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New Titanium Complexes Having Two Pyrrolide−Imine Chelate Ligands: Syntheses, Structures, and Ethylene Polymerization Behavior

Yasunori Yoshida, Shigekazu Matsui, Yukihiro Takagi, Makoto Mitani, Takashi Nakano, Hidetsugu Tanaka, Norio Kashiwa, and Terunori Fujita*

R&D Center, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba, Japan

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New titanium complexes **1**−**4** having two nonsymmetric bidentate pyrrolide−imine chelate ligands, $[2\text{-}(RNCH)C_4H_3N]_2TiCl_2$ (**1**, R = Ph; **2**, R = Et; **3**, R = *n*-hexyl; **4**, R = cyclohexyl), are prepared in good yields from the lithium salt of the corresponding ligands and $TiCl_4$. Complex **1** is suggested by DFT calculations to adopt a distorted-octahedral structure in which the two pyrrolide-N atoms are situated in trans positions, while the two imine-N atoms and the two Cl atoms are located cis to one another. The spatial disposition elucidated by X-ray crystallographic analysis of complex **1** is consistent with the preferred structure predicted by DFT calculations. The molecular structures of complexes **2** and **4** established by X-ray analyses are very similar to that of complex **1**. DFT calculations suggest that an active species derived from complex **1**, for ethylene polymerization, possesses cis-located active sites trans to the imine-N atoms. These complexes were investigated as ethylene polymerization catalysts. Using methylalumoxane (MAO) as a cocatalyst, these complexes display very high activities and produce high-molecular-weight polyethylenes. Among them, complex **4** exhibits the highest activity (14 100 kg of polymer/((mol of Ti) h) comparable to that of Cp_2TiCl_2 with a very high molecular weight (M_v) value of 2 601 000. Alternatively, using $Ph_3CB(C_6F_5)_4/i\text{-}Bu_3Al$ as a cocatalyst, these complexes produce ultrahigh-molecular-weight polyethylenes (M_v > 4 000 000) with high activities (1500−2000 kg of polymer/((mol of Ti)/h).

Introduction

Research and development of highly active, well-defined group 4 metallocene catalysts has stimulated the progress of organometallic chemistry and catalyst chemistry.[1] In addition, the above research and development has revolutionized polymer chemistry to create a variety of polymers having novel properties and uses.[2] Therefore, after the discovery of the metallocene catalysts, well-defined transition-metal complexes have been intensively investigated, aiming at discovering highly active new olefin polymerization catalysts.[3] Recent advances in the design and synthesis of well-defined transition-metal complexes have spurred the rapid development of highly active olefin polymerization catalysts. Thus, quite a few highly active olefin polymerization catalysts based on both early- and late-transition-metal complexes have been developed. Notable examples are nickel complexes with diimine ligands[4] or phenoxy−imine ligands,[5] iron or cobalt complexes with diimine−pyridine ligands,[6] titanium complexes with diamide ligands,[7] phosphine−imide ligands,[8] indolide−imine ligands,[9] or tris(pyrazolyl)-borate ligands,[10] zirconium complexes with diamide ligands[11] or bis(phenoxy)−amine ligands,[12] and tantalum complexes with amide−pyridine ligands.[13] These complexes display activities comparable to those of the group 4 metallocene catalysts.

Previously, we have investigated well-defined transition-metal complexes featuring nonsymmetric bidentate ligand(s)[14] on the basis of the ligand-oriented catalyst

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[1] Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390.

[2] For a review: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

[3] For reviews: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Matsui, S.; Mitani, M.; Fujita, T. *Petrotech* **2001**, *24*, 11.

[4] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320.

[5] (a) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149. (b) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

[6] (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.

[7] (a) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 524. (b) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008.

[8] Stephan, D. W.; Guerin, F.; Spence, R. E. v. H.; Koch, L.; Gao, X.; Brown, S. J.; Swabey, J. W.; Wang, Q.; Xu, W.; Zoricak, P.; Harrison, D. G. *Organometallics* **1999**, *18*, 2046.

[9] Matsugi, T.; Matsui, S.; Kojoh, S.; Takagi, Y.; Inoue, Y.; Fujita, T.; Kashiwa, N. *Chem. Lett.* **2001**, 566.

[10] Murtuza, S.; Casagrande, O. L., Jr.; Jordan, R. F. *Polym. Mater. Sci. Eng.* **2001**, *84*, 109.

[11] Gibson, V. C.; Kimberley, B. S.; White, A. J. P.; Williams, D. J.; Howard, P. *Chem. Commun.* **1998**, 313.

[12] Tshuva, E. Y.; Goldberg, I.; Kol, M.; Weitman, H.; Goldschmidt, Z. *Chem. Commun.* **2000**, 379.

[13] Hakala, K.; Lofgren, B.; Polamo, M.; Leskela, M. *Macromol. Rapid Commun.* **1997**, *18*, 635.

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design concept[15h] to develop highly active new olefin polymerization catalysts. As a result of this study, we have developed a new family of group 4 transition-metal complexes possessing two phenoxy–imine chelate ligands, named FI Catalysts, displaying high catalytic performance for olefin polymerization,[15] including living olefin polymerization.[16] These results inspired us to conduct further investigation along this research line. Recently, we have turned our efforts to group 4 transition metal complexes having two pyrrolide–imine chelate ligands[17] because the active species of these complexes for olefin polymerization may have cis-located active sites trans to the imine-N atoms, the same as the active species of highly active group 4 transition-metal complexes having two phenoxy–imine chelate ligands.[15] In this paper, we describe the syntheses and structures of new titanium complexes bearing two pyrrolide–imine chelate ligands. Ethylene polymerization results using these titanium complexes in the presence of methylalumoxane or $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al are also presented in order to introduce the high potential of these complexes for olefin polymerization.

Results and Discussion

Synthesis of Titanium Complexes Having Two Pyrrolide–Imine Ligands. A general synthetic route for the titanium complexes with two pyrrolide–imine ligands[18,19] used in this study is shown in Scheme 1.

Scheme 1

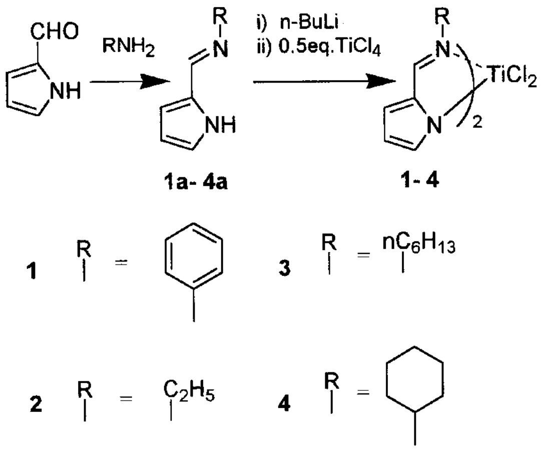
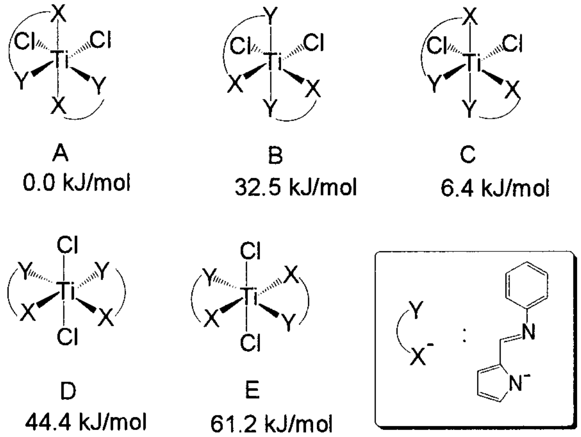


Chart 1. Five Idealized Octahedral Structures and Their Relative Formation Energies Based on Isomer A



The pyrrolide–imine ligands of structures **1a**–**4a** are prepared (yields: **1a**, 65%; **2a**, 66%; **3a**, 96%; **4a**, 96%) by the Schiff-base condensation of the desired primary amine with pyrrole-2-carboxaldehyde in dry EtOH using formic acid as a catalyst. The titanium complexes bearing two pyrrolide–imine ligands **1**–**4** are obtained as black powders (yields: **1**, 79%; **2**, 58%; **3**, 37%; **4**, 38%) by the treatment of $TiCl_4$ with 2 equiv of the lithium salt of the pyrrolide–imine ligand in dry diethyl ether. The overall yields starting from pyrrole-2-carboxaldehyde are fairly good (**1**, 51%; **2**, 38%; **3**, 36%; **4**, 36%).

Structure of Complex 1. The ^1H NMR spectra of complexes **1**–**4** display a single sharp resonance for the methine proton (–HN=C–) of the pyrrolide–imine chelate ligands, consistent with an octahedral coordination structure.

Five idealized octahedral structures (A–E, Chart 1) in which the titanium is bound to two cis-coordinated pyrrolide–imine chelate ligands are possible for each complex because the titanium complex possesses two nonsymmetric bidentate ligands. The relative formation energies for these five possible isomers of complex **1** were calculated using DFT to establish the most stable isomeric structure. Structure A was predicted to be the most favored (see Chart 1). The calculations suggest

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(14) Pioneering work concerning this field: (a) Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282. (b) Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3303. (c) Kim, I.; Nishihara, Y.; Jordan, R. F.; Rogers, R. D.; Rheingold, A. L.; Yap, P. A. *Organometallics* **1997**, *16*, 3314. (d) Jones, D.; Roberts, A.; Cavell, K.; Keim, W.; Englert, U.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 255.

(15) (a) Fujita, T.; Tohi, Y.; Mitani, M.; Matsui, S.; Saito, J.; Nitabaru, M.; Sigi, K.; Makio, H.; Tsutsui, T. Eur. Pat. 0874005, 1998; *Chem. Abstr.* **1998**, *129*, 331166. (b) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. *Chem. Lett.* **1999**, 1065. (c) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett.* **1999**, 1263. (d) Matsui, S.; Mitani, M.; Saito, J.; Matsukawa, N.; Tanaka, H.; Nakano, T.; Fujita, T. *Chem. Lett.* **2000**, 554. (e) Mitani, M.; Fujita, T. *Chem. Chem. Ind.* **2000**, *53*, 691. (f) Tohi, Y.; Mitani, M.; Tanaka, H.; Fujita, T. *Catal. Catal.* **2000**, *42*, 310. (g) Saito, J.; Mitani, M.; Matsui, S.; Kashiwa, N.; Fujita, T. *Macromol. Rapid Commun.* **2000**, *21*, 1333. (h) Matsui, S.; Fujita, T. *Catal. Today* **2001**, *66*, 61. (i) Matsukawa, N.; Matsui, S.; Mitani, M.; Saito, J.; Tsuru, K.; Kashiwa, N.; Fujita, T. *J. Mol. Catal. A* **2001**, *169*, 99. (j) Matsui, S.; Inoue, Y.; Fujita, T. *J. Synth. Org. Chem., Jpn.* **2001**, *59*, 232. (k) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847. (l) Saito, J.; Mitani, M.; Matsui, S.; Tohi, Y.; Makio, H.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Macromol. Chem. Phys.*, in press. (m) Ishi, S.; Saito, J.; Mitani, M.; Mohri, J.; Matsukawa, N.; Tohi, Y.; Matsui, S.; Kashiwa, N.; Fujita, T. *J. Mol. Catal. A*, in press. (n) Inoue, Y.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2000**, 1060.

(16) (a) Mitani, M.; Yoshida, Y.; Mohri, J.; Tsuru, K.; Ishii, S.; Kojoh, S.; Matsugi, T.; Saito, J.; Matsukawa, N.; Matsui, S.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. WO Pat. 01/55231 A1, 2001. (b) Fujita, T.; Yoshida, Y.; Tohi, Y.; Matsui, S.; Mitani, M.; Kojoh, S.; Kashiwa, N. *Catal. Catal.* **2001**, *43*, 67. (c) Saito, J.; Mitani, M.; Mohri, J.; Yoshida, Y.; Matsui, S.; Ishii, S.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2918. (d) Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 576. (e) Saito, J.; Mitani, M.; Onda, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Macromol. Rapid Commun.* **2001**, *22*, 1072. (f) Kojoh, S.; Matsugi, T.; Saito, J.; Mitani, M.; Fujita, T.; Kashiwa, N. *Chem. Lett.* **2001**, 822.

(17) (a) Matsui, S.; Nitabaru, M.; Yoshida, Y.; Mitani, M.; Fujita, T. Eur. Pat. 1008595, 2000; *Chem. Abstr.* **2000**, *133*, 43969. (b) Yoshida, Y.; Matsui, S.; Takagi, Y.; Mitani, M.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Fujita, T. *Chem. Lett.* **2000**, 1270. (c) Yoshida, Y.; Matsui, S.; Takagi, Y.; Mitani, M.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Catal. Catal.* **2001**, *43*, 103.

(18) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C. Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651.

(19) Matsuo, Y.; Mashima, K.; Tani, K. *Chem. Lett.* **2000**, 1114.

Table 1. Summary of Crystallographic Data for Complexes 1, 2, and 4

	1	**2**	**4**
formula	$C_{22}H_{18}N_4Cl_2Ti$	$C_{14}H_{18}N_4Cl_2Ti$	$C_{22}H_{30}N_4Cl_2Ti$
fw	457.22	361.13	469.31
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.606(2)	7.922(2)	14.064(9)
b (Å)	14.200(2)	17.862(8)	11.446(2)
c (Å)	14.294(2)	11.866(2)	14.354(2)
β (deg)	113.59(1)	97.18(1)	92.06(3)
V (Å)	2158.9(6)	1665.9(9)	2309(1)
Z	4	4	4
ρ(calcd) (g cm^{-3})	1.407	1.440	1.350
μ (cm^{-1})	6.59	8.32	6.18
λ (Å)	Mo Kα, 0.710 69	Mo Kα, 0.710 70	Mo Kα, 0.710 70
T	296 K	150K	150K
$2\theta_{\max}$ (deg)	55.0	55.2	57.1
no. of obsd rflns	5482	3490	4797
no. of unique rflns	5175	3462	4699
F_{000}	936	744	984
R^a	0.031	0.151	0.114
$R_w{}^b$	0.029	0.222	0.116

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ (complex **1**); $R = \sum(|F_o|^2 - |F_c|^2)/\sum|F_o|^2$ (complexes **2** and **4**). [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$ (complex **1**); $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$ (complexes **2** and **4**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 1, 2, and 4

	1	**2**	**4**
	Distances		
Ti−Cl(1)	2.2506(7)	2.275(1)	2.3542(8)
Ti−Cl(2)	2.2598(6)	2.285(1)	2.208(1)
Ti−N(1)	2.043(2)	2.044(3)	2.040(2)
Ti−N(2)	2.215(2)	2.168(3)	2.130(2)
Ti−N(3)	2.033(2)	2.049(3)	2.033(2)
Ti−N(4)	2.185(2)	2.174(3)	2.231(2)
	Angles		
Cl(1)−Ti−Cl(2)	97.82(3)	97.86(4)	100.40(4)
Cl(1)−Ti−N(1)	101.77(5)	103.69(9)	101.20(6)
Cl(1)−Ti−N(2)	90.95(4)	87.13(8)	91.64(6)
Cl(1)−Ti−N(3)	91.68(5)	90.17(9)	90.15(6)
Cl(1)−Ti−N(4)	165.45(4)	165.06(10)	166.67(5)
Cl(2)−Ti−N(1)	91.31(5)	89.00(9)	90.72(5)
Cl(2)−Ti−N(2)	165.47(4)	165.89(9)	163.51(5)
Cl(2)−Ti−N(3)	104.10(5)	100.29(9)	101.30(6)
Cl(2)−Ti−N(4)	93.03(4)	91.38(9)	93.03(4)
N(1)−Ti−N(2)	75.50(6)	77.0(1)	75.80(7)
N(1)−Ti−N(3)	158.04(6)	162.2(1)	161.77(7)
N(1)−Ti−N(4)	87.60(6)	88.1(1)	89.51(7)
N(2)−Ti−N(3)	87.12(6)	92.9(1)	89.80(7)
N(2)−Ti−N(4)	80.54(5)	86.7(1)	83.25(7)
N(3)−Ti−N(4)	76.22(6)	76.6(1)	77.57(7)

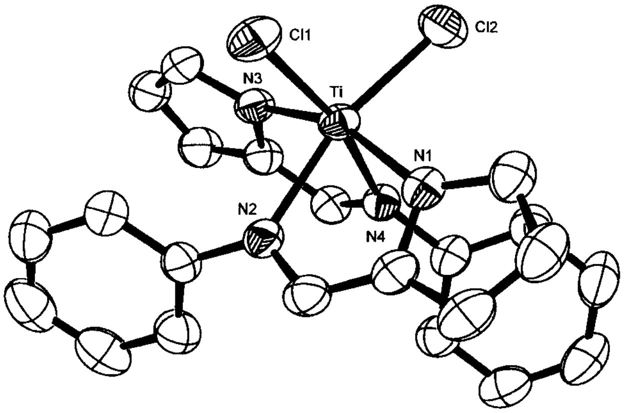

Figure 1. Molecular structure of complex **1**. Thermal ellipsoids at the 50% level are shown. Hydrogen atoms are omitted for clarity.

that complex **1** adopts a distorted-octahedral structure in which two pyrrolide-N (pN) atoms are trans (pN−Ti−pN, 172.5°; Ti−pN, 2.067 Å) and two imine-N (iN) atoms (iN−Ti−iN, 90.0°; Ti−iN, 2.128 Å) and two Cl atoms are cis (Cl−Ti−Cl, 97.3°; Ti−Cl, 2.353 Å). In the predicted structure the phenyl group on the iN swings out of the plane formed by the pyrrolide−imine chelate ring, forming a dihedral angle of 52.7°. In structure A, the short Ti−pN bonds are trans to each other to reduce steric congestion of the ligands. In addition, the pN can participate in Ti−pN π-bonding using different Ti d orbitals.

The molecular structure of complex **1** was established by a crystallographic analysis. The crystallographic data, collection parameters, and refinement parameters are summarized in Table 1. Selected bond angles and distances for complex **1** are listed in Table 2.

As shown in Figure 1, complex **1** adopts a distorted-octahedral geometry of the structure A type, having molecular C_2 symmetry. The two pN atoms are situated in trans positions (pN−Ti−pN, 158.04(6)°; Ti−pN, 2.033(2) and 2.043(2) Å), while the two iN atoms (iN−Ti−iN, 80.54(5)°; Ti−iN, 2.185(2) and 2.215(2) Å) and the two Cl atoms are oriented cis to each other (Cl−Ti−Cl, 97.82(3)°; Ti−Cl, 2.2506(7) and 2.2598(6) Å) at the central titanium metal. Thus, the spatial disposition predicted by DFT calculations is in good accordance with the results of the X-ray analysis, suggesting that DFT calculations are an effective tool for analyzing the molecular structure of a titanium complex having two pyrrolide−imine chelate ligands.

The Ti−pN, Ti−iN, and Ti−Cl bond distances of complex **1** are similar to those in known titanium complexes.[20] The cis angles associated with the chelated pyrrolide−imine ligands are acute (75.50(6) and 76.22(6)°). Alternatively, other cis angles between the ligands lie in the range of 80.54(5)° (iN−Ti−iN) to 101.77(5)° (pN−Ti−Cl), but most of the cis angles are around 90°, implying that constraints imposed by the chelation and steric interactions between the ligands are not significant for complex **1**. The trans angles between the ligands range from 158.04(6)° (pN−Ti−pN)

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[20] Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368.

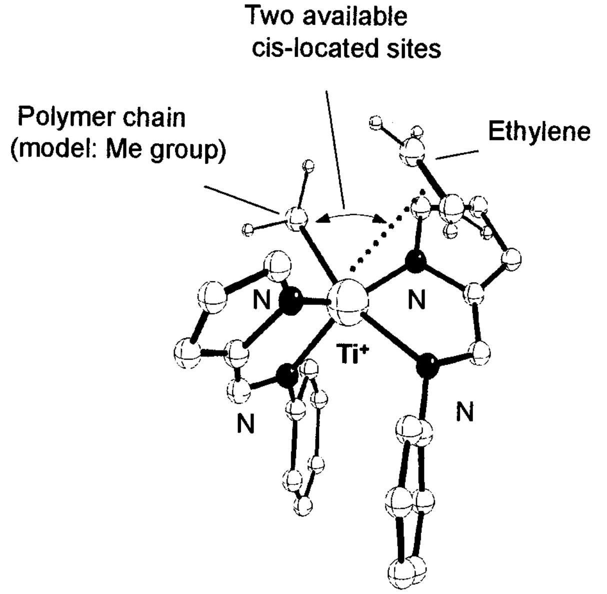

Figure 2. Calculated structure of the cationic active species generated from neutral complex **1**.

to 165.47(4)° (Cl−Ti−iN). The five-membered chelate rings are substantially flat and appear not to be significantly strained. The phenyl group on iN swings out of the plane formed by the chelate ring, making dihedral angles of 50.8(2) and 55.1(3)°, the values being in good accordance with those predicted by DFT calculations.

The catalytically active species derived from group 4 transition-metal complexes is known to be an alkyl cationic complex.[21] The results of DFT calculations on a methyl cationic complex generated from complex **1**, an initially active species derived from complex **1** with MAO for ethylene polymerization, indicate that the cationic complex has cis-located active sites; a methyl group and a coordinated ethylene are in a cis configuration (77.4°) and are trans to the iN's (Figure 2). Thus, the stereochemical relationship between the active sites and the iN's of the active species generated from complex **1** is the same as that for the active species of highly active group 4 transition-metal complexes having two phenoxy−imine chelate ligands,[15] which has cis-located active sites trans to the iN's. The results of DFT calculations as well as X-ray analysis suggest that complex **1** has a high potential for olefin polymerization.

Structures of Complexes 2−4. The molecular structures of complexes **2** and **4** were also elucidated by X-ray analyses. ORTEP views for complexes **2** and **4** are shown in Figures 3 and 4, and crystallographic details and selected bond distances and angles are listed in Tables 1 and 2. The molecular structures of complexes **2** and **4** are very similar to that of complex **1**, suggesting that substituents on iN give rise to no significant structural change of the complex. We assume that complex **3** adopts the similar structure.

Ethylene Polymerization. Ethylene polymerization behavior of complexes **1**−**4** were investigated in toluene at 25 °C using MAO as a cocatalyst under ethylene at atmospheric pressure. Polymerization results are summarized in Table 3. Complex **1** (R = Ph) displayed an activity of 6000 kg of polymer/((mol of Ti) h). This activity is very high for a titanium complex having no Cp ligands, under atmospheric pressure conditions. The

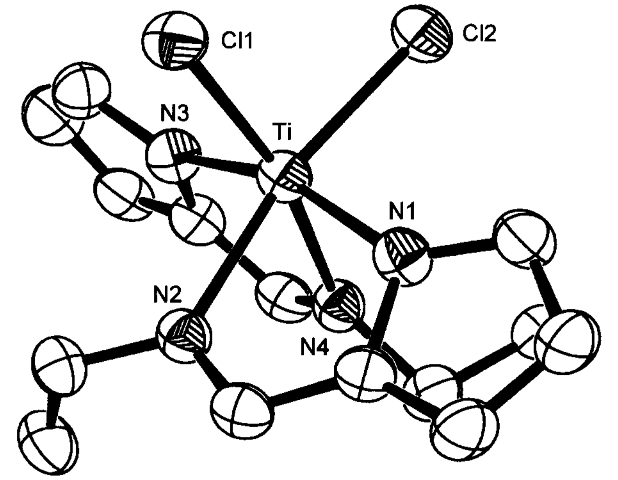

Figure 3. Molecular structure of complex **2**. Thermal ellipsoids at the 50% level are shown. Hydrogen atoms are omitted for clarity.

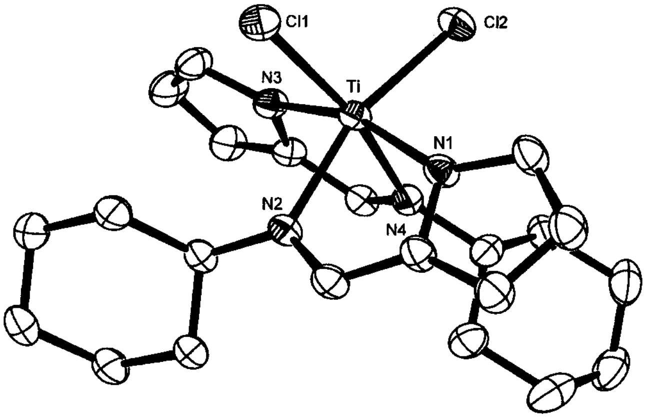

Figure 4. X-ray structure of complex **4**. Thermal ellipsoids at the 50% level are shown. Hydrogen atoms are omitted for clarity.

Table 3. Ethylene Polymerization Results[a]

entry	complex	yield (g)	activity (kg of polymer/((mol of Ti) h))	M_v
		cocatalyst MAO		
1	**1**	0.50	6000	75 000
2	**2**	0.03	400	412 000
3	**3**	0.07	800	441 000
4	**4**	1.18	14 100	2 601 000
5	Cp_2TiCl_2	1.39	16 700	1 253 000
		cocatalyst $Ph_3CB(C_6F_5)_4$/i-Bu_3Al		
6	**1**	0.16	1900	4 739 000[b]
7	**2**	0.14	1700	4 654 000[b]
8	**3**	0.13	1500	4 901 000[b]
9	**4**	0.17	2000	4 029 000[b]
10	Cp_2TiCl_2	0.29	3500	773 000

[a] Conditions: ethylene atmospheric pressure; ethylene gas flow, 100 L/h; toluene, 250 mL; polymerization temperature, 25 °C; polymerization time, 5 min; complex, 1 μmol; cocatalyst MAO (purchased from Albemarle), 1.25 mmol; $Ph_3CB(C_6F_5)_4$, 6 μmol; i-Bu_3Al, 0.25 mmol. [b] Polymer did not dissolve completely in decalin under the intrinsic viscosity measurement conditions. These values were obtained from the polyethylene soluble in decalin under the intrinsic viscosity measurement conditions.

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[21] (a) Tjaden, E. B.; Jordan, R. F. *Macromol. Symp.* **1995**, *89*, 231. (b) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 371.

viscosity-average molecular weight (M_v) value of the polymer was 75 000. The molecular weight distribution (M_w/M_n) of the polyethylene was 2.21 ($M_n = 30\,000$, $M_w = 67\,000$, GPC), indicating that the polymer is produced by a single-site catalyst. Complexes **2** and **3** (**2**, R = Et; **3**, R = *n*-hexyl) exhibited lower activities of 400 and 800 kg of polymer/((mol of Ti) h) with high M_v values of 412 000 and 441 000, respectively. Interestingly, complex **4** (R = cyclohexyl) showed a very high activity of 14 100 kg of polymer/((mol of Ti) h) with a very high M_v value of 2 601 000.[22−24] To our knowledge, the activity, 14 100 kg of polymer/((mol of Ti) h), represents one of the highest values reported to date for homogeneous titanium complexes with no Cp ligand and is comparable to those of Cp_2TiCl_2 (entry 5) and titanium tris(pyrazolyl)borate complexes.[10,25,26] The basic trend observed concerning the activity is that an increase in the bulk of R group on the iN results in enhanced activity. The enhancement in activity may be attributed to the effective separation between the cationic active species and the anionic cocatalyst as a result of the attachment of bulkier alkyl substituents to the iN. Using $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al as a cocatalyst in the place of MAO, these complexes provided polyethylenes which did not dissolve completely in decalin under the intrinsic viscosity measurement conditions, exhibiting high activities (**1**, 1900 kg of polymer/((mol of Ti) h); **2**, 1700 kg of polymer/((mol of Ti) h); **3**, 1500 kg of polymer/((mol of Ti) h); **4**, 2000 kg of polymer/((mol of Ti) h)). The M_v values for the soluble part of the polyethylenes are 4 739 000 (complex **1**), 4 654 000 (complex **2**), 4 901 000 (complex **3**), and 4 029 000 (complex **4**), suggesting that the polyethylenes formed with complexes **1**−**4**/$Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al cocatalyst systems are of exceptionally high molecular weight. Considering the great difference in molecular weight values obtained using MAO and $Ph_3CB(C_6F_5)_4$/*i*-BuAl as cocatalysts, the structures of the active species may be different depending on the cocatalyst employed.[29]

In conclusion, we have prepared new titanium complexes having two nonsymmetric bidentate pyrrolide−imine chelate ligands using the previously studied highly active FI Catalysts (group 4 transition-metal complexes having two phenoxy−imine chelate ligands) as a guide. X-ray analyses as well as DFT calculations indicate that these complexes adopt a distorted-octahedral structure with a trans-pN, cis-iN, and cis-Cl arrangement. An active species generated from complex **1** is suggested by DFT calculations to possess cis-located active sites trans to the iN's. While the choice of cocatalyst system has an effect on the catalytic performance of these titanium complexes, the highest activity obtained with MAO is comparable to that of Cp_2TiCl_2. Moreover, the molecular weight values obtained with $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al are exceptionally high and are some of the highest values encountered in homogeneous olefin polymerization catalysts, including the group 4 metallocene catalysts. The results introduced herein in combination with our previous results[9,15−17] suggest that group 4 transition-metal complexes bearing two nonsymmetric bidentate ligands are potentially viable catalysts for olefin polymerization.

Experimental Section

General Comments. All manipulations of air- and/or water-sensitive compounds were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a dry nitrogen glovebox.

Dried solvents (ethanol, diethyl ether, tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and *n*-hexane) used for ligand and complex syntheses were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Aniline derivatives and pyrrole-2-carboxaldehyde were purchased from Tokyo Kasei Kogyo Co., Ltd. An *n*-butyllithium hexane solution and $TiCl_4$ were obtained from Kanto Chemical Co., Inc. and Aldrich Chemical Co., Inc., respectively.

Toluene used as a polymerization solvent (Wako Pure Chemical Industries, Ltd.) was dried over Al_2O_3. Methanol and isobutyl alcohol were purchased from Wako Pure Chemical Industries, Ltd. Ethylene was purchased from Sumitomo Seika Co., Ltd. Methylalumoxane (MAO) was obtained from Albemarle as a 1.2 M toluene solution, and the remaining trimethylaluminum was evaporated in vacuo prior to use. Cp_2TiCl_2 (Tokyo Kasei Kogyo Co., Ltd.), *i*-Bu_3Al (Tosoh-Akuzo Co., Ltd.), and $Ph_3CB(C_6F_5)_4$ (Asahi Glass Co., Ltd.) were used as received.

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(22) Ethylene polymerization results using $TiCl_4$/MAO: activity, 90 kg of polymer/((mol of Ti) h); M_v, 296 000. Polymerization conditons were the same as those for entries 1−5, except for the catalyst amount (5 μmol) and polymerization time (30 min).

(23) Ethylene polymerization results using other titanium complexes having two pyrrolide−imine chelate ligands/MAO are as follows. **$[2\text{-}(4\text{-}CH_3O\text{-}C_6H_4\text{-}NCH)C_4H_3N]_2TiCl_2$**: activity, 3800 kg of polymer/((mol of Ti) h); M_v, 271 000. **$[2\text{-}(4\text{-}CF_3\text{-}C_6H_4\text{-}NCH)C_4H_3N]_2TiCl_2$**; activity, 800 kg of polymer/((mol of Ti) h); M_v, 335 000. **$[2\text{-}(3,5\text{-}(CF_3)_2\text{-}C_6H_3\text{-}NCH)C_4H_3N]_2TiCl_2$**: activity, 500 kg of polymer/((mol of Ti) h); M_v, 1 191 000. Polymerization conditions were the same as those for entries 1−5. The introduction of 4-CH_3O, 4-CF_3, and 3,5-$(CF_3)_2$ into the phenyl group resulted in a decrease in activity and an increase in M_v. **$[2\text{-}(4\text{-}CH_3O\text{-}C_6H_4\text{-}NCH)C_4H_3N]_2TiCl_2$**: overall yield 46%; ^1H NMR (270 MHz, $CDCl_3$, δ) 3.78 (t, $J = 7$ Hz, 6H, CH_3O−), 6.06 (dd, $J = 2$ Hz, 2H, pyrrole ring aromatic H), 6.42 (d, $J = 2$ Hz, 2H, pyrrole ring aromatic H), 6.6−7.8 (m, 2H, pyrrole ring aromatic H + 8H, benzene ring aromatic H + 2H, −CH═N−); FD-mass *m*/*z* 516 (M^+). Anal. Calcd for $C_{24}H_{22}N_4TiCl_2$: C, 53.57; H, 4.50; N, 11.36. Found: C, 53.52; H, 4.35; N, 11.69. **$[2\text{-}(4\text{-}CF_3\text{-}C_6H_4\text{-}NCH)C_4H_3N]_2TiCl_2$**: overall yield 46%; ^1H NMR (270 MHz, $CDCl_3$, δ) 6.18 (dd, $J = 2$ Hz, 2H, pyrrole ring aromatic H), 6.64 (d, $J = 2$ Hz, 2H, pyrrole ring aromatic H), 7.00−8.00 (m, 2H, pyrrole ring aromatic H + 8H, benzene ring aromatic H + 2H, −CH═N−) [Et_2O of crystallization, δ 1.20 (t, $J = 5$ Hz, 3H, CH_3−), 3.48 (q, $J = 5$ Hz, 2H, −CH_2−)]; FD-mass *m*/*z* 592 (M^+). Anal. Calcd for $C_{24}H_{16}F_6N_4TiCl_2 \cdot {}^1/_2Et_2O$: C, 49.55; H, 3.36; N, 8.89. Found: C, 49.92; H, 3.37; N, 9.42. **$[2\text{-}(3,5\text{-}(CF_3)_2\text{-}C_6H_3\text{-}NCH)C_4H_3N]_2TiCl_2$**: overall yield 33%; ^1H NMR (270 MHz, $CDCl_3$, δ) 6.18 (dd, $J = 2$ Hz, 2H, pyrrole ring aromatic H), 6.64 (d, $J = 2$ Hz, 2H, pyrrole ring aromatic H), 7.36 (s, 4H, benzene ring aromatic H), 7.62 (d, $J = 2$ Hz, 2H, pyrrole ring aromatic H), 7.80 (s, 2H, benzene ring aromatic H), 7.90 (s, 2H, −CH═N−); FD-mass *m*/*z* 728 (M^+). Anal. Calcd for $C_{26}H_{14}F_{12}TiCl_2$: C, 42.83; H, 1.94; N, 7.68. Found: C, 42.52; H, 2.13; N, 7.91.

(24) For propylene polymerization at 25 °C at atmospheric pressure, the complex **4**/MAO produced syndiotactic-rich polymer with low activity.

(25) Although the corresponding zirconium complexes possess practically the same molecular structure, they display considerably lower activities for the polymerization of ethylene under the same or similar conditions.[19,26] It is likely that strong binding of the cocatalyst to the electrophilic zirconium metal center[27,28] may result in reducing space for ethylene's coordination to the metal and its insertion into the metal−carbon bond.

(26) Yoshida, Y.; Matsui, S.; Nitabaru, M.; Fujita, T. Unpublished results.

(27) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562.

(28) Guérin, F.; McConville, D. H.; Vittal, J. *Organometallics* **1996**, *15*, 5586.

(29) One possible explanation for the M_v difference is that, in the case of $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al cocatalyst, the pyrrolide−imine ligand of the complex is converted to a pyrrolide−amine ligand by the reduction with *i*-Bu_3Al and/or its contaminant aluminum hydride compounds. The reduction of an imine to an amine has been observed for Ti or Zr complexes having two phenoxy−imine ligands/$Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al catalyst systems.[15k,l]

^{1}H NMR spectra were recorded on a JEOL270 spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard at ambient probe temperature (25 °C). Chemical shifts were reported in δ units.

FD-MS spectra were recorded on an SX-102A from Japan Electron Optics Laboratory Co., Ltd.

Elemental analysis for CHN was performed by a CHNO type from Helaus Co.

All calculations were performed using the gradient-corrected density functional method BLYP, by means of the Amsterdam Density Functional (ADF ver2.3.0) program.[30] For geometry optimizations, we used a triple-ζ basis set on Ti and a double-ζ STO basis set on N, Cl, and atoms constituting the ethylene and methyl group as a polymer model. A single-ζ STO basis set was employed on the other atoms. For energy calculations, a triple-ζ STO basis set on Ti and a double-ζ plus polarization STO basis set on the other atoms are used and the quasi-relativistic correction is also added.

Single crystals of complex **1**, **2**, and **4** suitable for X-ray analysis were grown from hexane/CH_2Cl_2 solutions. Details of the crystal data are listed in Table 1.

Data collection for complex **1** was performed on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation at 296 K. The data were corrected for Lorentz and polarization effects, but no decay collection was applied. The structure was solved by direct methods (SIR92)[31] and expanded using Fourier techniques (DIRDIF94).[32] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically.

Data collections for complex **2** and **4** performed made on a Rigaku RAXIS-IV imaging plate diffractometer with graphite-monochromated Mo Kα radiation at 150 K. The data were corrected for Lorentz and polarization effects, but no decay collection was applied. The structure was solved by heavy-atom Patterson methods (PATTY)[33] and expanded using Fourier techniques (DIRDIF94).[32] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

All calculations were performed using the teXsan crystallographic software package[34] of Molecular Structure Corp.

Intrinsic viscosity [η] was measured in decalin at 135 °C using an Ubbelohde viscometer (polyethylene 25 mg/decalin 25 mL). Viscosity average molecular weight (M_v) values of polyethylenes were calculated from the equation $[\eta] = (6.2 \times 10^{-4})M_v^{0.7}$. The molecular weight distribution (M_w/M_n) value of polyethylene was determined using a Waters 150-C gel permeation chromatograph at 145 °C using polyethylene calibration and equipped with three TSKgel columns (two sets of TSKgelGMH$_{HR}$-H(S)HT and TSKgelGMH$_6$-HTL). *o*-Dichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min.

Complex Synthesis. 2-(PhNCH)C_4H_3NH (1a). To a stirred solution of pyrrole-2-carboxyaldehyde (5.07 g, 53.3 mmol) in dried ethanol (150 mL), aniline (4.96 g, 53.3 mmol) and formic acid (1 mL), as a catalyst, were added. The reaction mixture was stirred for 72 h at room temperature. Evaporation of the ethanol gave a solid residue, which was purified by column chromatography on silica gel using hexane/ethyl acetate (9/1) as eluent to afford a flesh-colored solid. Recrystallization from *n*-hexane gave **1** as a flesh-colored powder in 65% yield (5.98 g, 35.2 mmol). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 6.30 (dd, $J = 2$ Hz, 1H, pyrrole ring aromatic H), 6.69 (d, $J = 2$ Hz, 1H, pyrrole ring aromatic H), 6.89 (d, $J = 2$ Hz, 1H, pyrrole ring aromatic H), 7.1−7.5 (m, 5H, benzene ring aromatic H), 8.29 (s, 1H, −CH=N−), 9.85 (br s, 1H, pyrrole ring NH). FD-mass: *m/z* 170. Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.73; H, 5.84; N, 16.33.

[2-(PhNCH)$C_4H_3N]_2TiCl_2$ (1). To a stirred solution of **1a** (1.035 g, 6.08 mmol) in dried diethyl ether (15.5 mL) at −78 °C was added dropwise a 1.54 M *n*-butyllithium hexane solution (4.15 mL, 6.38 mmol) over a 5 min period. The mixture was warmed to room temperature and stirred for 4 h. The resulting mixture was added dropwise over a 30 min period to a 0.5 M *n*-heptane solution of $TiCl_4$ (6.08 mL, 3.04 mmol) in dried diethyl ether (15.5 mL) at −78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h. Then, the reaction mixture was filtered through a glass filter, and the filtrate was concentrated in vacuo to give a solid. Dried diethyl ether (20 mL) was added to the solid, and the mixture was stirred for 10 min and filtered. The filtrate was concentrated in vacuo to yield a black solid. CH_2Cl_2 (5 mL) and *n*-hexane (10 mL) were added to the solid, and the mixture was stirred for 1 h and then filtered. Evaporation of the solvent gave **1** (1.10 g, 2.40 mmol) as a black solid in 79% yield. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 6.0−7.9 (m, 6H, pyrrole ring aromatic H + 10H, benzene ring aromatic H), 7.80 (s, 2H, −CH=N−). FD-mass: *m/z* 456 (M^+). Anal. Calcd for $C_{22}H_{18}N_4TiCl_2$: C, 57.80; H, 3.97; N, 12.25. Found: C, 58.29; H, 3.95; N, 12.62.

2-(EtNCH)C_4H_3NH (2a). 2a was prepared using a procedure similar to that for **1a**. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 1.26 (t, $J = 7$ Hz, 3H, CH_3−), 3.56 (q, $J = 7$ Hz, 2H, −CH_2−), 6.26 (dd, $J = 2$ Hz, 1H, aromatic H), 6.43 (d, $J = 2$ Hz, 1H, aromatic H), 6.89 (d, $J = 2$ Hz 1H, aromatic H), 8.13 (s, 1H, −CH=N−), 9.20 (br s, 1H, pyrrole ring NH). FD-mass: *m/z* 122. Anal. Calcd for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.93. Found: C, 68.39; H, 8.30; N, 23.12.

[2-(EtNCH)$C_4H_3N]_2TiCl_2$ (2). 2 was prepared using a procedure similar to that for **1**. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 1.05 (t, $J = 7$ Hz, 6H, CH_3−), 3.09 (q, $J = 7$ Hz, 4H, −CH_2−), 6.30 (dd, $J = 2$ Hz, 2H, aromatic H), 6.58 (d, $J = 2$ Hz, 2H, aromatic H), 7.80 (d, $J = 2$ Hz, 2H, aromatic H), 8.00 (s, 2H, −CH=N−). FD-mass: *m/z* 360 (M^+). Anal. Calcd for $C_{14}H_{18}N_4TiCl_2$: C, 46.57; H, 5.02; N, 15.52. Found: C, 47.01; H, 4.97; N, 15.94.

2-(*n*-hexyl-NCH)C_4H_3NH (3a). 3a was prepared using a procedure similar to that for **1a**. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.90 (d, $J = 7$ Hz, 3H, CH_3−), 1.30 (m, 6H, *n*-hexyl H), 1.65 (dd, $J = 7$ Hz, 2H, *n*-hexyl H), 3.52 (t, 2H, $J = 7$ Hz, *n*-hexyl H), 6.24 (dd, $J = 2$ Hz, 1H, aromatic H), 6.45 (d, $J = 2$ Hz, 1H, aromatic H), 6.88 (d, $J = 2$ Hz, 1H, aromatic H), 8.08 (s, 1H, −CH=N−), 9.48 (br s, 1H, pyrrole ring NH). FD-mass: *m/z* 178. Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 73.95; H, 10.93; N, 15.99.

[2-(*n*-hexyl-NCH)$C_4H_3N]_2TiCl_2$ (3). 3 was prepared by the procedure outlined for **1**. The yield was 37%. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.8−1.6 (m, 22H, *n*-hexyl H), 2.7−3.3 (m, 4H, *n*-hexyl H), 6.30 (dd, $J = 2$ Hz, 2H, aromatic H), 6.58 (d, $J = 2$ Hz, 2H, aromatic H), 7.80 (d, $J = 2$ Hz, 2H, aromatic H), 7.88 (s, 2H, −CH=N−). FD-mass: *m/z* 472 (M^+). Anal. Calcd for $C_{22}H_{34}N_4TiCl_2$: C, 55.83; H, 7.24; N, 11.84. Found: C, 55.49; H, 7.04; N, 12.23.

2-(cyclohexyl-NCH)C_4H_3NH (4a). 4a was prepared using a procedure similar to that for **1a**. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 1.1−1.9 (m, 10H, cyclohexyl H), 3.0−3.2 (m, 1H, cyclohexyl H), 6.21 (dd, $J = 2$ Hz, 1H, aromatic H), 6.48 (d, $J = 2$ Hz, 1H, aromatic H), 6.89 (d, $J = 2$ Hz, 1H, aromatic H), 8.13 (s, 1H, −CH=N−), 8.35 (br s, 1H, pyrrole ring NH). FD-mass: *m/z*:

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(30) Guerra, C. F.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acta* **1998**, *99*, 391.

(31) SIR92: Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1994**, *26*, 343.

(32) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. In The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(33) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. In The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(34) teXsan: Crystal Structure Analysis Package; Molecular Structure Corpo., The Woodlands, TX, 1985 and 1999.

176. Anal. Calcd for $C_{11}H_{16}N_2$: C, 74.96; H, 9.15; N, 15.89. Found: C, 74.54; H, 9.31; N, 15.93.

[2-(cyclohexyl-NCH)C_4H_3N]$_2$TiCl$_2$ (4). 4 was prepared by the procedure outlined for **1**. The yield was 38%. ^{1}H NMR (270 MHz, CDCl$_3$, δ): 0.7−2.7 (m, 22H, cyclohexyl H), 6.28 (dd, J = 2 Hz, 2H, aromatic H), 6.60 (d, J = 2 Hz, 2H, aromatic H), 7.80 (d, J = 2 Hz, 2H, aromatic H), 8.00 (s, 2H, −CH═N−). FD-mass: m/z 468 (M$^+$). Anal. Calcd for $C_{22}H_{30}N_4TiCl_2$: C, 56.31; H, 6.44; N, 11.94. Found: C, 56.79; H, 6.71; N, 12.12.

Ethylene Polymerization. Ethylene polymerization was performed in a glass flask (500 mL) equipped with a mechanical stirrer, a temperature probe, and a condenser. Toluene (250 mL) was introduced to the nitrogen-purged reactor and stirred 600 rpm. The solvent was kept at the prescribed polymerization temperature, and then the ethylene gas feed (100 L/h) was started. After 10 min, polymerization was initiated by the addition of 1.25 M solution of MAO in toluene (1 mL, 1.25 mmol) and then a 0.002 M solution of a complex in toluene (0.5 mL, 1 μmol) into the reactor. The polymerization was quenched after the prescribed time by the addition of isobutyl alcohol (5 mL). The resulting mixture was added to the acidic methanol (1000 mL including 5 mL of concentrated HCl). The polyethylene was collected by filtration, washed with methanol, and then dried at 80 °C in vacuo for 10 h. In the case of using $Ph_3CB(C_6F_5)_4$/i-Bu_3Al cocatalyst in the place of MAO, a 0.5 M solution of i-Bu_3Al in toluene (0.5 mL, 0.25 mmol), a 0.002 M solution of complex in toluene (0.5 mL, 1 μmol), and then a 0.002 M solution of $Ph_3CB(C_6F_5)_4$ in toluene (3 mL, 6 μmol) were added, in this order, into the reactor.

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Supporting Information Available: Tables of atomic coordinates and $B_{\mathrm{iso}}/B_{\mathrm{eq}}$ values, anisotropic displacement parameters, and bond distances and angles for complexes **1**, **2**, and **4** and text giving synthetic procedures for complexes **1**−**4**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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