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# *Articles*

# Sterically Controlled Silacycloalkyl Diamide Complexes of Titanium(IV): Synthesis, Structure, and Catalytic Behavior of (cycl)Si(NBu$^t$)$_2$TiCl$_2$ [(cycl)Si = Silacyclobutane, Silacyclopentane, Silacyclopentene, and Silacyclohexane]

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The chemistry of titanium complexes stabilized by a series of cyclic silyldiamide ligands-(cycl)Si(HNBu$^t$)$_2$ (**2**) derived from the silacycloalkyl unit -(CH$_2$)$_n$Si-, with $n = 3$, 4, and 5, has been studied. Thus, a variety of *spiro*-siladiazatitanacyclobutane complexes (cycl)Si(NBu$^t$)$_2$TiCl$_2$ (**3**) has been prepared by the reaction of the dilithium salt of **2** with titanium tetrachloride. The reaction of **2** with Ti(NMe$_2$)$_4$ in refluxing toluene yields (cycl)Si(NBu$^t$)$_2$Ti(NMe$_2$)$_2$ (**4**), and the product **4** is converted to **3** in a moderate isolated yield by treatment with excess Me$_3$SiCl. Dimethyl complexes of the type (cycl)Si(NBu$^t$)$_2$TiMe$_2$ (**5**) were prepared by the reaction of **3** with MeMgBr. Complexes **3** have been characterized by X-ray crystallography. As a result of the formation of the siladiazatitanacyclobutane ring, the titanium atoms in **3** exhibit distorted-tetrahedral configurations with the two chloride ligands. In addition, the crystallographic results establish that steric interactions between the silacycloalkyl and *tert*-butyl groups influence the C(Bu$^t$)−N−Ti angles and, hence, the steric environment at titanium. The compounds **3** were further investigated as potential catalysts for the polymerization of ethylene. While sterically less demanding silacyclobutyl and -pentyl diamide complexes (**3a** and **3b**) exhibit low ethylene polymerization activity (4.0−5.8 kg PE mol$_{cat}^{-1}$ h$^{-1}$) in the presence of methylalumoxane, the highly puckered silacyclohexyl diamide complex **3c** shows better activity (14 kg PE mol$_{cat}^{-1}$ h$^{-1}$) for ethylene polymerization when it is activated with MAO.

## Introduction

A bidentate diamide ligand with a silyl substituent[1] is of considerable interest as a ligand in the coordination chemistry of main group elements[2] and transition metals.[3] Such a complex is also attractive as an "open" chelating diamide ligand for the synthesis of olefin polymerization precatalysts.[4] In this context, recent reports describing the use of zirconium−diamide complexes [{Me$_2$Si(NBu$^t$)$_2$}ZrR]$^+$ for alkene and alkyne insertion are noteworthy.[5] To extend this structure−reactivity method to the preparation of silyldiamides, we are exploring the reactivity of Si-functionalized cyclic silyldiamides of varying sizes toward titanium metal. Because the two amide groups should ideally dispose a restricted wedgelike opening, the bulky cyclic silyldiamide would seem well-suited as a supporting ligand for early transition metals. One important aspect of our work on cyclic silyldiamide complexes is the influence of the Si-(cycl) and N-Bu$^t$ substituents on the steric environment at the titanium center. Therefore, through modification of the organic substituents at the bridge silicon position, there is the potential for making

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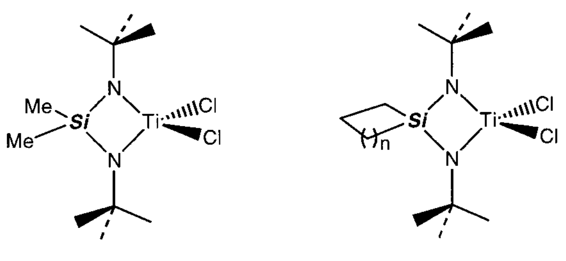
**Chart 1**



**A** **3**

rational modifications that can be used to stabilize desired structural and reactivity characterics.

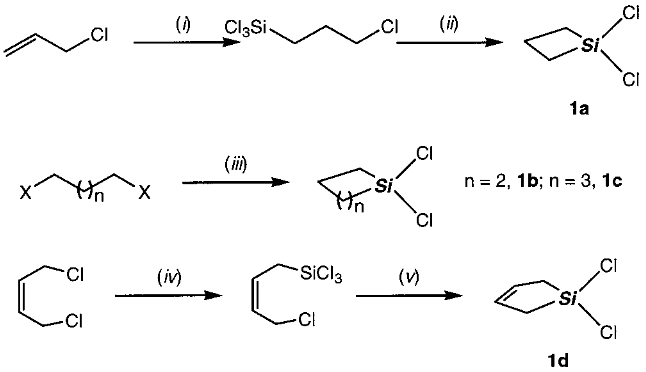
On the basis of these general structural considerations, we set out to synthesize titanium complexes of *spiro*-siladiazatitanacyclobutane, (cycl)Si(NBu$^t$)$_2$TiCl$_2$ (**3**) [(cycl)Si = silacyclobutane, silacyclopentane, silacyclopentene, and silacyclohexane], which are of interest for applications in olefin polymerization (Chart 1). Comparison of key bond angles around the siladiazatitanacyclobutane core as a fuction of the Si-(cycl) and N-Bu$^t$ substituents provides insight into this structure–reactivity relationship.

## Results and Discussions

**Synthesis of the Dichlorosilacycloalkanes or -alkene (1).** In an effort to extend the range of available silyldiamide ligands, we have been investigating the introduction of a variety of silacycloalkyl groups in the bridging position. The dichlorosilacycloalkane and -alkene derivatives **1** have been prepared using a standard procedure involving the appropriate chloroalkylchlorosilanes or dichloroalkanes. Thus, our synthetic methodology is based on the reaction of chloroalkylchlorosilanes or dichloroalkanes with magnesium to generate the corresponding dichlorosilacycloalkane[6,7] or -alkene[8] species **1** as shown in Scheme 1.

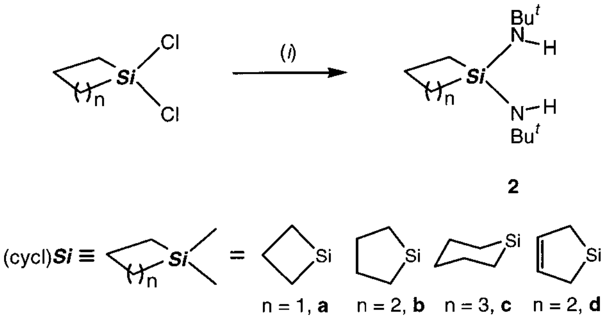
**Synthesis of the Silacycloalkyl or -alkenyl Diamides (2).** Chelating diamides with silyl substituents are readily accessible by the reaction of lithium amide with dichlorosilacycloalkane or -alkene **1**. Compound **2** (colorless liquid) is readily accessible via a procedure (Scheme 2) analogous to that for the synthesis of the silyldiamide ligand Me$_2$Si(NHBu$^t$)$_2$ (**A**).[9] For example, the reaction of *tert*-butylamine with *n*-butyllithium followed by the addition of **1** gives silyldiamide derivatives **2** in good yield. The ligand systems used were the bidentate amines **2**; the lithium salt was taken as the starting material for the synthesis of the titanium(IV) amides **3**.

**Scheme 1. Synthesis of Dichlorosilacycloalkane or -alkene 1**[a]



[a] Legend: (i) HSiCl$_3$, H$_2$PtCl$_6$, PPh$_3$, 25 °C; (ii) Mg, THF, 25 °C; (iii) (a) Mg, Et$_2$O, 25 °C; (b) SiCl$_4$, Et$_2$O, 25 °C; (iv) HSiCl$_3$, CuCl, NEt$_3$, 25 °C; (v) Mg, Et$_2$O, 25 °C.

**Scheme 2. Synthesis of Cyclic Silyldiamide Ligand 2**[a]



[a] Legend: (i) 2 LiNBu$^t$H, Et$_2$O, −78 °C.

**Synthesis of the *spiro*-Siladiazatitanacyclobutane Complexes, (cycl)Si(NBu$^t$)$_2$TiCl$_2$ (3).** The reaction of TiCl$_4$ (1.0 mmol) and the dilithium salt of **2** (1 equiv) in diethyl ether leads to (cycl)Si(NBu$^t$)$_2$TiCl$_2$ (**3**) in good yield (45–88%). Compounds **3** were purified by low-temperature recrystallization from pentane as red crystals. Satisfactory elemental analyses were obtained for **3**, and the $^1$H and $^{13}$C NMR spectral data are consistent with the presence of the bidentate cyclic silyldiamide ligand (see Experimental Section).

The $^1$H NMR signals for N-Bu$^t$ in **3** are at a lower field than those for the free ligand. This can be explained on the basis of a tetrahedral geometry with amide and chloride ligands and evidence of Ti–N coordination in solution. This observation is consistent with similar findings for the siladiazatitanacyclobutane ring of the Me$_2$Si(NBu$^t$)$_2$TiCl$_2$ (**A**) (Chart 1). The data for **3** also reveal that the replacement of a cyclic alkyl or an alkenyl group on the central silicon atom has little

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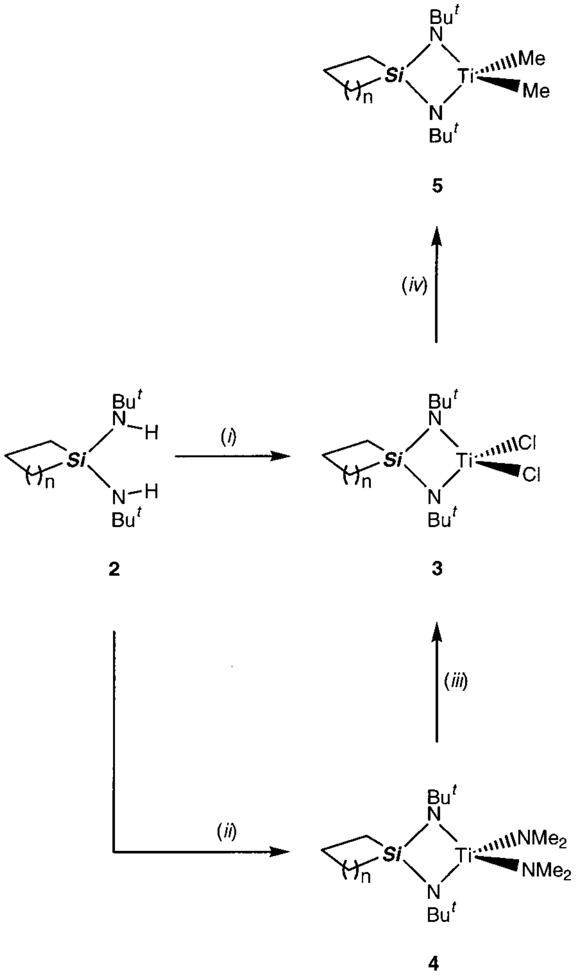
**Scheme 3. Synthesis of Titanium Complexes Incorporating Ligand 2**[a]



[a] Legend: (i) (a) LiBu$^n$, Et$_2$O, −78 °C; (b) TiCl$_4$, Et$_2$O, −78 °C; (ii) Ti(NMe$_2$)$_4$, toluene, 110 °C; (iii) Me$_3$SiCl, CH$_2$Cl$_2$, 25 °C; (iv) MeMgBr, Et$_2$O, −78 °C.

effect on the N-Bu$^t$ values in both the $^1$H and $^{13}$C NMR spectra. The reaction proceeds with high yield, giving preferential formation of the tetrahedral Ti complexes. In addition, the increased kinetic stability of the products **3** is most likely a consequence of the formation of a *spiro* ring that is imposed by the cyclic silyl backbone.

**Synthesis and Reactivity of the Diamido Ti(IV) Complexes, (cycl)Si(NBu$^t$)$_2$Ti(NMe$_2$)$_2$ (4).** The diamido titanium(IV) complexes **4** were prepared through an amine elimination. The reaction of Ti(NMe$_2$)$_4$ with **2** under N$_2$ in refluxing toluene for 12 h afforded the diamido titanium(IV) complexes (cycl)Si(NBu$^t$)$_2$Ti(NMe$_2$)$_2$ (**4**) in 90% yield. Crystallization from toluene afforded pure (cycl)Si(NBu$^t$)$_2$Ti(NMe$_2$)$_2$ (**4**) as orange-red crystals in 40−61% yield (Scheme 3). The evolved Me$_2$NH was allowed to escape from the reaction vessel via an oil bubbler. The $^1$H and $^{13}$C NMR spectra of **4** are consistent with pseudo $C_{2v}$-symmetric structures and symmetrical bidentate coordination of the diamide ligand. $^1$H NMR data suggest that the yield of **4** is essentially quantitative, but the high solubility of **4** in hydrocarbon solvents evidently prevents it from being isolated in higher yield. The addition of excess chlorotrimethylsilane to the bright yellow solution of **4** in CH$_2$Cl$_2$ resulted in an immediate color change to orange-red, indicating the conversion to (cycl)Si(NBu$^t$)$_2$TiCl$_2$ (**3**). Thus, addition of excess trimethylchlorosilane to **4** gave **3** in 72−92% isolated yield (Scheme 3). The NMR spectra of these products were identical with those of **3** prepared by the method of Scheme 3.

**Table 1. Data for Ethylene Polymerization**[a]

| entry | catalyst | [cat.] ($\mu$mol) | time (min) | activity[b] | $T_m$ (°C)[c] |
|---|---|---|---|---|---|
| 1 | **A** | 10 | 30 | 2.6 | 129.8 |
| 2 | **3a** | 10 | 30 | 4.0 | 128.1 |
| 3 | **3b** | 10 | 30 | 5.8 | 131.1 |
| 4 | **3c** | 10 | 30 | 14.0 | 129.7 |
| 5 | **3d** | 10 | 30 | 19.8 | 130.4 |
| 6 | Cp$_2$TiCl$_2$[d] | 12 | 10 | 323.0 | 138.1 |

[a] MMAO-4 (Al:M = 1000:1), 70 mL of toluene, 40 °C, 1 atm of ethylene. [b] kg PE/mol$_{cat}$ h atm. [c] Measured by differential scanning calorimetry (DSC). [d] 100 mL of hexane.

**Synthesis of the *spiro*-Siladiazatitanacyclobutane Complexes, (cycl)Si(NBu$^t$)$_2$TiMe$_2$ (5).** Because dialkyl species are important precursors for active polyolefin catalysts, we synthesized the dimethyl derivatives of these diamide complexes **5**. Methylation of a diethyl ether solution of **3** (1.0 mmol) with MeMgBr (2.4 mmol) at room temperature for 2 h afforded high yields of **5** (66−86%) as pale yellow solids. The composition of **5** was confirmed by elemental analysis. As expected, the $^1$H NMR spectra of **5** are consistent with a species with pseudo $C_{2v}$ symmetry. Characteristic $^1$H and $^{13}$C NMR resonances of the Ti-Me groups were observed at around $\delta$ 0.2 and 3.4, respectively. The cyclo alkylsilyl groups exhibit unresolved multiplets between $\delta$ 0.7 and 1.9, and the signal of the chemically equivalent *tert*-butyl protons is observed as a singlet at around $\delta$ 1.5. Although the reaction produces the desired product almost quantitatively, as indicated by NMR spectroscopy, we failed to isolate the analytically pure crystalline product. The product was isolated as a sticky solid which was difficult to recrystallize due to its high solubility even in pentane.

Given the sterically open nature of the silicon-bridged diamide ligand, it was expected that the cations would exhibit distinct structural and reactive chemistry compared to that of the analogous silyl diamide complex [{Me$_2$Si(NBu$^t$)$_2$}ZrR]$^+$.[5] The reaction of **5** with 1 equiv of B(C$_6$F$_5$)$_3$ was carried out at low temperature, but only intractable product was obtained. It was observed that the ionic species decomposed slowly to yield unidentifiable species at room temperature in several hours.[10] Despite considerable efforts, however, attempts to isolate and characterize the decomposition product have been unsuccessful.

**Polymerization of Ethylene.** Multiple experiments were carried out with complexes **3**. Although we have not yet prepared alkyl cations of the type [{(cycl)Si(NBu$^t$)$_2$}TiMe]$^+$ in order to isolate polyolefin catalysts, we have already conducted preliminary catalytic ethylene polymerization tests on **3**, using MMAO (modified methylalumoxane) as cocatalyst (Al/Ti 1000/1) in hexane at 40 °C (1 atm of ethylene). Table 1 compiles the results of homogeneous ethylene polymerizations obtained using **3** as catalyst. Activities were low, 4.0 (**3a**), 5.8 (**3b**), 14 (**3c**), and 20 (**3d**) (kg PE mol$_{cat}^{-1}$ h$^{-1}$), compared to an activity of 323 with Cp$_2$TiCl$_2$ under the same

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**Table 2. X-ray Crystallographic Data and Processing Parameters for Compounds 3a−d**

| | **3a** | **3b** | **3c** | **3d** |
|---|---|---|---|---|
| formula | $C_{11}H_{24}C_{l2}N_2SiTi$ | $C_{12}H_{26}C_{l2}N_2SiTi$ | $C_{13}H_{28}C_{l2}N_2SiTi$ | $C_{12}H_{24}C_{l2}N_2SiTi$ |
| fw | 331.22 | 345.24 | 359.26 | 343.22 |
| cryst class | monoclinic | orthorhombic | orthorhombic | orthorhombic |
| space group | $C2/c$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ |
| Z | 8 | 4 | 4 | 4 |
| cell constants | | | | |
| $A$, Å | 10.1089(4) | 8.9124(4) | 9.0699(6) | 8.9424(5) |
| $B$, Å | 14.0311(3) | 8.9092(9) | 13.4358(7) | 8.9421(5) |
| $C$, Å | 12.5670(5) | 23.257(2) | 16.0787(1) | 22.736(3) |
| $V$, Å$^3$ | 1736.6(1) | 1846.6(3) | 1959.4(2) | 1818.0(2) |
| $\beta$, deg | 103.034(7) | | | |
| $\mu$, cm$^{-1}$ | 8.54 | 8.06 | 7.62 | 8.18 |
| cryst size, mm | 0.3 × 0.5 × 0.5 | 0.35 × 0.4 × 0.5 | 0.25 × 0.5 × 0.7 | 0.2 × 0.15 × 0.3 |
| $D_{calcd}$, g/cm$^3$ | 1.267 | 1.242 | 1.218 | 1.254 |
| $F(000)$ | 696 | 728 | 760 | 720 |
| radiation | Mo Kα ($\lambda = 7170$ Å) | | | |
| $\theta$ range, deg | 2.53−26.14 | 1.75−25.98 | 1.98−25.96 | 1.79−25.95 |
| $h, k, l$ collected | +12, +10, ±15 | +10, +10, +28 | +11, +16, +19 | +11, +11, +28 |
| no. of rflns measd | 3511 | 4099 | 2228 | 3997 |
| no. of unique rflns | 1708 | 3600 | 2192 | 3542 |
| no. of rflns used in refinement ($I > 2\sigma(I)$) | 1353 | 3063 | 1070 | 1070 |
| no. of params | 82 | 170 | 178 | 171 |
| data/param ratio | 20.83 | 21.18 | 12.31 | 20.71 |
| $R_1{}^a$ | 0.0335 | 0.0542 | 0.0482 | 0.0683 |
| $wR_2{}^b$ | 0.1110 | 0.1488 | 0.1109 | 0.1582 |
| GOF | 0.922 | 0.966 | 0.697 | 0.874 |

[a] $R_1 = \sum|F_o| - |F_c|$ (based on reflections with $F_o^2 > 2\sigma F^2$). [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$(also with $F_o^2 > 2\sigma F^2$).

conditions. The dimethyl complex **A** has shown little activity (2.6 kg PE $mol_{cat}{}^{-1}$ $h^{-1}$) under comparable conditions. Molecular weights of the polymer samples could not be measured, because they showed low solubility even in refluxing 1,2,4-trichlorobenzene. However, melting temperatures ($T_m$) measured by differential scanning calorimetry (DSC) are typical of high-density polyethylene. No methyl bending resonances at around 1376 cm$^{-1}$ were observed in the IR spectra of the polymers prepared with these catalytic systems, which suggests the branching might be absent.[11]

The low catalytic activities of **3** are presumably due to decomposition of the active catalysts generated with MMAO. One explanation might be the cleavage of the N−Si bond of the ligand in our complexes by the large excess of MMAO cocatalyst, as already observed on silylamido group 4 metal complexes.[4a,12] Although their catalytic activities are low, they still show differences in polymerization activity. Consequently, the catalyst **3c** bearing the silacyclohexyl group shows higher activity than that of the silacyclobutyl-substituted analogue **3a**. It is interesting to observe that the catalyst **3d** bearing the silacyclopentenyl group shows higher activity than that of the silacycloalkyl-substituted analogues (**3a**−**c**). The reasons for higher activity of **3d** under these conditions are not clear. However, this complex has proved less prone to decomposition than the silacycloalkyl analogues **3a**−**c**.

**Molecular Geometry and Crystal Structures of 3.** Suitable crystals for X-ray analysis of **3** have been obtained by cooling a pentane solution to −45 °C, and the crystal structures of the four compounds were determined by X-ray diffraction. Crystal data for complexes **3** are summarized in Table 2, refinement details are discussed in the Experimental Section, and selected bond distances and angles are collected in Tables 3 and 4, respectively. The molecular geometries and atom-labeling schemes are shown in Figures 1−4. The structural analysis of **3** reveals a molecular core with similarities to that of complex **A**:[13] the metal center is in a distorted tetrahedral environment consisting of the two nitrogen atoms of the silyldiamide ligand with the chloride ligands completing the coordination sphere.

**Table 3. Selected Interatomic Distances (Å) in 3a−d**

| | | | | | |
|---|---|---|---|---|---|
| Compound **3a** | | | | | |
| Ti(1)−N(1) | 1.832(2) | Ti(1)−Cl(1) | 2.250(8) | Ti(1)−Si(1) | 2.596(9) |
| Si(1)−N(1) | 1.759(2) | Si(1)−C(1) | 1.863(2) | Si(1)−C(2) | 2.351(4) |
| N(1)−C(3) | 1.477(3) | C(1)−C(2) | 1.535(4) | | |
| Compound **3b** | | | | | |
| Ti(1)−N(1) | 1.826(4) | Ti(1)−N(2) | 1.834(4) | Ti(1)−Cl(2) | 2.252(2) |
| Ti(1)−Cl(1) | 2.253(2) | Ti(1)−Si(1) | 2.605 (1) | Si(1)−N(1) | 1.770(4) |
| Si(1)−N(2) | 1.773(4) | Si(1)−C(1) | 1.867(5) | Si(1)−C(4) | 1.872(5) |
| N(1)−C(5) | 1.484(6) | N(2)−C(9) | 1.476(6) | C(1)−C(2) | 1.550(9) |
| C(2)−C(3) | 1.48 (1) | C(3)−C(4) | 1.542(9) | | |
| Compound **3c** | | | | | |
| Ti(1)−N(2) | 1.832(6) | Ti(1)−N(1) | 1.834(5) | Ti(1)−Cl(1) | 2.247(3) |
| Ti(1)−Cl(2) | 2.252(3) | Ti(1)−Si(1) | 2.609(2) | Si(1)−N(2) | 1.778(6) |
| Si(1)−N(1) | 1.778(6) | Si(1)−C(1) | 1.847(7) | Si(1)−C(5) | 1.853(8) |
| N(1)−C(6) | 1.461(9) | N(2)−C(10) | 1.476(9) | C(1)−C(2) | 1.50(1) |
| C(2)−C(3) | 1.50(1) | C(3)−C(4) | 1.49(1) | C(4)−C(5) | 1.51(1) |
| Compound **3d** | | | | | |
| Ti(1)−N(1) | 1.82(1) | Ti(1)−N(2) | 1.83(1) | Ti(1)−Cl(1) | 2.24(5) |
| Ti(1)−Cl(2) | 2.24 (5) | Ti(1)−Si(1) | 2.59 (4) | Si(1)−N(1) | 1.75(1) |
| Si(1)−N(2) | 1.77(1) | Si(1)−C(1) | 1.86(2) | Si(1)−C(4) | 1.88(1) |
| N(1)−C(5) | 1.49(2) | N(2)−C(9) | 1.48(2) | C(1)−C(2) | 1.48(2) |
| C(2)−C(3) | 1.27(2) | C(3)−C(4) | 1.51(2) | | |

Overall, the four structures are tetrahedral with a planar conformation for the diamido-titanium ring, similar to what is observed in complex **A** (Table 5). Thus, in all of the compounds **3** studied, the (cycl)Si(NBu$^t$)$_2$Ti core forms a nearly planar siladiazatitanacyclobutane

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[11] Koenig, J. L. *Chemical Microstructure of Polymer Chains*; Wiley: New York, 1982; p 63.

[12] Schrock, R. R.; Seidel, S. W.; Schrodi, Y.; Davis, W. M. *Organometallics* **1999**, *18*, 428.

[13] Jones, R.; Seeberger, M. H.; Atwood, J. L.; Hunter, W. E. *J. Organomet. Chem.* **1983**, *247*, 1.

**Table 4. Selected Interatomic Angles (deg) in 3a−d**

| | | | | | |
|---|---|---|---|---|---|
| | | Compound **3a** | | | |
| N(1*)−Ti(1)−N(1) | 85.2(1) | N(1)−Ti(1)−Cl(1) | 113.3(6) | Cl(1)−Ti(1)−Cl(1*) | 112.5(5) |
| N(1)−Si(1)−N(1*) | 89.6(1) | N(1)−Si(1)−C(1) | 123.4(1) | C(1*)−Si(1)−C(1) | 81.4(2) |
| C(3)−N(1)−Si(1) | 130.6(1) | C(3)−N(1)−Ti(1) | 136.5(1) | Si(1)−N(1)−Ti(1) | 92.6(8) |
| C(2)−C(1)−Si(1) | 87.0(2) | | | | |
| | | Compound **3b** | | | |
| N(1)−Ti(1)−N(2) | 85.6(2) | N(1)−Ti(1)−Cl(2) | 113.9(1) | N(2)−Ti(1)−Cl(2) | 114.6(1) |
| N(1)−Ti(1)−Cl(1) | 115.0(1) | N(2)−Ti(1)−Cl(1) | 114.2(1) | Cl(2)−Ti(1)−Cl(1) | 111.4(8) |
| N(1)−Si(1)−N(2) | 89.2(2) | N(1)−Si(1)−C(1) | 118.3(2) | N(2)−Si(1)−C(1) | 118.4(2) |
| N(1)−Si(1)−C(4) | 118.0(2) | N(2)−Si(1)−C(4) | 118.1(2) | C(1)−Si(1)−C(4) | 96.9(3) |
| C(5)−N(1)−Si(1) | 131.3(3) | C(5)−N(1)−Ti(1) | 135.8(3) | Si(1)−N(1)−Ti(1) | 92.8(2) |
| C(9)−N(2)−Si(1) | 131.7(3) | C(9)−N(2)−Ti(1) | 135.7(3) | Si(1)−N(2)−Ti(1) | 92.5(2) |
| C(2)−C(1)−Si(1) | 102.7(4) | C(3)−C(2)−C(1) | 109.7(5) | C(2)−C(3)−C(4) | 110.3(5) |
| C(3)−C(4)−Si(1) | 102.6(4) | | | | |
| | | Compound **3c** | | | |
| N(2)−Ti(1)−N(1) | 85.8(2) | N(2)−Ti(1)−Cl(1) | 114.4(2) | N(1)−Ti(1)−Cl(1) | 113.0(2) |
| N(2)−Ti(1)−Cl(2) | 113.7(2) | N(1)−Ti(1)−Cl(2) | 114.8(2) | Cl(1)−Ti(1)−Cl(2) | 112.6(1) |
| N(2)−Si(1)−N(1) | 89.1(3) | N(2)−Si(1)−C(1) | 117.8(3) | N(1)−Si(1)−C(1) | 113.4(3) |
| N(2)−Si(1)−N(1) | 115.1(4) | N(1)−Si(1)−C(5) | 115.7(3) | C(1)−Si(1)−C(5) | 105.6(3) |
| C(6)−N(1)−Si(1) | 132.8(5) | C(6)−N(1)−Ti(1) | 134.2(5) | Si(1)−N(1)−Ti(1) | 92.5(3) |
| C(10)−N(2)−Si(1) | 135.0(5) | C(10)−N(2)−Ti(1) | 132.4(5) | Si(1)−N(2)−Ti(1) | 92.6(3) |
| C(2)−C(1)−Si(1) | 116.3(6) | C(3)−C(2)−C(1) | 114.8(7) | C(4)−C(3)−C(2) | 116.3(8) |
| C(3)−C(4)−C(5) | 116.6(8) | C(4)−C(5)−Si(1) | 112.1(5) | | |
| | | Compound **3d** | | | |
| N(1)−Ti(1)−N(2) | 85.1(5) | N(1)−Ti(1)−Cl(1) | 113.5(4) | N(2)−Ti(1)−Cl(1) | 114.3(5) |
| N(1)−Ti(1)−Cl(2) | 115.3(5) | N(2)−Ti(1)−Cl(2) | 114.1(4) | Cl(1)−Ti(1)−Cl(2) | 112.0(2) |
| N(1)−Si(1)−N(2) | 89.1(5) | N(1)−Si(1)−C(1) | 118.3(7) | N(2)−Si(1)−C(1) | 117.3(7) |
| N(1)−Si(1)−C(4) | 118.4(8) | N(2)−Si(1)−C(4) | 119.3(7) | C(1)−Si(1)−C(4) | 96.5(7) |
| C(5)−N(1)−Si(1) | 130(1) | C(5)−N(1)−Ti(1) | 136(1) | Si(1)−N(1)−Ti(1) | 93.3(6) |
| C(9)−N(2)−Si(1) | 130(1) | C(9)−N(2)−Ti(1) | 137(1) | Si(1)−N(2)−Ti(1) | 92.4(6) |
| C(2)−C(1)−Si(1) | 102(1) | C(3)−C(2)−C(1) | 120(2) | C(2)−C(3)−C(4) | 121(2) |
| C(3)−C(4)−Si(1) | 100(1) | | | | |

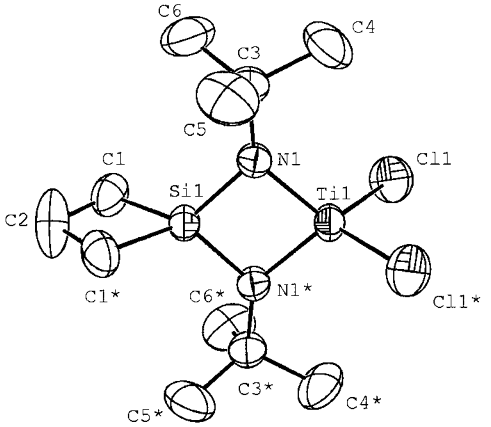

**Figure 1.** Molecular structure of $(C_3H_6)Si(NBu^t)_2TiCl_2$ (**3a**) with thermal ellipsoids drawn at the 30% level.

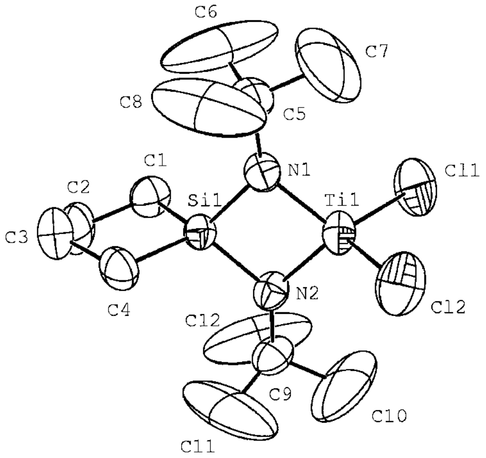

**Figure 2.** Molecular structure of $(C_4H_8)Si(NBu^t)_2TiCl_2$ (**3b**) with thermal ellipsoids drawn at the 30% level.

metallacyclic ring (torsional angles of N−Ti−N−Si < 1°). The cyclic silyldiamide ligand nearly symmetrically chelates the titanium center to form a planar siladiazatitanacyclobutane ring with a bite angle (N−Ti−N) of 85.4° (average). The Ti−N distances are shorter than those found in other four-coordinate amido complexes,[14] which are in the 1.824−1.833 Å range. In addition, the Ti−Cl bond lengths (2.239−2.253 Å) are substantially shorter than those of $Cp_2TiCl_2$.[15] Overall, the Ti−N and Ti−Cl bond lengths are comparable to those in the titanium silyldiamido complex **A**.[13] It is of note that the Cl−Ti−Cl angle of **3** is significantly larger, by about 15°, than the corresponding angle in complex **A** (96.89°) and much closer to the ideal tetrahedral value. This opening of the Cl−Ti−Cl angle in these cyclic silyldiamide complexes **3** is likely an indication of less steric crowding in the equatorial plane of these compounds. The somewhat "open" and "closed" Cl−Ti−Cl and N−Ti−N angles (112.13 and 85.42°, respectively) presumably reflect the constraint on the geometry provided by the (cycl)Si link of the diamide ligand.

**Structure−Catalytic Activity Realtionship of Complex 3.** While the gross structural features of **3** correlate well as shown in Table 5, closer inspection reveals some interesting differences among the four complexes. As expected, the silacyclic linkage moiety of

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(14) (a) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562. (b) Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994**, *13*, 2907. (c) Hebner, B.; Manners, I.; Paetzold, P. *Chem. Ber.* **1987**, *120*, 1065. (d) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010. (e) Brauer, D. J.; Bürger, H.; Wiegel, K. *J. Organomet. Chem.* **1978**, *150*, 215. (f) Alcock, N. M.; Pierce-Butler, M.; Willey, G. R. *J. Chem. Soc., Chem. Commun.* **1974**, 627.

(15) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622.

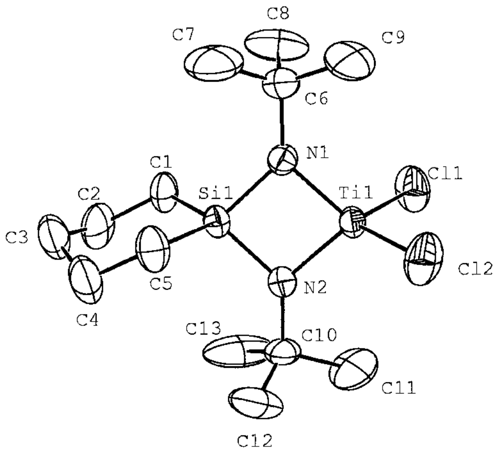

**Figure 3.** Molecular structure of $(C_5H_{10})Si(NBu^t)_2TiCl_2$ (**3c**) with thermal ellipsoids drawn at the 30% level.

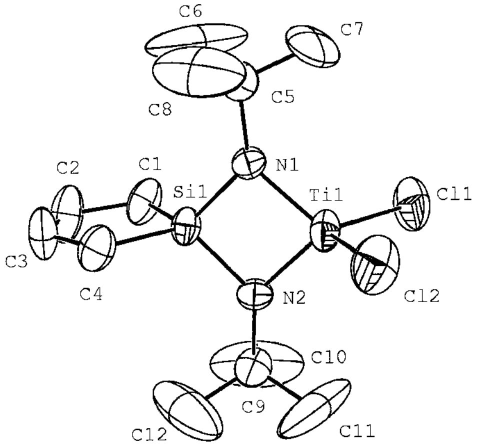

**Figure 4.** Molecular structure of $(C_4H_6)Si(NBu^t)_2TiCl_2$ (**3d**) with thermal ellipsoids drawn at the 30% level.

the diamide ligands has considerable influence on the structure of the titanium dichloride complexes. For easy comparison, the structural features of *spiro*-siladiazatitanacyclobutane rings in **3** are schematically represented (Charts 2 and 3).

Interestingly, the silacycloalkyl ring itself in **3** is gradually distorted from planarity as the chain growth continues in the silacycloalkyl unit $\text{-}(CH_2)_nSi\text{-}$, with $n = 3$, 4, and 5. Replacing the methyl substituents at the central silicon atom with a cyclobutyl group has a minimal steric effect on the structure of the metallacycle core as shown in Chart 2. The planar arrangement about silicon is retained, and the alkyl substituents remain in the plane of the silacycle in **3a**. The average $C(Bu^t)-N-Ti$ angles ($\theta_f$) in **3a** (136.5°) are comparable to those of complex **A** (136.1°).

In contrast, a slightly puckered five-membered silacyclopentyl ring is formed in **3b** (Chart 3). Therefore, two *tert*-butyl groups on the nitrogens are directed away from this silacyclopentyl ring pointing in the opposite directions to reduce steric crowding. For **3c**, the chelate ring is isostructural to that of **3b**, except that the steric demand of the highly puckered six-membered silacyclohexyl ring causes two *tert*-butyl groups on the nitrogens to project more significantly toward the titanium center.

In fact, the increase in the $Si-N-C(Bu^t)$ angles ($\theta_b$) and a concomitant decrease in the $C(Bu^t)-N-Ti$ angles ($\theta_f$) for **3c** relative to **3a** and **3b** are presumably due principally to steric interactions. The average $C(Bu^t)-N-Ti$ angles ($\theta_f$) in **3b** (135.8°) and **3c** (133.3°) are 0.3° and 2.8° smaller than those of complex **A** (136.1°), respectively. Steric interactions between the Si-(cycl) and the N-$Bu^t$ groups thus influence the steric environment at the titanium center. It seems that the puckering of the silacyclohexyl ring in **3c** generates steric protection at the titanium. The resulting difference in steric protection at the titanium center strongly influences the catalytic activity.[16] It may be these features which contribute to the observed increase in catalytic activity for **3c** relative to **3a** and **3b**, as shown in Table 1. Similar control of steric crowding at the metal center has been observed in bulky amidinate complexes of aluminum,[17] gallium,[18] and tin.[19]

At this point, it is not possible to make a clear statement regarding the catalytic potential of the silacycloalkyl or -alkenyl groups. Nevertheless, we believe that there is sufficient scope for optimizing the Si-bridged diamido complexes reported herein for possible applications. Obviously, the silacyclopentenyl derivative **3d** has proven to be most promising as a homogeneous polymerization catalyst. It combines electronic and steric effects to provide an ideal complex for polymerization catalysis.

## Summary

A series of cyclic silyldiamide chelates **2** react with titanium tetrachloride to yield kinetically stabilized *spiro*-siladiazatitanacyclobutane complexes **3** that are fully characterized by X-ray crystallography. Cyclic silyldiamide ligands are useful for fundamental studies of the relationships between ligand structure and metal coordination geometry, because their steric properties can be modified by variation in the silacycloalkyl substituents. This feature is likely due to the relative steric interaction experienced by the Si-(cycl) and N-$Bu^t$ groups. It can be concluded that the diamide ligand linked by the sterically demanding silacyclohexyl group chelates the titanium center with greater steric protection than in the planar silacyclobutyl case. In general, these titanium(IV) complexes **3** exhibit low ethylene polymerization activity in the presence of MAO, but increased activity for the polymerization was observed when the sterically demanding silacyclohexyl diamide ligand **3c** was tested.

## Experimental Section

**General Procedures.** All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. Diethyl ether, toluene, hexane, and pentane were distilled under nitrogen from sodium/benzophenone. Dichloromethane was dried with $CaH_2$. Benzene-$d_6$ was distilled under nitrogen from sodium and stored in a Schlenk storage flask until needed. $CDCl_3$ was predried under $CaH_2$ and vacuum-transferred. Chlorotrimethylsilane, *n*-BuLi (1.6 M in

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[16] Deng, L.; Ziegler, T.; Woo, T. K.; Margl, P.; Fan, L. *Organometallics* **1998**, *17*, 3240.

[17] Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 5183.

[18] Dagorne, S.; Jordan, R. F.; Young, V. C., Jr. *Organometallics* **1999**, *18*, 4619.

[19] Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1997**, *36*, 501.

**Table 5. Comparison of Important Structure Parameters of 3**

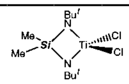
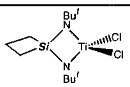
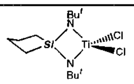
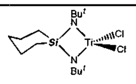
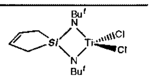
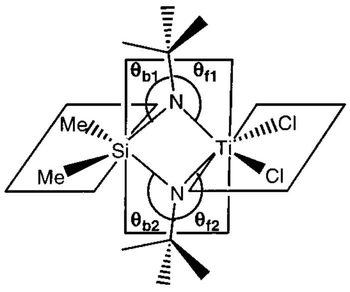
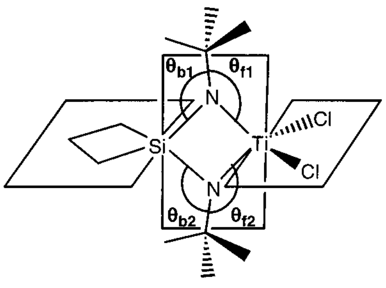
| | A | 3a | 3b | 3c | 3d |
|---|---|---|---|---|---|
| |  |  |  |  |  |
| Ti-N(Å) | 1.829 | 1.832(2) | 1.830(4) | 1.833(5) | 1.824(1) |
| Ti-Cl(Å) | 2.250 | 2.250(8) | 2.253(2) | 2.250(3) | 2.239(5) |
| Si-N(Å) | 1.766 | 1.759(2) | 1.772(4) | 1.778(6) | 1.759(1) |
| N-Ti-N(°) | 85.27 | 85.18(1) | 85.61(2) | 85.8(2) | 85.1(5) |
| Cl-Ti-Cl(°) | 111.01 | 112.51(5) | 111.40(8) | 112.6(1) | 112.0(2) |
| N-Si-N(°) | 89.10 | 89.6(1) | 89.2(2) | 89.1(3) | 89.1(5) |
| C-Si-C(°) | 111.90 | 81.4(2) | 96.9(3) | 105.6(3) | 96.5(7) |
| C-N-N-C(°) | 14.6 | 94.3 | 70.0 | 169.3 | 56.2 |

**Chart 2**



A

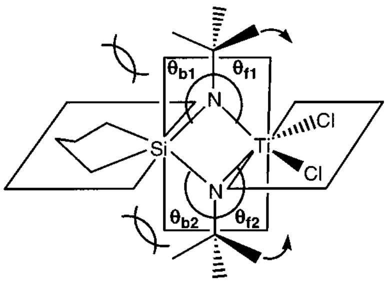
θb1 = 131.1(4)°, θb2 =131.1(4)°;
θf1 = 136.1(5)°, θf2 = 136.1(5)°



3a

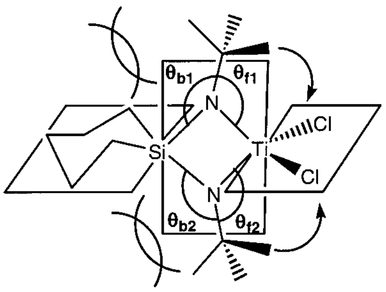
θb1 = 130.6(1)°, θb2 =130.6(1)°;
θf1 = 136.5(1)°, θf2 = 136.5(1)°

**Chart 3**



3b

θb1 = 131.3(3)°, θb2 =131.7(3)°;
θf1 = 135.8(3)°, θf2 = 135.7(3)°



3c

θb1 = 132.8(5)°, θb2 =135.0(5)°;
θf1 = 134.2(5)°, θf2 = 132.4(5)°

hexanes), $TiCl_4$, and ethylene (99.5+%) were used as received from Aldrich. 1,1-Dichlorosilacyclobutane,[6] 1,1-dichlorosilacyclopentane,[7] 1,1-dichlorosilacyclohexane,[7] and 1,1-dichlorosilacyclopent-3-ene[8] were obtained by literature methods. $Ti(NMe_2)_4$ was prepared according to a literature procedure.[20] $B(C_6F_5)_3$ was synthesized[21] and recrystallized from cold pentane. Methylalumoxane (Akzo, type 4) modified with an isobutyl group was purchased as a toluene solution. All $^1H$ (300.1 MHz, measured in $CDCl_3$) and $^{13}C$ (75.4 MHz, measured in $CDCl_3$) NMR spectra were recorded on a Varian Mercury-300BB spectrometer unless otherwise stated. $^1H$ and $^{13}C$ NMR chemical shifts are reported relative to $Me_4Si$ and were determined by reference to the residual $^1H$ or $^{13}C$ solvent peaks. Elemental analyses were performed at either Galbraith Laboratories, Inc., or the chemical analysis laboratory of the Korea Institute of Science and Technology.

**Preparation of Silacycloalkyl or -alkenyl Diamides (2). Representative Procedure.** *tert*-Butylamine (2.31 mL, 22.0 mmol) in THF (50 mL) was added to a 250 mL flask equipped with a magnetic stirrer, an argon inlet, and a condenser. The solution was cooled to 0 °C, and then 15.12 mL of *n*-BuLi (1.6 M in hexanes) was added dropwise. The reaction mixture was warmed to room temperature and stirred additionally for 5 h. The resulting solution was cooled to 0 °C again, and then $(cycl)SiCl_2$ (10.0 mmol) was added. The mixture was heated to reflux for 2 h. After the mixture was stirred for an additional 12 h at room temperature, all volatiles were removed by drying in vacuo. The resulting residue was extracted with pentane, filtered through a Celite pad, and dried in vacuo to afford a pale yellow oil.

**2a:** colorless oil (1.35 g, 63.08%) was obtained by vacuum distillation (75 °C, 0.3 Torr). $^1H$ NMR: $\delta$ 0.968 (m, 4H, $SiCH_2$), 1.201 (s, 18H, $NBu^t$), 1.719 (m, 2H, $CH_2CH_2$). $^{13}C\{^1H\}$ NMR: $\delta$ 13.652 ($SiCH_2$), 23.095 ($CH_2CH_2$), 33.822 ($NCMe_3$), 49.332 ($NCMe_3$). Anal. for $C_{11}H_{26}N_2Si$: found C 61.73, H 12.36, N 13.11; calcd C 61.62, H 12.22, N 13.06.

**2b:** colorless oil (1.49 g, 65.07%) was obtained by vacuum distillation (87 °C, 0.3 Torr). $^1H$ NMR: $\delta$ 0.477 (m, 4H, $SiCH_2$),

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[20] Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.
[21] Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

1.184 (s, 18H, N$Bu^t$), 1.563 (m, 4H, CH$_2$C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 15.452 (Si$C$H$_2$), 26.139 (CH$_2$$C$H$_2$), 33.752 (NC$Me_3$), 49.276 (N$C$Me$_3$). Anal. for $C_{12}H_{28}N_2Si$: found C 63.15, H 12.42, N 12.30; calcd C 63.09, H 12.35, N 12.26.

**2c:** colorless oil (1.75 g, 72.02%) was obtained by vacuum distillation (103 °C, 0.3 Torr). $^1$H NMR: $\delta$ 0.620 (m, 4H, SiC$H_2$), 1.193 (s, 18H, N$Bu^t$), 1.384 (m, 2H, CH$_2$CH$_2$C$H_2$), 1.672 (m, 4H, CH$_2$C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 17.970 (Si$C$H$_2$), 25.507 (CH$_2$CH$_2$$C$H$_2$), 30.683 (CH$_2$$C$H$_2$), 33.994 (NC$Me_3$), 49.458 (N$C$Me$_3$). Anal. for $C_{13}H_{30}N_2Si$: found C 64.43, H 12.53, N 11.60; calcd C 64.39, H 12.47, N 11.55.

**2d:** colorless oil (1.20 g, 53.05%) was obtained by distillation (35 °C). $^1$H NMR: $\delta$ 0.808 (m, 4H, SiC$H_2$), 1.127 (s, 18H, N$Bu^t$), 5.900 (m, 2H, ═C$H$). $^{13}$C{$^1$H} NMR: $\delta$ 19.926 (Si$C$H$_2$), 33.691 (NC$Me_3$), 49.316 (N$C$Me$_3$), 130.891 (═$C$H). Anal. for $C_{12}H_{26}N_2Si$: found C 63.69, H 11.62, N 12.30; calcd C 63.65, H 11.57, N 12.37.

**Preparation of the *spiro*-Siladiazatitanacyclobutane Complexes, (cycl)Si(NBu$^t$)$_2$TiCl$_2$ (3). Representative Procedure.** To a solution of **2** (1.0 mmol) in 20 mL of diethyl ether, precooled to −78 °C, was added 1.3 mL of *n*-BuLi (1.6 M in hexanes). The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon it was transferred, via cannula, to a suspension of 1.1 equiv of titanium tetrachloride in 20 mL of Et$_2$O that was cooled to −78 °C. The resultant yellow mixture was allowed to warm to room temperature and stirred for 2 h. Removal of the volatiles provided the final crude product which was further crystallized from pentane at −45 °C to provide pure (cycl)Si(NBu$^t$)$_2$TiCl$_2$ **(3)** as a reddish-yellow solid.

**3a:** red crystals (0.15 g, 45.03%) were obtained by recrystallization (−45 °C, pentane). $^1$H NMR: $\delta$ 1.474 (m, 4H, SiC$H_2$), 1.543 (s, 18H, N$Bu^t$), 2.149 (m, 2H, CH$_2$C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 12.941 (Si$C$H$_2$), 26.979 (CH$_2$$C$H$_2$), 33.412 (NC$Me_3$), 66.541 (N$C$Me$_3$). Anal. for $C_{11}H_{24}N_2Cl_2SiTi$: found C 39.99, H 7.20, N 8.32; calcd C 39.89, H 7.30, N 8.46.

**3b:** red crystals (0.30 g, 88.05%) were obtained by recrystallization (−45 °C, pentane). $^1$H NMR: $\delta$ 1.047 (m, 4H, SiC$H_2$), 1.503 (s, 18H, N$Bu^t$), 1.905 (m, 4H, CH$_2$C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 12.541 (Si$C$H$_2$), 25.720 (CH$_2$$C$H$_2$), 33.544 (NC$Me_3$), 66.204 (N$C$Me$_3$). Anal. for $C_{12}H_{26}N_2Cl_2SiTi$: found C 41.88, H 7.73, N 8.25; calcd C 41.75, H 7.59, N 8.11.

**3c:** red crystals (0.27 g, 76.05%) were obtained by recrystallization (−45 °C, pentane). $^1$H NMR: $\delta$ 1.205 (m, 4H, SiC$H_2$), 1.528 (s, 18H, N$Bu^t$), 1.594 (m, 2H, CH$_2$C$H_2$CH$_2$), 2.000 (m, 4H, CH$_2$C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 17.706 (Si$C$H$_2$), 26.092 (CH$_2$CH$_2$$C$H$_2$), 29.069 (CH$_2$$C$H$_2$), 33.527 (NC$Me_3$), 65.626 (N$C$Me$_3$). Anal. for $C_{13}H_{28}N_2Cl_2SiTi$: found C 43.60, H 7.70, N 7.70; calcd C 43.46, H 7.86, N 7.80.

**3d**: red crystals (0.23 g, 67.06%) were obtained by recrystallization (−45 °C, pentane). $^1$H NMR: $\delta$ 1.468 (s, 18H, N$Bu^t$), 1.693 (m, 4H, SiC$H_2$), 6.163(m, 2H, ═C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 16.569 (Si$C$H$_2$), 33.054 (NC$Me_3$), 66.408 (N$C$Me$_3$), 130.567 (═$C$H$_2$). Anal. for $C_{12}H_{24}N_2Cl_2SiTi$: found C 42.12, H 7.11, N 8.24; calcd C 42.00, H 7.05, N 8.16.

**Preparation of the *spiro*-Siladiazatitanacyclobutane Complexes, (cycl)Si(NBu$^t$)$_2$Ti(NMe$_2$)$_2$ (4). Representative Procedure.** Complex **2** (1.0 mmol) in toluene (10 mL) was added to Ti(NMe$_2$)$_4$ (0.23 mL, 1.0 mmol) in toluene (10 mL) at room temperature. The reaction mixture was heated to refluxing temperature and stirred for 12 h. The resulting orange solution was dried under vacuum to afford a yellow solid. The solid was extracted with pentane, and the filterate was concentrated and cooled to −45 °C. Yellow solid **4** was isolated by the filtration, washing with cold pentane, and drying in vacuo.

**4a:** yellow powder (0.15 g, 43.1%). $^1$H NMR: $\delta$ 1.041 (m, 4H, SiC$H_2$), 1.202 (s, 18H, N$Bu^t$), 1.697 (m, 2H, CH$_2$C$H_2$), 3.252(s, 12H, Ti(N$Me_2$)). $^{13}$C{$^1$H} NMR: $\delta$ 13.644 (Si$C$H$_2$), 23.187 (CH$_2$$C$H$_2$), 33.860 (NC$Me_3$), 38.829 (N$C$Me$_3$), 43.995 (TiN$Me_2$). Anal. for $C_{15}H_{36}N_4SiTi$: found C 51.79, H 10.46, N 16.15; calcd C 51.71, H 10.41, N 16.08.

**4b:** yellow powder (0.19 g, 52.34%). $^1$H NMR: $\delta$ 0.463 (m, 4H, SiC$H_2$), 1.163 (s, 18H, N$Bu^t$), 1.558 (m, 4H, CH$_2$C$H_2$), 3.238(s, 12H, TiN$Me_2$). $^{13}$C{$^1$H} NMR: $\delta$ 15.351 (Si$C$H$_2$), 26.043 (CH$_2$$C$H$_2$), 33.656 (NC$Me_3$), 38.778 (N$C$Me$_3$), 43.842 (TiN$Me_2$). Anal. for $C_{16}H_{38}N_4SiTi$: found C 53.16, H 10.65, N 15.53; calcd C 53.02, H 10.57, N 15.46.

**4c:** yellow powder (0.15 g, 39.79%); $^1$H NMR: $\delta$ 0.591 (m, 4H, SiC$H_2$), 1.159 (s, 18H, N$Bu^t$), 1.351 (m, 2H, CH$_2$CH$_2$C$H_2$), 1.640 (m, 4H, CH$_2$C$H_2$), 3.235 (s, 12H, TiN$Me_2$). $^{13}$C{$^1$H} NMR: $\delta$ 17.616 (Si$C$H$_2$), 25.153 (CH$_2$CH$_2$$C$H$_2$), 30.344 (CH$_2$$C$H$_2$), 33.661 (NC$Me_3$), 38.498 (N$C$Me$_3$), 43.528 (TiN$Me_2$). Anal. for $C_{17}H_{40}N_4SiTi$: found C 54.26, H 10.75, N 14.95; calcd C 54.23, H 10.71, N 14.88.

**4d:** yellow powder (0.22 g, 61.11%). $^1$H NMR: $\delta$ 1.171 (s, 18H, N$Bu^t$), 3.244 (s, 12H, TiN$Me_2$), 1.195 (m, 4H, SiC$H_2$), 5.855(m, 2H, ═C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 19.885 (Si$C$H$_2$), 33.635 (NC$Me_3$), 38.792 (N$C$Me$_3$), 43.958 (TiN$Me$), 130.871(═$C$H$_2$). Anal. for $C_{16}H_{36}N_4SiTi$: found C 53.40, H 10.14, N 15.65; calcd C 53.31, H 10.07, N 15.54.

**Conversion of 4 to 3.** Complex **4** (0.50 mmol) was dissolved in methylene chloride (20 mL), and then excess Me$_3$SiCl (10 equiv) was added. After an additional 30 min of stirring, all volatiles were removed under vacuum, and the resulting residue was washed with pentane three times. Drying in vacuo produced red solid **3**.

**3a:** red powder (0.12 g, 72.46%). **3b:** red powder (0.16 g, 92.69%). **3c:** red powder (0.15 g, 83.51%). **3d:** red powder (0.14 g, 81.58%).

**Preparation of the *spiro*-Siladiazatitanacyclobutane Complexes, (cycl)Si(NBu$^t$)$_2$TiMe$_2$ (5). Representative Procedure.** To a solution of **3** (1.0 mmol) in 20 mL of diethyl ether, precooled to −78 °C, was added MeMgBr (3.0 M in ether, 0.80 mL, 2.4 mmol). The reaction mixture was warmed to room temperature and stirred for 2 h. The resulting yellow solution was dried under vacuum to afford a pale yellow solid. The solid was extracted with pentane, and the filterate was concentrated and cooled to −45 °C. Yellow solid **5** was isolated by filtration, washing with cold pentane, and drying in vacuo.

**5a:** yellow powder (0.25 g, 86.21%). $^1$H NMR: $\delta$ 0.249 (s, 6H, Ti$Me$), 1.265 (m, 4H, SiC$H_2$), 1.553 (s, 18H, N$Bu^t$), 1.861 (m, 2H, CH$_2$C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 11.929 (Si$C$H$_2$), 22.474 (CH$_2$$C$H$_2$), 34.267 (Ti$Me$), 35.374 (NC$Me_3$), 65.983 (N$C$Me$_3$). Anal. for $C_{13}H_{30}N_2SiTi$: found C 53.88, H 10.52, N 9.72; calcd C 53.78, H 10.41, N 9.65.

**5b:** yellow powder (0.22 g, 72.37%). $^1$H NMR: $\delta$ 0.191 (s, 6H, Ti$Me$), 0.737 (m, 4H, SiC$H_2$), 1.520 (s, 18H, N$Bu^t$), 1.765 (m, 4H, CH$_2$C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 13.091 (Si$C$H$_2$), 25.931 (CH$_2$$C$H$_2$), 34.202 (Ti$Me$), 35.561 (NC$Me_3$), 65.938 (N$C$Me$_3$). Anal. for $C_{14}H_{32}N_2SiTi$: found C 55.33, H 10.71, N 9.10; calcd C 55.24, H 10.60, N 9.20.

**5c:** yellow powder (0.21 g, 66.04%). $^1$H NMR: $\delta$ 0.147 (s, 6H, Ti$Me$), 0.928 (m, 4H, SiC$H_2$), 1.484 (m, 2H, CH$_2$CH$_2$C$H_2$), 1.546 (s, 18H, N$Bu^t$), 1.884 (m, 4H, CH$_2$C$H_2$). $^{13}$C{$^1$H} NMR: $\delta$ 18.703 (Si$C$H$_2$), 26.083 (CH$_2$CH$_2$$C$H$_2$), 30.617 (CH$_2$$C$H$_2$), 34.025 (Ti$Me$), 34.742 (NC$Me_3$), 65.816 (N$C$Me$_3$). Anal. for $C_{15}H_{34}N_2SiTi$: found C 56.65, H 10.83, N 8.91; calcd C 56.58, H 10.76, N 8.80.

**5d:** yellow powder (0.26 g, 86.09%). $^1$H NMR: $\delta$ 0.247 (s, 6H, Ti$Me$), 1.294 (m, 4H, SiC$H_2$), 1.496 (s, 18H, N$Bu^t$), 6.062 (m, 2H, ═C$H$). $^{13}$C{$^1$H} NMR: $\delta$ 17.322 (Si$C$H$_2$), 31.344 (Ti$Me$), 34.449 (NC$Me_3$), 65.801 (N$C$Me$_3$), 130.931 (═$C$H$_2$). Anal. for $C_{14}H_{30}N_2SiTi$: found C 55.72, H 10.14, N 9.10; calcd C 55.61, H 10.00, N 9.26.

**Polymerization of Ethylene.** In a glovebox, a 100 mL Schlenk tube was charged with the catalyst together with MAO and hexane. Typically, each solid catalyst (10 $\mu$mol) was added to a MAO (0.269 g, 10.0 mmol) solution in toluene (2.6 mL). The mixture was stirred at 40 °C for 30 min. Ethylene gas was then allowed into the tube, and its pressure was maintained continuously at 1 atm by means of bubbling. The polymerization was quenched by stopping the ethylene supply and subsequent addition of a methanolic solution of 1 M HCl. The white precipitate was filtered and washed with an aqueous solution of 1 M HCl, copious methanol, and acetone. The resulting powder was finally dried in an oven at 80 °C for 12 h.

**Crystal Structure Determination.** Crystals of **3** were obtained from toluene, sealed in glass capillaries under argon, and mounted on the diffractometer. Data were collected and corrected for Lorentz and polarization effects. Each structure was solved by the application of direct methods using the SHELXS-96 program[22a] and least-squares refinement using SHELXL-97.[22b] After anisotropic refinement of all non-H atoms, several H atom positions could be located in difference Fourier maps. These were refined isotropically while the remaining H atoms were calculated in idealized positions and included into the refinement with fixed atomic contributions. Further detailed information is listed in Table 1.

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**Supporting Information Available:** Crystallographic data (excluding structure factors) for structures **3a**−**d** reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148326 (**3c**), -148327 (**3b**), -148328 (**3a**), and -148329 (**3d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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