, when a solution of **5** in toluene was treated with MAO in toluene, the ^{47}Ti signal appeared at −875 ppm with a line width of 1000 Hz and a ^{49}Ti signal at −1075 ppm with a line width of 1000 Hz (with respect to $TiCl_4$ as external standard). A strikingly similar spectrum of two signals at 870 and 1070 ppm with a line width of 1000 Hz attributable respectively to ^{47}Ti and ^{49}Ti nuclei was seen when **4** in toluene was treated with MAO. We surmise, therefore, that both the tetranuclear **5** and the mononuclear **4** give rise to the same or similar cationic titanium species. At present we are not sure if this indeed is the active species for catalysis, as the metal center lacks the required number of vacant coordination sites. However, the removal of a ligated oxygen atom by MAO, to facilitate the approach of monomer ethylene, also cannot be ruled out. For example, Eisen has explained the reactivity of a C_3-symmetric zirconium catalyst attached to three benzamidinate ligands, by removing one of the ligating units from the metal center by MAO.[12a] Another recent report on ostensibly similar titanium(IV) compounds of triaryloxoamine ligands suggests a delinking of the metal−oxygen bond prior to initiating ethylene polymerization.[12b] Bruno[12c] offers a similar route for styrene polymerization by a titanium compound containing tripodal aryloxide ligands in the presence of MAO.

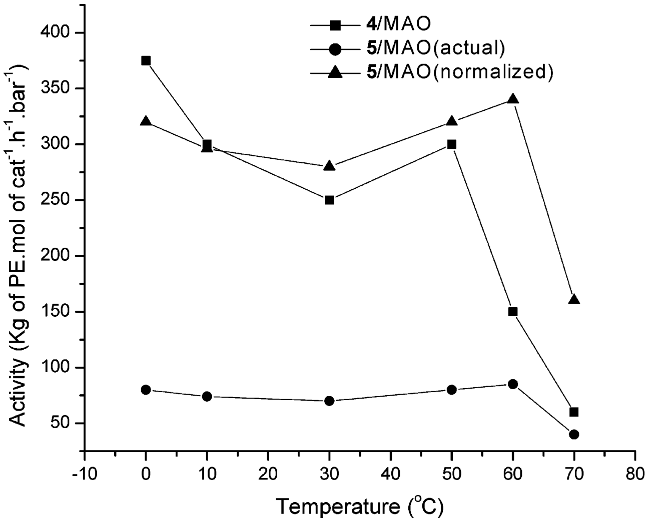

Figure 2. Temperature dependence on catalytic activity.

The polyethylenes obtained had good solubility in *o*-dichlorobenzene, 1,2,4-trichlorobenzene, xylene, mesitylene, etc. at high temperatures (>100 °C). The ^{13}C NMR of the polyethylene obtained showed a single peak at 28.27 ppm, and the melting points of polymers obtained from DSC studies were in the region 130−135 °C, consistent with a linear polyethylene architecture. Varying the ethylene pressures (1−3 bar) and polymerization temperatures has no effect on the linearity of the resultant polyethylene, whereas M_η was found to increase with increasing pressure (Table 3).

Conclusion

To summarize, we have synthesized and characterized two novel titanatrane compounds bearing a C_3-

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(11) (a) Boyle, T. J.; Alamond, T. H.; Mechenbier, E. R. *Inorg. Chem.* **1997**, *36*, 3293. (b) Foris, A. *Magn. Reson. Chem.* **2000**, *38*, 1044.

(12) (a) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640. For the suggestion of a formal loss of an aryloxide arm of a tripodal ligand from the metal center during polymerization, see: (b) Wang, W.; Fujiki, M.; Nomura, K. *Macromol. Rapid Commun.* **2004**, *25*, 504. (c) Michalczyk, L.; Gala, S.; Bruno, J. W. *Organometallics* **2001**, *20*, 5547.

symmetric aminotriol ligand. The compounds polymerize ethylene with high catalytic activities, and the polymerization data suggest the formation of mononuclear catalytically active species from a tetranuclear system. Further studies to understand the nature of the active species in polymerization and to evaluate the use of these precatalysts for polymerization of α-olefins are in progress.

Experimental Section

General Procedures. All manipulations were done under an atmosphere of dry, oxygen-free argon employing vacuum or Schlenk line techniques, unless otherwise stated. Argon was purified by passage through columns of MnO anchored on silica gel catalyst[13] and 4 Å molecular sieves. All polymerizations were performed in a Buchi type I high-pressure reactor equipped with BDS (Buchi Database System). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ at ambient temperature with tetramethylsilane (TMS) as the internal standard, and ^{47}Ti NMR (22.5 MHz) spectra were recorded with $TiCl_4$ as an external standard using a Bruker AV400 spectrometer. ^{13}C NMR spectra of polyethylene samples were obtained in 1,2,4-trichlorobenzene at 120 °C with DMSO-d_6 as lock solvent under the following conditions: pulse angle 25°, acquisition time 0.655 s, pulse delay 6 s, and number of scans 6000. Intrinsic viscosities of the polyethylene samples were determined by dissolving 10 mg of polymer in 20 mL of Decalin (98% cis/trans) using an Ubbelohde viscometer kept at 135 °C. Thermal analyses were performed on a Stanton Redcrofts simultaneous thermal analyzer (781 series). Flash chromatography was carried out on 230−400 mesh silica gel following the procedure of Still.[14] IR spectra of samples were recorded as CH_2Cl_2 solutions on a JASCO FTIR 400 spectrometer.

Synthesis and Isolation of Ligands 1 and 2. To 2 M ammonia in methanol solution (7.0 mL, 14.0 mmol) was added styrene epoxide (5.0 g, 41.6 mmol) at −78 °C. The mixture was stirred overnight at room temperature and then heated in an 80 °C oil bath for 4 days. The product was obtained as a colorless syrupy liquid. The diastereomeric mixture containing the C_3-symmetric ligand **1** and C_s-symmetric ligand **2** was purified from other impurities by flash chromatography using 70:30 hexane−ethyl acetate (yield: 60%). This mixture was further dissolved in 50:50 toluene−hexane under hot conditions and cooled to room temperature. Ligand **1** crystallizing out as colorless crystals was further purified by repeated crystallization from 2-propanol solution. Ligand **2** was freed from residual **1** using semipreparative HPLC using 80:20 methanol−water mixture. The overall yields of **1** and **2** were 20% and 42%, respectively.

1 was obtained as colorless needlelike crystals. Mp: 142−144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.73 (dd, $J = 7.2$, 2, N−CH_2, 3H), 2.97 (dd, $J = 7.4$, 4, N−CH_2, 3H), 5.00 (dd, $J = 3.5$, 4, O−CH, 3H), 5.22−5.71 (br s, C−OH, 3H), 7.28−7.44 (m, Ph, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.6 (N−CH_2), 70.5 (O−CH), 126.0 (Ph C), 127.6 (Ph C), 128.4 (Ph C), 141.8 (Ph C). IR (CH_2Cl_2, cm^{-1}): 3427, 3031, 2888, 1603, 1494, 1453, 1334, 1201, 1063, 887. Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.39; H, 7.16; N, 3.71. Found: C, 76.26; H, 7.08; N, 3.78.

2 was obtained as a colorless syrupy liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.82−2.87 (m, N−CH_2, 6H), 4.21−4.84 (br s, C−OH, 3H), 4.77−4.81 (m, O−CH, 3H), 7.26−7.35 (m, Ph, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.1 (N−CH_2), 65.4 (N−CH_2), 71.7 (O−CH), 73.6 (O−CH), 125.5 (Ph C), 127.1 (Ph C), 127.9 (Ph C), 141.4 (Ph C). IR (CH_2Cl_2, cm^{-1}): 3400, 3020, 2880, 1600, 1490, 1450, 1220, 1200, 1050, 887. Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.39; H, 7.16; N, 3.71. Found: C, 76.16; H, 7.31; N, 3.66.

Synthesis of 3. A solution of **1** (3.8 g, 10 mmol) in diethyl ether (10 mL) was added to a solution of Ti(O^{i}Pr)$_4$ (2.84 g, 10 mmol) in toluene (20 mL) at −78 °C. The mixture was stirred for 3 h at room temperature. Removal of the solvent afforded the titanium isopropoxide compound **3** (4.3 g, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.22 (d, $J = 7.4$, 3, CH_3, 6H), 3.15−3.40 (m, N−CH_2, 6H), 5.20 (septet, $J = 4.2$, 3, CH(CH_3)$_2$, 1H), 5.95 (m, Ph−CH−O, 3H), 7.38−7.84 (m, Ph, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.1 (CH_3), 63.8 (N−CH_2), 71.1 (CH(CH_3)$_2$), 81.3 (O−CH), 125.9 (Ph C), 127.4 (Ph C), 128.4 (Ph C), 142.2 (Ph C). IR (CH_2Cl_2, cm^{-1}): 3270, 3048, 2973, 1754, 1494, 1454, 1374, 1219, 1067, 946, 850. Anal. Calcd for $C_{27}H_{31}NO_4Ti$: C, 67.36; H, 6.49; N, 2.91. Found: C, 67.41; H, 6.53; N, 2.90.

Synthesis of 4. The Ti isopropoxide compound **3** (4.6 g, 10.0 mmol) prepared as shown above was dissolved in toluene (25 mL), and acetyl chloride (0.98 g, 12.5 mmol) was added. The mixture was stirred at room temperature for 2 h to give a clear yellow solution and was precipitated in hexane. Hexane was removed by cannula, and the white solid was redissolved in CH_2Cl_2 and reprecipitated in hexane. Removal of the solvent afforded a white solid (3 g, 65%) that was dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.21−3.52 (m, N−CH_2, 6H), 5.95 (m, O−CH, 3H), 7.38−7.84 (m, Ph, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.8 (N−CH_2), 81.3 (O−CH), 125.9 (Ph C), 127.4 (Ph C), 128.4 (Ph C), 142.2 (Ph C). IR (CH_2Cl_2, cm^{-1}): 3267, 3052, 2973, 1753, 1494, 1454, 1374, 1220, 1067, 946, 849. Anal. Calcd for $C_{24}H_{24}NO_3TiCl$: C, 62.34; H, 5.24; N, 3.06. Found: C, 61.64; H, 5.32; N, 3.28.

Synthesis of the Tetranuclear Ti Compound 5. The mononuclear compound **4** (4.57 g, 10.0 mmol) was dissolved in toluene (10 mL) and distilled water (5.0 mmol). The reaction mixture was stirred at room temperature for 30 min, and the toluene was removed by distillation under reduced pressure. The product separated from the residual toluene as a viscous liquid and slowly crystallized on cooling. **5**: yield 2.465 g, 55%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.12−3.60 (m, N−CH_2, 6H), 6.12 (m, O−CH, 3H), 7.21−7.80 (m, Ph, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 64.1 (N−CH_2), 81.7 (O−CH), 126.2 (Ph C), 127.9 (Ph C), 128.7 (Ph C), 142.9 (Ph C). IR (CH_2Cl_2, cm^{-1}): 3244, 3053, 2970, 1958, 1754, 1603, 1533, 1494, 1453, 1374, 1219, 1065, 943, 913, 847. Anal. Calcd for $C_{96}H_{96}N_4O_{14}Ti_4$: C, 66.99; H, 5.58; N, 3.25. Found: C, 65.43; H, 5.47; N, 3.33.

Ethylene Polymerization. An autoclave of capacity 1 L was dried under vacuum (10^{-1} mmHg) for several hours. Toluene (300 mL) was transferred into the vessel under a positive pressure of nitrogen and was heated to 30 °C. The temperature was controlled (to ca. ±2 °C) with an external heating/cooling bath and was monitored by a thermocouple that extended into the polymerization vessel. A solution of MAO in toluene was then injected, and the mixture was stirred for 3 min at 200 rpm. The precatalyst in a solution of toluene was then injected, and the reaction mixture was stirred for an additional 3 min at the same rate. The rate of stirring was increased to 1000 rpm, and the vessel was vented of nitrogen and pressurized with ethylene. Any recorded exotherm was within the allowed temperature differential of the heating/cooling system. The solution was stirred for 1 h, after which time the reaction was quenched with 1 M HCl in MeOH. The precipitated polymer was subsequently washed with MeOH and dried at 100 °C for at least 24 h prior to weighing.

X-ray Crystallographic Data Collection and Refinement of Structure. Colorless crystals of the compound **5**, suitable for X-ray diffraction studies, were grown by slow evaporation of a toluene−hexane (10:1) mixture. A crystal of approximate size 0.3 × 0.3 × 0.25 mm^3 was mounted in a Lindemann tube with paraffin oil to protect it from atmo-

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(13) (a) Shriver, D. F.; Drezdzen, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986; Chapter 3. (b) Sundararajan, G.; Shivasubramaniam, V. *Res. Ind.* **1991**, *36*, 26.

(14) Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *48*, 2923.

spheric air and moisture during data collection. The X-ray diffraction data at room temperature were measured in frames with increasing ω (width, 0.3°/frame) at a scan speed of 8 s/frame using a Bruker SMART APEX CCD diffractometer, equipped with a fine-focus sealed-tube X-ray source. The SMART software was used for data acquisition and the SAINT software for data extraction. The structure was solved by the heavy-atom method and refined by full-matrix least squares using the SHELX system of programs.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms in the compound were generated and assigned isotropic thermal parameters, riding on their parent carbon atoms, and used for structure factor calculation only. The hydrogen atoms of the ligands were located from the difference Fourier maps, and they were refined for two cycles isotropically at the initial stage. At the final stage of refinement, their thermal parameters were only refined isotropically.

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Supporting Information Available: A CIF file giving crystallographic data for compound **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034408R

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(15) Sheldrick, G. M. SHELX-97: Programs for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, Germany, 1997.