Cyclopentadienyl−Hydrazido Titanium Complexes: Synthesis, Structure, Reactivity, and Catalytic Properties

Joon T. Park,*,† Sung Cheol Yoon,† Byoung-Jae Bae,† Won Seok Seo,† Il-Hwan Suh,‡ Taek Kyu Han,§ and Joon Ryeo Park§

Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea, Department of Physics, Chungnam National University, Taejon 305-764, Korea, and SK Corporation, Daeduk Institute of Technology, Taejon 305-712, Korea

An η^1-hydrazido bis(dimethylamido) complex, $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2)]Ti(NMe_2)_2$ (**2**), has been prepared from a neat reaction of $(C_5Me_4H)SiMe_2(NHNMe_2)$ (**1**) with $Ti(NMe_2)_4$ at 130 °C via amine elimination. Treatment of **2** with Me_3SiCl gives an η^2-hydrazido dichloro compound, $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiCl_2$ (**3**). The reaction of **2** with excess $AlMe_3$ (ca. 5 equiv) affords an $AlMe_3$ adduct, $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2AlMe_3)]TiMe_2$ (**4**), which is converted to a dimethyl complex, $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiMe_2$ (**5**), upon treatment with NEt_3. The reaction of **5** with $B(C_6F_5)_3$ affords a methyl−triarylborate complex, $[(\eta^5\text{-}C_5Me_4)SiMe_2(NNMe_2)]TiMe(\mu\text{-}Me)B(C_6F_5)_3$ (**6**). The reaction of **2** with H_2O produces a tetrameric organotitanoxane $[(\eta^5\text{-}C_5Me_4)(SiMe_2NHNMe_2)Ti]_4O_6$ (**7**) with an adamantane-like cage structure. However, the reaction of **2** with H_2O in the presence of HCl affords a dimeric complex $[\mu\text{-}(OSiMe_2\text{-}\eta^5\text{-}C_5Me_4)TiCl_2]_2$ (**8**). Compounds **1**−**8** have been characterized by spectroscopic and analytical data. Molecular structures of **2**, **3**, **4**, **5**, **7**, and **8** have been determined by single-crystal X-ray diffraction studies. Complexes **2**−**5** contain η^1-hydrazido (**2** and **4**) and η^2-hydrazido (**3** and **5**) groups depending on the electronic nature of the titanium center. Reversible interconversion between η^1- and η^2-hydrazido moieties has been observed upon addition of either NEt_3 (**4** → **5**) or $AlMe_3$ (**5** → **4**). Complexes **2**−**5** exhibit moderate catalytic activities for the polymerization of ethene in the presence of either methyaluminoxane (MAO) or $Al^iBu_3/Ph_3C^+B(C_6F_5)_4^-$.

Introduction

The *ansa*-monocyclopentadienyl−amido (CpA) titanium catalysts $[(\eta^5\text{-}C_5R'_4)SiMe_2(NR)]TiX_2$ (R = alkyl, aryl; X = Me, Cl) have received much attention as olefin polymerization catalysts.[1] They have shown remarkable activity for copolymerization of ethene with other olefins such as hexene, octene, and cyclic olefins.[1b−d] The sterically open nature of the catalyst active site is considered to facilitate incorporation of various olefins into growing polymer chains. Since initial introduction of an *ansa*-ligand $(C_5Me_4H)SiMe_2(HNN^tBu)$ by Bercaw and co-workers for scandium olefin polymerization catalysts,[2] the components of the CpA catalysts have been systematically varied to achieve a desired catalytic behavior.[3−8] Changing the cyclopentadienyl group from Me_4Cp to Cp or indenyl ligand results in a steady drop in productivity and less comonomer incorporation.[3] As expected, increasing the size of the bridging group for $(CH_2)_2$ or $(Me_2Si)_2$ leads to similar unfavorable outcomes due to the resulting diminution of the catalytic active site.[4] Efforts of changing the *tert*-butyl group on the amido moiety to various alkyl and aryl groups have not been successful in improving the catalytic activity, although it was possible to incorporate chiral amines to obtain optically active polymerization catalysts.[5] Variations of the metal include Sc,[2] Y,[6] Ti, Zr, Hf, V,[7]

* To whom correspondence should be addressed. E-mail: jtpark@sorak.kaist.ac.kr. Fax: +82-42-869-2810.
† Korea Advanced Institute of Science and Technology.
‡ Chungnam National University.
§ SK Corporation.

(1) (a) Canich, J. A. M. (Exxon) U.S. Pat. 5,026,798, 1991. (b) Canich, J. A. M. (Exxon) Eur. Pat. Appl. 0420 436 A1, 1991. (c) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. A.; Lai, S. Y. (Dow) Eur. Pat. Appl. 0416 815 A2, 1991. (d) Canich, J. A. M. (Exxon) U.S. Pat. 5,096,867, 1992. (e) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649. (f) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

(2) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623.

(3) (a) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649. (b) Okuda, J.; Schatterman, F. J.; Wocaldo, S.; Massa, W. *Organometallics* **1995**, *14*, 789. (c) Devore, D.-D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132. (d) McKnight, A. L.; Masood, M. A.; Waymouth, R. M. *Organometallics* **1997**, *16*, 2879. (e) Brown, S. J.; Gao, X.; Harrison, D. G.; Koch, L.; Spence, R. E. v. H.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5445.

(4) (a) Stevens, J. C. *Stud. Surf. Sci. Catal.* **1994**, *89*, 277. (b) Dias, H. V. R.; Wang, Z.; Bott, S. G. *J. Organomet. Chem.* **1996**, *508*, 91. (c) Foster, P.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **1997**, *545*, 35. (d) Sinnema, P.-J.; Veen, L.; Spek, A. L. Veldman, N.; Teuben, J. H. *Organometallics* **1997**, *16*, 4245. (e) Duba, L.; Erker, G.; Fröhlich, R.; Zippel, F. *Eur. J. Inorg. Chem.* **1998**, 1153.

(5) (a) Okuda, J.; Eberle, T.; Spaniol, T. P. *Chem Ber.* **1997**, *130*, 209. (b) Eberle, T.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **1998**, 237.

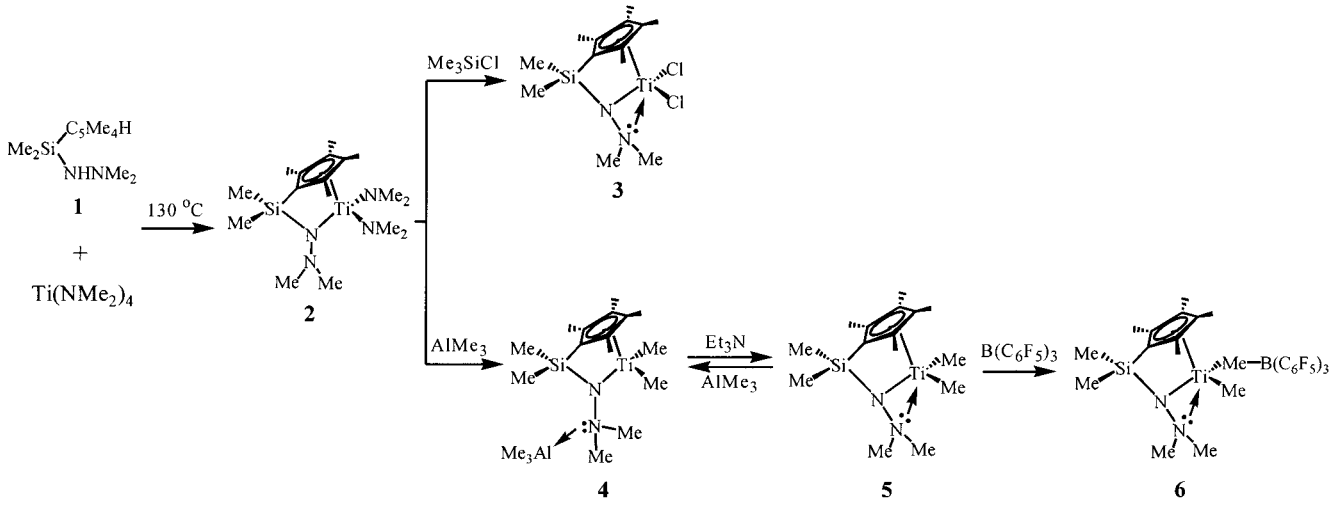
(6) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227.

(7) Witte, P. T.; Meetsma, A.; Hessen, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **1997**, *119*, 10561.

(8) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284.

10.1021/om990841i CCC: $19.00
Publication on Web 03/08/2000

Scheme 1



and Cr[8] atoms. Thus far it appears that $[(\eta^5\text{-}C_5Me_4)SiMe_2(N^tBu)]TiCl_2$ is the most optimized catalyst for ethene polymerization.

As an extension of the structural variation in CpA titanium complexes, we have employed the hydrazido moiety as a donor group instead of the amido ligand. The strong donor nature of the hydrazido moiety is expected to stabilize the catalytically active cationic species compared to the amido ligand, which may result in interesting polymerization characteristics. Two η^2-hydrazido complexes, $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}NHNMe_2)]TiCl_2$ and $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}NPhNH_2)]TiCl_2$, are the only known hydrazido titanium complexes before this work.[9] However, Okuda and co-workers have reported structurally related tridentate CpA complexes, $[(\eta^5\text{-}C_5Me_4)SiMe_2(NCH_2CH_2X)]MCl_2$ (M = Zr, Hf), in which the two-electron-donor moiety (X = OMe or NMe_2) was found to act as a labile coordinating ligand for the electron-deficient metal center.[10] Herein we report synthesis, characterization, and reactivity of various *ansa*-tetramethylcyclopentadienyl−hydrazido titanium complexes, together with their ethene polymerization properties. A preliminary account of this work has appeared.[11]

Results and Discussion

Synthesis and Characterization of 1−6. Overall reaction conditions and structural consequences of **1**−**6** are summarized in Scheme 1. An *N*,*N*-dimethyl hydrazido ligand, $(C_5Me_4H)SiMe_2(NHNMe_2)$ (**1**), is prepared by the reaction of $LiNHNMe_2$ with $(C_5Me_4H)SiMe_2Cl$ as a greenish liquid in 63% yield after purification by vacuum distillation. Treatment of $(C_5Me_4H)SiMe_2Cl$ with H_2NNMe_2 in the presence of Et_3N, however, affords **1** in a lower yield (40%). Neat reaction of **1** with $Ti(NMe_2)_4$ at 130 °C affords an η^1-hydrazido bis(dimethylamido) complex, $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2)]Ti(NMe_2)_2$ (**2**), as red crystals in 42% yield after recrystallization in pentane. This amine elimination reaction, however, did not proceed in toluene solvent.[12] Treatment of **2** with excess Me_3SiCl in dichloromethane gives an η^2-hydrazido dichloro compound, $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiCl_2$ (**3**), as an orange solid in 63% yield after recrystallization in toluene. Direct synthesis of **3** has been attempted from the metathesis reaction of the dilithio salt of **1** with $TiCl_3(THF)_3$ or $TiCl_4(THF)_2$, but was unsuccessful.

Synthesis of a dimethyl derivative **5** was attempted from the reaction of **3** with 2 equiv of trimethylaluminum, but the reaction was sluggish. However, when an excess amount (ca. 5 equiv) of trimethylaluminum is used, a trimethylaluminum adduct of **5** is unexpectedly isolated in 43% yield as air-sensitive brownish yellow crystals by recrystallization in pentane. The trimethylaluminum molecule is coordinated to the hydrazido nitrogen with dimethyl groups to yield an η^1-hydrazido complex, $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2AlMe_3)]TiMe_2$ (**4**). Upon treatment of **4** with triethylamine at −78 °C in toluene, the trimethylaluminum molecule could be eliminated to produce the dimethyl complex $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiMe_2$ (**5**) as a green solid in 77% yield. Monitoring the conversion of **5** to **4** by ^1H NMR spectroscopy reveals that the conversion is complete within 10 min upon addition of 1.5 equiv of $AlMe_3$ to a $CDCl_3$ solution of **5**.

The ^1H NMR spectral data of compounds **1**−**5** are summarized in Table 1. Two singlet resonances are observed for the four methyl groups on the cyclopentadienyl ligands of **1**−**5**, indicating that all the compounds have C_s symmetry in solution. The methyl proton resonance on the silicon atom of free ligand **1** at −0.06 ppm shifts significantly downfield by ca. 0.5−0.8 ppm upon coordination to the titanium metal. The methyl proton resonances on the hydrazido moiety of **2**, **3**, and **5** appear at 2.49, 2.95, and 2.99 ppm, respectively. This

(9) (a) Latham, I. A.; Leigh, G. J.; Huttner, G. *J. Chem. Soc., Dalton Trans.* **1986**, 385. (b) Latham, I. A.; Leigh, G. J.; Huttner, G. *J. Chem. Soc., Dalton Trans.* **1986**, 377. (c) Hughes, D. L.; Latham, I. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1986**, 393. (d) Hammer, R.; Thewalt, U.; Hughes, D.; Leigh, G. J.; Walker, D. G. *J. Organomet. Chem.* **1987**, *323*, C29.

(10) (a) du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129. (b) Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836. (c) Amor, F.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **1998**, *558*, 139.

(11) Yoon, S. C.; Bae, B.-J.; Suh, I.-H.; Park, J. T. *Organometallics* **1999**, *18*, 2049.

(12) (a) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (b) Herrmann, W. A.; Morawietz, M. J. *J. Organomet. Chem.* **1994**, *482*, 169. (c) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5. (d) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024.

Table 1. ^{1}H NMR Spectral Data (300 MHz, $CDCl_3$, 25 °C) of 1−5

compound	C_5Me_4	$SiMe_2$	$NNMe_2$	$TiNMe_2$	$TiMe$	$AlMe_3$
1	1.94, 1.78	−0.06	2.37			
2	2.11, 2.02	0.49	2.49	2.99		
3	2.20, 1.91	0.66	2.95			
4	2.18, 1.98	0.60	3.29		0.40	−0.84
5	2.17, 1.72	0.43	3.00		−0.39	

downfield shift (0.46−0.5 ppm) for **3** and **5** compared to **2** supports the structural characterization that the hydrazido moieties in **3** and **5** are η^2-coordinated to the titanium metal center (vide infra). The methyl proton resonance on the hydrazido group of **4** is shifted further downfield to 3.29 ppm due to the Lewis acid coordination, although the hydrazido moiety in **4** adopts an η^1-bonding mode.

The coordination mode of the hydrazido moiety in **1**−**5** can be tuned either by the electronic property of the two terminal ligands on the titanium center or by addition of Lewis acids and bases. Complex **2** with NMe_2 donor ligands contains an electron-rich titanium center, which consequently results in η^1-coordination of the hydrazido moiety. Complexes **3** and **5**, however, have η^2-hydrazido groups because of the relatively electron-poor titanium metal with electron-withdrawing Cl and Me ligands. Interestingly, reversible interconversion (**4** ⇄ **5**) between η^1- and η^2-hydrazido ligands has been observed upon addition of external NEt_3 and $AlMe_3$ reagents.

The general preparation of "cation-like" metal alkyl complexes has been performed by the reaction of the corresponding dialkyl compounds with $B(C_6F_5)_3$ or $Ph_3C^+B(C_6F_5)_4^-$.[13] Reaction of **5** with 1 equiv of $B(C_6F_5)_3$ in pentane affords a methyltriarylborate complex, [(η^5-C_5Me_4)$SiMe_2$($NNMe_2$)]Ti(Me)B(C_6F_5)$_3$ (**6**), which was isolated as orange crystals by recrystallization from a mixture of pentane and toluene at −20 °C. The ^{1}H NMR spectrum of **6** (see Figure 1) exhibits four singlets for the four methyl groups on the C_5Me_4 ring and two singlets for the two methyl groups on the $SiMe_2$ group, implying an unsymmetric nature of **6**. The methyl resonance on the titanium atom appears at δ 0.22 ppm as a sharp singlet and the μ-Me resonance at δ 0.45 ppm as a broad signal. Suitable crystals of **6** for the structural characterization by X-ray diffraction study could not be obtained, but the ^{1}H NMR spectrum of **6** reveals a similar structural correspondence to the structurally characterized [η^5-1,2-$(Me)_2C_5H_3$]$_2$ZrMe(μ-Me)B(C_6F_5)$_3$ and [η^5-1,3-$(SiMe_3)_2C_5H_3$]$_2$ZrMe(μ-Me)B(C_6F_5)$_3$.[13]

Crystal Structures of 2−5. The X-ray crystal structures of **2**−**5** have been determined to examine the structural details of the hydrazido moieties. The overall molecular geometries and the atomic labeling schemes of **2**−**5** are illustrated in Figures 2−5, respectively. Selected bond lengths and angles of **2**−**5** are presented in Table 2.

The structure of **2** (see Figure 2) exhibits a distorted tetrahedral geometry consisting of a bifunctional tetramethylcyclopentadienyl−hydrazido ligand and two terminal dimethylamido groups. There are two equivalent molecules (**2**-A and **2**-B) in the crystallographic asymmetric unit (see Supporting Information). In subsequent discussions bond lengths and angles will be given with the values for molecule A. General structural features of **2** are comparable to those previously reported for [(η^5-C_5H_4)$SiMe_2$(N^tBu)]Ti(NMe_2)$_2$ and [(η^5-C_5Me_4)$SiMe_2$(N^tBu)]Zr(NMe_2)$_2$.[14] Complex **2** has a pseudo-C_s symmetry with a mirror plane including the Ti, Si, N1, and N2 atoms, and bisecting the Me_2N−Ti−NMe_2 angle and the Cp ring. The short Ti−N3 and Ti−N4 bond lengths (1.927(8) and 1.912(8) Å) and the planar geometry of the N3 and N4 nitrogen atoms indicate sp^2 hybridization of the two nitrogen atoms with the out-of-plane lone pairs, giving an N(pπ) → M(dπ) interaction.

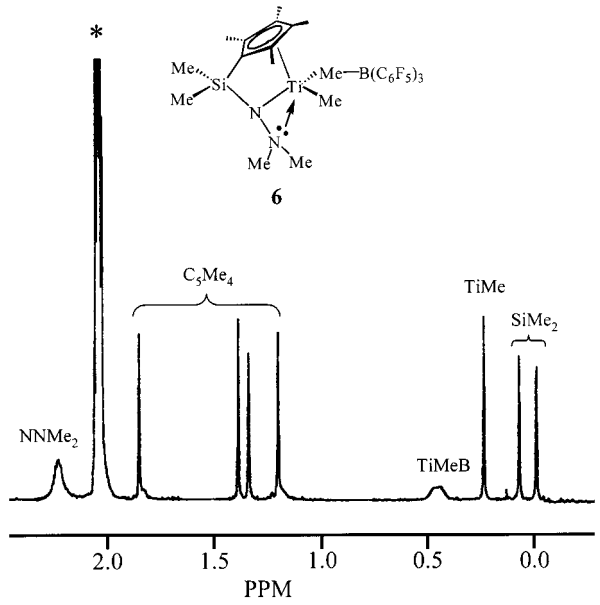


Figure 1. ^{1}H NMR spectrum (300 MHz, toluene-d_8, 25 °C) of [(η^5-C_5Me_4)$SiMe_2$($NNMe_2$)]Ti(Me)(μ-Me)B(C_6F_5)$_3$ (**6**): (*) solvent peaks.

Table 2. Selected Bond Lengths (Å) and Angles (deg) with Esd's for 2−5

	2-A	**3**-A	**4**	**5**
		Bond Lengths		
Ti−N(1)	1.977(7)	1.857(11)	1.952(12)	1.862(7)
Ti−N(2)		2.364(11)		2.466(6)
Ti−N(3)	1.927(7)			
Ti−N(4)	1.912(8)			
Ti−Cl(1)		2.303(4)		
Ti−Cl(2)		2.305(4)		
Ti−C(14)			2.115(14)	2.114(8)
Ti−C(15)			2.122(14)	2.112(8)
N(1)−N(2)	1.449(10)	1.405(14)	1.461(16)	1.390(8)
Ti−Cp′(Cen[a])	2.098	2.060	2.011	2.059
		Bond Angles		
N(3)−Ti−N(4)	100.7(4)			
Cl(1)−Ti−Cl(2)		105.7(2)		
C(14)−Ti−C(15)			101.8(6)	103.4(4)
Ti−N(1)−Si	105.7(4)	114.5(5)	106.2(6)	112.7(3)
C(1)−Si−N(1)	91.8(4)	84.5(5)	88.3(6)	86.3(3)
Cp′ (Cen)−Ti−N(1)	103.85	101.12	105.19	102.76
Cp′ (Cen)−Ti−N(2)	121.31	137.54		136.71

[a] Cen = ring centroid.

(13) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (b) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1. (c) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 623. (d) Bochmann, M.; Langcaster, S. J.; Hursthouse, M. B.; Abdul Malik, K. M. *Organometallics* **1994**, *13*, 2235. (e) Bochmann, M.; Langcaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634. (f) Yang, X.; Stern, C. L. Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (g) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842.

(14) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Perterson, J. L. *Organometallics* **1996**, *15*, 1572.

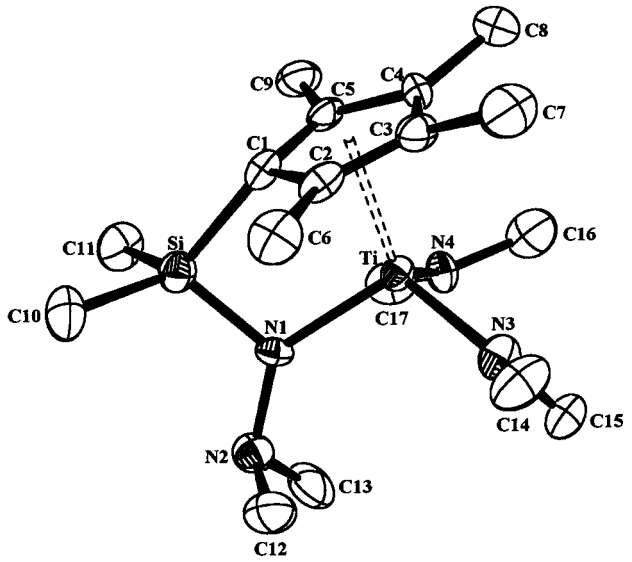


Figure 2. Molecular structure of $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2)]Ti(NMe_2)_2$ (**2**-A).

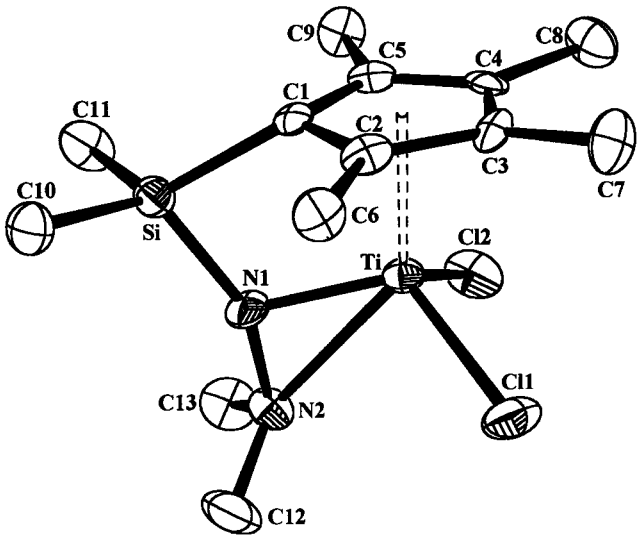


Figure 3. Molecular structure of $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiCl_2$ (**3**-A).

The electron-rich nature of the titanium center due to the d−p−π interaction appears to cause the hydrazido moiety to be η^1-bonded to the titanium metal (cf. Ti···N(2) = 3.173 Å). The Ti−N1 bond length (1.977(7) Å) is similar to that (1.972(4) Å) of $[(\eta^5\text{-}C_5H_4)SiMe_2(N^tBu)]Ti(NMe_2)_2$,[14] but longer than that for cyclopentadienyl−amido dichloro complexes such as $[(\eta^5\text{-}C_5Me_4)SiMe_2(N^tBu)]TiCl_2$ (1.907(4) Å),[14] $[(\eta^5\text{-}C_5H_4)SiMe_2(N^tBu)]TiCl_2$ (1.901(3) Å),[14] and $[(\eta^5\text{-}C_5H_4)SiMe_2(N^iPr)]TiCl_2$ (1.878(2) Å).[5b] This observed difference in the Ti−N1 bond lengths is probably a consequence of a decrease in the relative degree of N ⇌ Ti π-overlap for complexes with terminal amido moieties compared to those with dichloro ligands.

The molecular structure of **3** is similar to that of **2** except that the hydrazido moiety is η^2-bound to the titanium metal (see Figure 3). The crystallographic asymmetric unit contains two equivalent molecules (**3**-A and **3**-B; see Supporting Information), and molecule A is discussed. The Ti−N1 and Ti−N2 bond lengths (1.857(1) and 2.364(1) Å) are comparable to those of known η^2-hydrazido titanium complexes, $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}NHNMe_2)]TiCl_2$ (1.83 and 2.22 Å) and $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}NPhNH_2)]TiCl_2$ (1.88 and 2.14 Å).[9] The hydrazide (−1) fragment can be best represented formally as a six-electron donor with a N1 ⇌ Ti π-interaction and a N2 → Ti dative bond. Complex **3**, therefore, can be considered to be a 16-electron species.

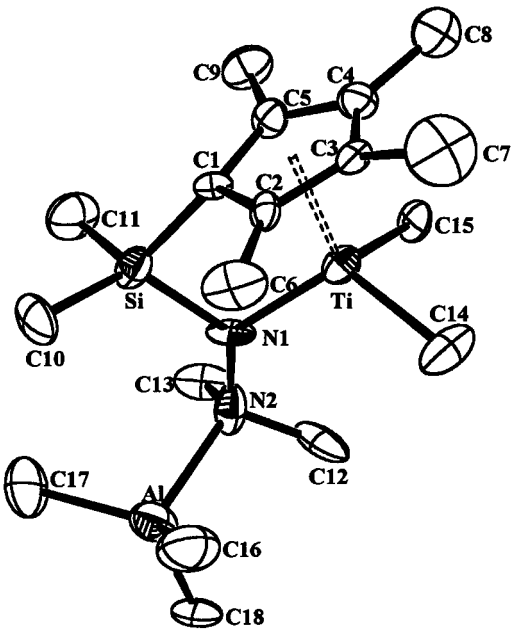


Figure 4. Molecular structure of $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2AlMe_3)]TiMe_2$ (**4**).

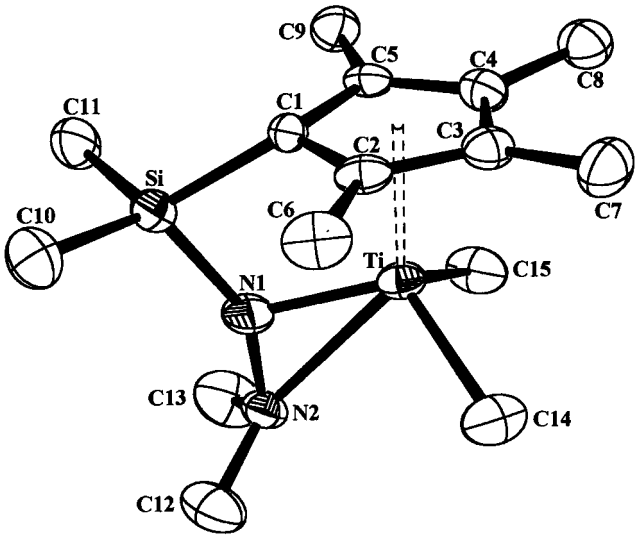
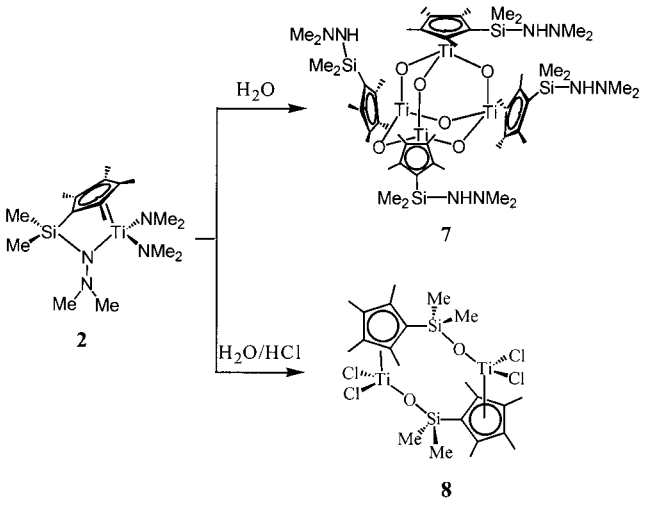


Figure 5. Molecular structure of $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiMe_2$ (**5**).

The overall structure of **4** (cf. Ti···N(2) = 3.058 Å) is similar to that of **2** with an η^1-hydrazido ligand (see Figure 4). A trimethylaluminum molecule is coordinated to the N(2) atom and disposed away from the metal center. The Ti−N(1) bond length (1.952(12) Å) is comparable to that of **2**, but longer than those of η^2-hydrazido complexes (1.857(11) Å for **3** and 1.862(7) Å for **5**). The bond length of Al−N(2) is 2.071(14) Å, which is within the general range of Al−N lengths (ca. 2.06 Å) for typical nitrogen−$AlMe_3$ adducts.[15]

(15) (a) Whitt, C. D.; Parker, L. M.; Atwood, J. L. *J. Organomet. Chem.* **1971**, *32*, 291. (b) Bradford, A. M.; Bradley, D. C.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1992**, *11*, 111.

Scheme 2



The molecular structure of **5** is essentially the same as that of **3** with an η^2-hydrazido moiety (see Figure 5). The bond lengths of Ti−N(1) (1.862(7) Å) and Ti−N(2) (2.466(6) Å) are slightly longer than those of **3**. The titanium center in **3** with more electronegative chlorine ligands is less electron-rich than that in **4** with methyl ligands and thus results in stronger Ti ⇌ N(1) π-interaction and a N(2) → Ti dative bond in **3** compared to those in **4**.

Synthesis and Structural Characterization of 7 and 8. To understand water sensitivity of **2**, the reaction of **2** with H_2O was investigated (see Scheme 2). The reaction of **2** with H_2O at room temperature yields a tetrameric organotitanoxane, $[(\eta^5\text{-}C_5Me_4)(SiMe_2NHNMe_2)Ti]_4O_6$ (**7**), as green crystals in 52% yield. The ^{1}H NMR spectrum of **7** shows two singlet resonances at 2.11 and 2.42 ppm with an intensity ratio of 1:6, indicating that the Ti−N bond in **2** is broken and the $NHNMe_2$ moiety is formed. X-ray structural analysis of **7** (see Figure 6) reveals an adamantane-like cage structure with a tetrahedral Ti_4O_6 core, which is similar to that previously reported for $[(\mu^5\text{-}C_5Me_5)Ti]_4O_6$ by Klemperer and co-workers.[16] The coordination geometry of each Ti atom is pseudo-tetrahedral with three sites being occupied by bridging oxygen atoms and the remaining site by a π-bonded η^5-tetramethylcyclopentadienyl ligand with a hydrazidodimethylsilyl substituent. Selected bond lengths and angles are presented in Table 3. The average bond lengths of Cp′(Cen)−Ti and Ti−O are 2.07 and 1.84 Å, respectively. The average bond angles Cp′(Cen)−Ti−O, Ti−O−Ti, and O−Ti−O are 116.7°, 124.0°, and 101.3°, respectively. Compound **7** is likely to be formed by hydrolysis and condensation reaction similar to that proposed for the formation of $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$ from hydrolysis of $(\eta^5\text{-}C_5Me_5)TiCl_3$ under basic conditions.[16]

Reaction of **2** with 5 equiv of HCl in wet diethyl ether solution produces a dinuclear compound $[\mu\text{-}(OSiMe_2\text{-}\eta^5\text{-}C_5Me_4)TiCl_2]_2$ (**8**) as red crystals in 45% yield after recrystallization in diethyl ether. The ^{1}H NMR spectrum of **8** exhibits only two kinds of resonances due to the methyl groups on the Si atom (0.49 ppm) and the C_5Me_4 ring (2.25 and 2.37 ppm). This implies that both the Si−N and Ti−N bonds are hydrolyzed in the presence of acid and the hydrazido moiety does not exist in **8**. The molecular structure of **8** is illustrated in Figure 7. Selected bond lengths and angles are listed in Table 4. The molecular structure of **8** consists of a dimeric molecule formed by two $[(\eta^5\text{-}C_5Me_4)SiMe_2O]TiCl_2$ fragments related by an inversion center, in which two oxygen atoms connect the silicon and titanium atoms. The bond lengths of Ti−O, Si−O, and Cp′(Cen)−Ti are

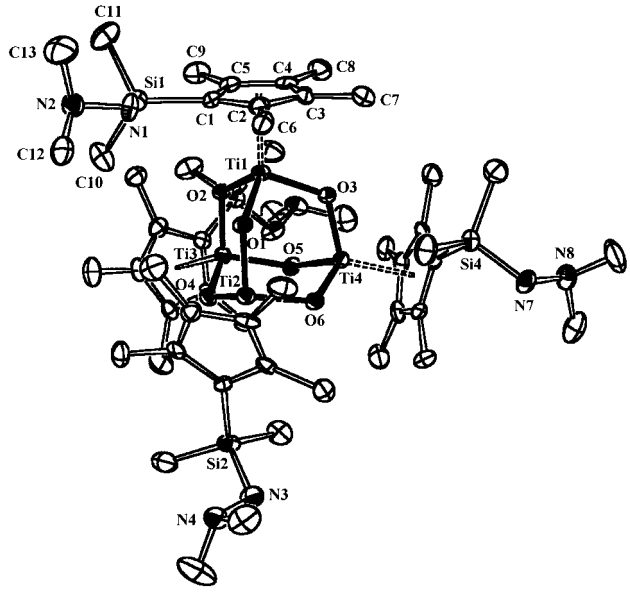


Figure 6. Molecular structure of $[(\eta^5\text{-}C_5Me_4)(SiMe_2\text{-}NHNMe_2)Ti]_4O_6$ (**7**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) with Esd's for 7

Bond Lengths			
Ti(1)−C(1)	2.385(8)	Si(1)−C(1)	1.884(9)
Ti(1)−C(2)	2.396(9)	Si(1)−C(10)	1.858(9)
Ti(1)−C(3)	2.421(8)	Si(1)−C(11)	1.861(9)
Ti(1)−C(4)	2.408(8)	Si(1)−N(1)	1.704(7)
Ti(1)−C(5)	2.402(8)	Ti−O (av)	1.84
N(1)−N(2)	1.419(9)	Ti−Cp′(Cen[a]) (av)	2.074

Bond Angles			
O−Ti−O (av)	101.3	C(1)−Si(1)−N(1)	108.7(4)
Ti−O−Ti (av)	124.0	C(10)−Si(1)−C(11)	108.9(5)
N(2)−N(1)−Si	116.0(6)	Cp′ (Cen)−Ti−O (av)	116.7

[a] Cen = ring centroid.

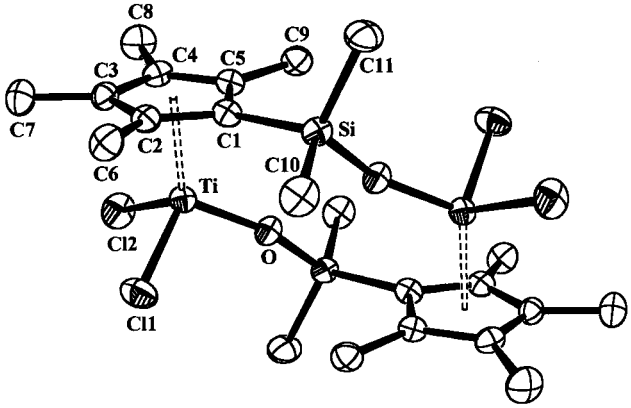


Figure 7. Molecular structure of $[\mu\text{-}(OSiMe_2\text{-}\eta^5\text{-}C_5Me_4)\text{-}TiCl_2]_2$ (**8**).

(16) (a) Babcock, L. H.; Day, V. W.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* **1987**, 858. (b) Babcock, L. M.; Klemperer, W. G. *Inorg. Chem.* **1989**, *38*, 2003. (c) Gomez-Sal, M. P.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *358*, 147.

Table 4. Selected Bond Lengths (Å) and Angles (deg) with Esd's for 8

Bond Lengths			
Ti−Cl(1)	2.254(2)	Ti−C(5)	2.325(5)
Ti−Cl(2)	2.258(2)	Ti−O	1.771(4)
Ti−C(1)	2.297(5)	Si−C(1)	1.877(5)
Ti−C(2)	2.390(5)	Si−C(10)	1.841(6)
Ti−C(3)	2.425(5)	Si−C(11)	1.837(6)
Ti−C(4)	2.384(5)	Si−O	1.650(4)
		Ti−Cp′(Cen[a])	2.031
Bond Angles			
Cl(1)−Ti−Cl(2)	102.6(1)	Ti−O−Si	159.8(2)
Cl(1)−Ti−O	103.1(1)	C(1)−Si-O	108.3(2)
Cl(2)−Ti−O	101.2(1)	C(10)−Si−C(11)	111.4(3)
		Cp′ (Cen)−Ti−O	120.2

[a] Cen = ring centroid.

1.771(4), 1.650(4), and 2.03 Å, respectively. The Ti−O−Si bond angle is 159.8(2)°. Complex **8** is isomorphous with $[\mu$-$(OSiMe_2$-η^5-$C_5H_4)TiCl_2]_2$, which was prepared from the reaction of $(\eta^5$-$C_5H_4SiMe_2Cl)TiCl_3$ and water by Royo and co-workers.[17] They proposed that both Si−Cl and Ti−Cl are simultaneously hydrolyzed to from $[(\eta^5$-$C_5H_4SiMe_2(OH)]TiCl_2(OH)$, and subsequent intermolecular condensation would produce the dimer. Similarly, hydrolysis of both Si−N and Ti−N bonds in the hydrazido moiety and metathesis of the two Ti−NMe_2 bonds by HCl from **2** will give an analogous intermediate and in turn the dimeric product **8**. The metrical parameters of **8** are similar to those previously observed for $[\mu$-$(OSiMe_2$-η^5-$C_5H_4)TiCl_2]_2$.

Polymerization. A summary of the polymerization results is shown in Table 5. Complexes **2**−**4** activated by methylaluminoxane (MAO) and **5** by $Al^iBu_3/Ph_3C^+B(C_6F_5)_4^-$ reveal moderate catalytic activities for the polymerization of ethene. Overall, the catalytic activities of **2**−**5** are lower than that of the best known $[(\eta^5$-$C_5Me_4)SiMe_2(N^tBu)]TiCl_2$,[5b] but comparable to that of a heteroatom-substituted cyclopentadienyl−amido complex, $[(\eta^5$-$C_5Me_4)SiMe_2(\eta^1$-$NCH_2CH_2OMe)]TiCl_2$.[10b] The molecular weights of produced polymers are very high ($>1.0 \times 10^6$), and their molecular weight distributions are broad. The structural characterization of trimethylaluminum adduct **4** suggests that the hydrazido (NMe_2) moiety of these catalysts could be coordinated by the aluminum atom of the cocatalysts. This coordination in **2**−**5** causes the enhancement of both the electron-withdrawing property and steric bulkiness of the hydrazido moiety, which consequently results in instability and low activity of the catalysts. Piccolrovazzi and co-workers previously proposed a similar coordination of the $[Al(CH_3)O]$ units of MAO to the methoxy oxygen to explain low productivity and low molecular weight of polymers with $[\eta^5$-4,7-$(MeO)_2C_9H_5]_2Zr(CH_2C_6H_5)_2$ catalyst.[18] The reason for the formation of high molecular weight polymers with catalysts **2**−**5** is not clear at the moment, but a plausible explanation could be the decreased β-hydride elimination for the chain termination due to steric hindrance by the bulky MAO-coordinated hydrazido group. The gpc curves are very broad and show multiple peaks. The broad polydispersities of polymers may be attributed to the formation of various active sites by the unstable cationic species. This thermal instability of the catalytically active cationic species is further supported by observation that the productivity is significantly decreased at high polymerization temperatures with catalyst precursor **5** in ethene/1-octene copolymerization (see runs 8 and 9).

Conclusion

We have prepared and fully characterized various titanium complexes with a new *ansa*-cyclopentadienyl−hydrazido ligand, **2**−**6**, which involve η^1- and η^2-bound hydrazido moieties depending on the electronic nature of the titanium metal center and, to our knowledge, are the first examples of η^1- and η^2-hydrazido ligand interconversion. Furthermore, we have shown reversible interconversion between the η^1- and η^2-hydrazido ligands (**4** ⇄ **5**) by tuning the electronic property of the hydrazido moiety upon addition of external Lewis base or acid reagent. Complex **2** reacts with water to produce a tetrameric organotitanoxane complex **7** by scission of the Ti−N bond, but in the presence of HCl both the Ti−N and Si−N bonds are cleaved to afford a dimeric oxo complex **8**. Complexes **2**−**5** in the presence of cocatalysts exhibit moderate catalytic activities for ethene polymerization, but produce very high molecular weight polymers. The cocatalysts appear to coordinate through the aluminum atom on the basic $-NMe_2$ moiety of the hydrazido group, which may cause the low activity and thermal instability of the catalysts.

Experimental Section

General Comments. All reactions were carried out under an inert atmosphere of argon by using either standard Schlenk or glovebox techniques. Tetrahydrofuran (THF), diethyl ether, pentane, and toluene were distilled from Na/K alloy under N_2 atmosphere. Dichloromethane was refluxed over CaH_2 and then distilled under N_2 atmosphere. $(C_5Me_4H)SiMe_2Cl$ was prepared according to the literature procedure.[2b] The ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AC-200 or AM-300 FT NMR spectrometer. Mass spectra were recorded on a JEOL SX 102 spectrometer. All *m*/*z* values are referenced to ^{28}Si and ^{35}Cl. Microanalytical data were provided by ORS (Oneida Research Services).

Molecular masses of polymers were determined by gel permeation chromatography on a Waters 150CV$^+$ instrument in 1,2,4-trichlorobenzene at 135 °C.

Preparation of $(C_5Me_4H)SiMe_2(NHNMe_2)$ (1). A hexane solution of *n*-butyllithium (1.56 M, 15.3 mL, 23.8 mmol) was added to an ether solution (100 mL) of NH_2NMe_2 (1.43 g, 23.8 mmol) at −78 °C. The reaction mixture was stirred for 12 h, and the formation of white suspension of $LiNHNMe_2$ was observed. To the white suspension was slowly added an ether solution (100 mL) of $(C_5Me_4H)SiMe_2Cl$ (4.26 g, 19.83 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature, stirred for 24 h, and filtered. The solvent of the filtrate was evaporated in vacuo, and the residue was distilled at 80 °C and 10^{-2} Torr to give **1** (2.97 g, 63%) as a green oil: ^1H NMR ($CDCl_3$, 25 °C) δ 2.44 (s, SiC*H*), 2.37 (s, 6H, NNMe_2), 1.94, 1.78 (s, 12H, C_5Me_4), −0.06 (s, 6H, SiMe_2).

Preparation of $[(\mu^5$-$C_5Me_4)SiMe_2(\eta^1$-$NNMe_2)]Ti(NMe_2)_2$ (2). A neat mixture of **1** (0.73 g, 3.1 mmol) and $Ti(NMe_2)_4$ (0.70 g, 3.1 mmol) in a 250 mL Schlenk flask was heated at 130 °C for 4 h. The reaction mixture was cooled to room temperature and placed under vacuum to remove volatiles. Recrystallization of the orange residue in pentane at −20 °C afforded **2** (0.48 g,

(17) (a) Ciruelos, S.; Cuenca, T.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Organometallics* **1995**, *14*, 177. (b) Ciruelos, S.; Cuenca, T.; Gómez, R.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Organometallics* **1996**, *15*, 1577.

(18) Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098.

Table 5. Homo- and Copolymerization of Ethene with 2−5

run[a] no.	cat. (μmol)	cocat.[b]	Al/Ti	octene (mL)	pressure[c] (atm)	T_p[d] (°C)	t_p[e] (h)	yield (g)	A[f]	M_w (×10^{-3})	MWD[g]
1	**2** (20)	MAO	500	0	30	140	0.5	0.43	43	860	63.6
2	**2** (60)	MAO	500	50	30	140	0.5	1.62	162	150	33.0
3	**3** (20)	MAO	570	0	8	50	2.0	2.60	65	790	27.0
4	**3** (20)	MAO	570	0	8	80	2.0	2.60	65	2200	140.0
5	**3** (20)	MAO	570	50	30	140	0.5	0.50	50	900	41.6
6	**4** (20)	MAO	500	0	30	140	0.5	0.76	76	520	23.7
7	**4** (60)	MAO	500	50	30	140	0.5	0.36	36		
8	**5** (100)	Al^{i}Bu$_3$/B	80	50	30	140	0.5	1.40	28	1316	29.2
9	**5** (100)	Al^{i}Bu$_3$/B	80	50	30	80	0.5	20	400	2314	9.0

Table 6. Crystallographic Data for 2, 3, 4, 5, 7, and 8

	2	**3**	**4**
formula	$C_{17}H_{36}N_4SiTi$	$C_{13}H_{24}N_2SiTiCl_2$	$C_{18}H_{39}N_2SiAlTi$
fw	372.49	355.20	386.48
temp, K	293	293	293
λ (Mo Kα), Å	0.7107	0.7107	0.7107
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$Pbc2_1$	$Pbca$
a, Å	9.171 (6)	7.717 (1)	13.866 (5)
b, Å	15.428 (2)	16.735 (2)	15.676 (3)
c, Å	16.488 (2)	26.731 (3)	21.455 (3)
α, deg	70.75 (1)	90	90
β, deg	76.35 (2)	90	90
γ, deg	89.21 (2)	90	90
V, Å^3	2135.0 (1)	3452.2 (9)	4663.4 (2)
Z	4[a]	8[a]	8
D_{calcd}, Mg m^{-3}	1.159	1.367	1.101
abs coeff, mm^{-1}	0.462	0.862	0.456
F(000)	808	1488	1680
cryst dimens, mm	0.726 × 0.099 × 0.155	0.560 × 0.120 × 0.170	0.132 × 0.330 × 0.264
θ range for data collcn, deg	2.25−20.00	2.43−23.00	2.18−20.00
no. of rflns measd	4161	2474	2174
no. of indepdt rflns	3976 [R_{int} = 0.0347]	2474 [R_{int} = 0.0000]	2174 [R_{int} = 0.0000]
no. of data/restraints/params	3976/0/415	2474/1/343	2174/12/209
GOF[b]	1.073	1.054	1.056
final *R* indices[c] [$I > 2\sigma(I)$]	R = 0.0692, R_w = 0.1320	R = 0.0494, R_w = 0.1087	R = 0.0873, R_w = 0.1539
R indices (all data)	R = 0.1462, R_w = 0.1738	R = 0.0739, R_w = 0.1295	R = 0.2356, R_w = 0.2395
D(*r*) and hole, e Å^{-3}	0.286 and −0.287	0.323 and −0.397	0.307 and −0.263

	5	**7**	**8**
formula	$C_{15}H_{30}N_2SiTi$	$C_{52}H_{100}N_8O_6Si_4Ti_4$	$C_{22}H_{36}O_2Si_2Ti_2Cl_4$
fw	314.37	1237.36	626.236
temp, K	293	293	293
λ(Mo Kα), Å	0.7107	0.7107	0.7107
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a, Å	13.572(2)	12.321(5)	8.716(4)
b, Å	7.840(1)	15.958(2)	19.5220(10)
c, Å	16.977(5)	19.194(3)	9.5410(10)
α, deg	90	79.64(1)	90
β, deg	95.50(1)	71.47(2)	114.60
γ, deg	90	67.27(1)	90
V, Å^3	1798.1(6)	3293.4(2)	1476.1(7)
Z	4	2	4
D_{calcd}, Mg m^{-3}	1.161	1.248	1.414
abs coeff, mm^{-1}	0.532	0.589	0.999
F(000)	680	1320	652
cryst dimens, mm	0.528 × 0.165 × 0.297	0.660 × 0.130 × 0.230	0.660 × 0.430 × 0.170
θ range for data collcn, deg	2.41−22.00	2.24−21.00	2.09−23.00
no. of rflns measd	2305	7338	2194
no. of indepdt rflns	2210 [R_{int} = 0.0349]	7068 [R_{int} = 0.0421]	2054 [R_{int} = 0.0681]
no. of data/restraints/params	2210/0/172	7068/0/667	2054/0/145
GOF	1.050	1.078	1.047
final *R* indices [$I > 2\sigma(I)$]	R = 0.0669, R_w = 0.1350	R = 0.0633, R_w = 0.1148	R = 0.0560, R_w = 0.1471
R indices (all data)	R = 0.1379, R_w = 0.1772	R = 0.1385, R_w = 0.1519	R = 0.0754, R_w = 0.1558
D(*r*) and hole, e Å^{-3}	0.306 and −0.260	0.320 and −0.302	0.736 and −0.601

42%) as red crystals: ^{1}H NMR ($CDCl_3$, 25 °C) *δ* 2.99 (s, 12H, TiN*Me*$_2$), 2.49 (s, 6H, NN*Me*$_2$), 2.11, 2.02 (s, 12H, C_5*Me*$_4$), 0.49 (s, 6H, Si*Me*$_2$); ^{13}C NMR ($CDCl_3$, 25 °C) *δ* 127.6, 124.9, 103.1 (C_5Me$_4$), 51.1 (NN*Me*$_2$), 48.6 (TiN*Me*$_2$), 14.0, 11.7 (C_5*Me*$_4$), 4.6 (Si*Me*$_2$). Anal. Calcd for $C_{17}H_{36}N_4SiTi$: C, 54.82; H, 9.74; N, 15.04. Found: C, 54.51; H, 9.34; N, 14.64.

Preparation of [(η^5-C_5Me_4)$SiMe_2$(η^2-$NNMe_2$)]$TiCl_2$ (3). A dichloromethane solution (10 mL) of Me_3SiCl (0.36 g, 3.4 mmol) was slowly added to a dichloromethane solution (30 mL) of **2** (0.50 g, 1.3 mmol). The reaction mixture was stirred at room temperature for 5 h, and the solvent was removed in vacuo. The orange residue was washed with ether (3 × 10 mL) and extracted with toluene. Evaporation of the solvent and recrystallization in toluene at −20 °C yielded **3** (0.30 g, 63%) as orange crystals: ^{1}H NMR ($CDCl_3$, 25 °C) δ 2.95 (s, 6H, NN*Me*$_2$), 2.20, 1.92 (s, 12H, C_5*Me*$_4$), 0.66 (s, 6H, Si*Me*$_2$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 136.4, 133.1, 96.5 (*C*$_5$Me$_4$), 50.0 (NN*Me*$_2$), 15.5, 12.2 (C_5*Me*$_4$), 4.2 (Si*Me*$_2$). Anal. Calcd for $C_{13}H_{24}Cl_2N_2SiTi$: C, 43.96; H, 6.81; N, 7.89. Found: C, 43.62; H, 6.40; N, 7.86.

Preparation of [(η^5-C_5Me_4)$SiMe_2$(η^1-$NNMe_2AlMe_3$)]$TiMe_2$ (4). A pentane solution (10 mL) of $AlMe_3$ (0.98 g, 13.6 mmol) was added to a toluene solution (30 mL) of **2** (1.01 g, 2.7 mmol) at −50 °C. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. The solvent was removed in vacuo, and the residue was extracted with pentane (3 × 10 mL). Evaporation of the solvent and recrystallization in pentane at −20 °C gave **4** (0.45 g, 43%) as green crystals: ^{1}H NMR ($CDCl_3$, 25 °C) δ 3.29 (s, 6H, NN*Me*$_2$), 2.18, 1.98 (s, 12H, C_5*Me*$_4$), 0.60 (s, 6H, Si*Me*$_2$), 0.40 (s br, 6H, Ti*Me*$_2$), −0.84 (s, 9H, Al*Me*$_3$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 135.7, 131.5, 101.1 (*C*$_5$Me$_4$), 55.8 (NN*Me*$_2$), 52.8 (Ti*Me*$_2$), 15.2, 12.4 (C_5*Me*$_4$), 6.01 (Si*Me*$_2$), −7.4 (Al*Me*$_3$).

Preparation of [(η^5-C_5Me_4)$SiMe_2$(η^2-$NNMe_2$)]$TiMe_2$ (5). A toluene solution (10 mL) of Et_3N (0.28 g, 2.7 mmol) was added dropwise to a toluene solution (30 mL) of **4** (1.00 g, 2.6 mmol) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. The solvent was evaporated, and the yellow residue was extracted with pentane (3 × 10 mL). Evaporation of the solvent and recrystallization of the residue in pentane at −20 °C afforded **5** (0.63 g, 77%) as yellow crystals: ^{1}H NMR ($CDCl_3$, 25 °C) δ 3.00 (s, 6H, NN*Me*$_2$), 2.17, 1.72 (s, 12H, C_5*Me*$_4$), 0.43 (s, 6H, Si*Me*$_2$), −0.39 (s, 6H, Ti*Me*$_2$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 129.4, 125.5, 91.4 (*C*$_5$Me$_4$), 52.2 (NN*Me*$_2$), 41.2 (Ti*Me*$_2$), 14.5, 11.7 (C_5*Me*$_4$), 5.1 (Si*Me*$_2$). Anal. Calcd for $C_{15}H_{30}N_2SiTi$: C, 57.31; H, 9.62; N, 8.91. Found: C, 57.26; H, 9.37; N, 8.87.

Preparation of [(η^5-C_5Me_4)$SiMe_2$($NNMe_2$)]TiMe(μ-Me)B-(C_6F_5)$_3$ (6). A pentane solution (30 mL) of **5** (0.15 g, 0.48 mmol) was added to a white suspension of $B(C_6F_5)_3$ (0.25 g, 0.48 mmol) in pentane (30 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature. A green solution was observed initially, but it became cloudy as a yellow solid began to precipitate. After stirring for 3 h, the resulting mixture was filtered. The yellow solid was washed with pentane (2 × 10 mL) and recrystallized from a mixture of toluene and pentane at −20 °C to produce **6** (0.09 g, 23%) as orange crystals: ^{1}H NMR (C_7D_8, 25 °C) δ 2.24 (br, 6H, NN*Me*$_2$), 1.84, 1.38, 1.33, 1.19 (s, 12H, C_5*Me*$_4$), 0.45 (br, 3H, B*Me*), 0.22 (s, 3H, Ti*Me*), 0.06, −0.02 (s, 6H, Si*Me*$_2$).

Preparation of [(η^5-C_5Me_4)($SiMe_2NHNMe_2$)Ti]$_4O_6$ (7). Deoxygenated water (24 μL, 1.34 mmol) was added to a toluene solution (50 mL) of **2** (0.50 g, 1.3 mmol) at room temperature. The reaction mixture was stirred for 5 h and turned to a yellow solution. The solvent was removed in vacuo, and the yellow residue was extracted with pentane (3 × 10 mL). Evaporation of the solvent and recrystallization of the residue in pentane at −20 °C yielded **6** (0.22 g, 52%) as green crystals: ^{1}H NMR ($CDCl_3$, 25 °C) δ 2.42 (s, 24H, N*Me*$_2$), 2.22, 1.99 (s, 48H, C_5*Me*$_4$), 2.11 (s, 4H, N*H*), 0.42 (s, 24H, Si*Me*$_2$). Anal. Calcd for $C_{52}H_{100}O_6N_8Si_4Ti_4$: C, 50.48; H, 8.15; N, 9.06. Found: C, 50.11; H, 7.98; N, 8.81.

Preparation of [μ-($OSiMe_2$-η^5-C_5Me_4)$TiCl_2$]$_2$ (8). An ether solution of HCl (1.0 M, 8.1 mL, 8.05 mmol) was added to a wet ether solution (50 mL) of **2** (0.6 g, 1.61 mmol) at −78 °C. The reaction mixture was slowly warmed to room temperature, stirred for 3 h, and filtered. The solvent of the filtrate was evaporated, and recrystallization of the residue in ether at −20 °C afforded red crystals of **8** (0.23 g, 45%): ^{1}H NMR ($CDCl_3$, 25 °C) δ 2.37, 2.25 (s, 24H, C_5*Me*$_4$), 0.49 (s, 12H, Si*Me*$_2$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 140.2, 139.4, 129.4 (*C*$_5$Me$_4$), 16.4, 13.1 (C_5*Me*$_4$), 2.4 (Si*Me*$_2$); MS (70 eV) *m*/*z* 626 (M^+). Anal. Calcd for $C_{22}H_{36}Cl_4O_2Si_2Ti_2$: C, 42.19; H, 5.79. Found: C, 41.68; H, 5.52.

Polymerization Procedure. Ethene polymerizations were carried out in an autoclave reactor. A toluene solution of MAO was introduced into the reactor, and the temperature was increased to the polymerization temperature. Toluene solutions of complexes **2**−**4** were injected into the reactor, respectively, and polymerization was started by introducing ethene into the reactor. In the case of ethene/1-octene copolymerization, 1-octene was added before ethene introduction. When $Al^iBu_3/Ph_3C^+B(C_6F_5)_4^-$ was used as a cocatalyst, a toluene solution of the cocatalyst was introduced before injection of a toluene solution of complex **5**. Polymerization was terminated by introducing ethanol.

X-ray Data Collection and Structure Determination. Crystals of **2**, **4**, **5**, and **7** suitable for X-ray structure determination were obtained by slow crystallization from pentane, and crystals of **3** and **8** from toluene and ether at −20 °C, respectively. All single crystals were mounted in thin-walled glass capillaries under an argon atmosphere. The determinations of the unit cell parameters, the orientation matrix, and the collection of intensity data were made on an Enraf-Nonius CAD-4 diffractometer, employing graphite-monochromated Mo Kα radiation. Lorentz and polarization corrections were applied to the intensity data. A semiempirical absorption correction was applied for **8**, but no absorption correction was made for **2**, **3**, **4**, **5**, and **7**. Relevant crystallographic data are summarized in Table 6.

All calculations were performed using the SHELXTL system of computer programs.[19] Scattering factors for all atoms were included in the software package. The structures were solved using direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. In the final cycle of refinement, the mean shift/esd's were less than 0.001.

Acknowledgment. We are grateful to SK Corporation for financial support of this work.

Supporting Information Available: A complete atomic labeling scheme for **7** and tables of atomic coordinates, thermal parameters, bond distances, and angles for **2**, **3**, **4**, **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990841I

(19) (a) SHELXS86: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) SHELXL93: Sheldrick, G. M. *Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1993.