A Versatile Synthetic Route for Cyclopentadienyl–Amido Titanium(IV) Compounds. NMR Spectroscopy Study and X-ray Molecular Structure of [Ti{η⁵-C₅H₄SiMe₂NMe(CH₂)₂-η-NMe}Cl₂]

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The reaction of the chlorosilyl-substituted cyclopentadienyltitanium compound [Ti(η^5-C$_5$H$_4$-SiMe$_2$Cl)Cl$_3$] with N,N-dimethylethylenediamine in the presence of 2 equiv of NEt$_3$ gave a mixture of two complexes, [Ti{η^5-C$_5$H$_4$SiMe$_2$NMe(CH$_2$)$_2$-η-NMe}Cl$_2$] (**1**) and [Ti{η^5-C$_5$H$_4$SiMe$_2$-η-N(CH$_2$)$_2$-η-NHMe}Cl$_2$] (**2**), in a molar ratio of 3:1. However, a similar reaction with N-methylethylenediamine afforded complex **2** regiospecifically. The dialkyl derivatives [Ti-{η^5-C$_5$H$_4$SiMe$_2$NMe(CH$_2$)$_2$-η-NMe}R$_2$] (R = Me (**3**), CH$_2$Ph (**4**)) were prepared by reacting the dichloride complex **1** with 2 equiv of MgClMe or 1 equiv of Mg(CH$_2$Ph)$_2$·2THF, respectively. The analogous reaction with LiNMe$_2$ afforded the diamido derivative [Ti{η^5-C$_5$H$_4$SiMe$_2$NMe(CH$_2$)$_2$-η-NMe}(NMe$_2$)$_2$] (**5**) in high yield. Complex **1** reacts with dry CO$_2$ via insertion of a molecule of CO$_2$ into each of the Ti–N and Si–N bonds to yield the dicarbamate compound [Ti{(η^5-C$_5$H$_4$SiMe$_2$OC(O)NMe(CH$_2$)$_2$NMe(η^2-CO$_2$)}Cl$_2$] (**6**), in which the carbamate groups are bound in η^2- and η^1-fashion. Thermal decomposition of complex **6** afforded the known oxo derivatives [Ti{μ-(η^5-C$_5$H$_4$SiMe$_2$-η-O)}Cl$_2$]$_2$ and [(TiCl$_2$)$_2$(μ-O)-[μ-{(η^5-C$_5$H$_4$SiMe$_2$)$_2$-(μ-O)}] with elimination of CO$_2$ and 1,3-dimethyl-2-imidazolidinone. The conformational interconversion of **1** and **6** and the reversible coordination of the terminal "NHMe" group to the metal center in **2** were studied in solution by DNMR spectroscopy. The crystal structure of **1** was determined by X-ray diffraction methods.

Introduction

Early-transition-metal complexes have provided important classes of catalysts for α-olefin polymerization[1] and related processes.[2] The most extensively investigated compounds are those based on group 4 bent metallocenes (MCp$_2$X$_2$), which upon activation with suitable coactivators, typically methylaluminoxane (MAO), offer highly active catalysts for olefin polymerization. Modification of the ligand environment at the metal centers (i.e., by linking cyclopentadienyl ligands with an intraannular bridge or by introducing sterically bulky substituents onto the Cp rings) allowed not only

the activity to be optimized but also stereochemical control over polymer composition and structure. Over the last few years, ligand design has played a key role in developing new homogeneous Ziegler–Natta catalysts,[3] with increasing interest in industrial and academic laboratories, and new ligand systems for both early[4] and late[5] transition metals.

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In this context, bifunctional cyclopentadienyl ligands containing an appended donor substituent are attracting considerable attention due to their ability to modify steric congestion and Lewis acidity at the electrophilic metal center.[6,7] Several synthetic strategies have been used to prepare these derivatives. The most usual are metathesis[6e−g] reactions of the dilithium salts or Grignard reagents of $[(C_5R_4)LNR']^{2-}$ dianions with the appropriate metal halide, thermally induced amine[6h,8] or alkane[6i,9] elimination in the reactions of the neutral ligand with amido or alkyl precursors, and the HCl elimination from metal chlorides in the presence of a base.[10] Green[11a] and Teuben[11b] employed the desilylation reaction for the preparation of *ansa*-monocyclopentadienyl−alkoxo and −imido complexes, respectively. In all of these examples the N or O functionalities are incorporated directly into the backbone of the cyclopentadienyl substituent prior to metal coordination. Recently we reported[12] an alternative approach which entails assembling the ligand framework at the metal coordination sphere.

As part of our current research on such bidentate ligands, we have investigated the reaction of the chlorodimethylsilyl-substituted monocyclopentadienyltitanium $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ complex[13] with different diamines to expand this synthetic methodology. It has allowed us to prepare different types of complexes bearing chelating cyclopentadienyl−amido ligands. Here, we report a simple, efficient, and versatile entry into the chemistry of titanium complexes with cyclopentadienyl−silyl−amido functions bridged by a spacer of varying length. The derivatization of the dichloride complex to new dialkyl and diamido derivatives, $[Ti\{\eta^5\text{-}C_5H_4SiMe_2NMe(CH_2)_2\text{-}\eta\text{-}NMe\}R_2]$, has been studied.

Currently, there is a substantial interest in exploring the use of carbon dioxide as a renewable source of carbon for producing chemicals in metal-mediated catalytic processes.[14] This moved us to study the reactivity of **1** with CO_2.

Results and Discussion

The reaction of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$[13] with diamines provides a useful synthetic route to various cyclopentadienyl−silyl−amido titanium derivatives. Its reaction with 1 equiv of the diamine $NHMe(CH_2)_2NHMe$ in toluene at −78 °C in the presence of 2 equiv of NEt_3 gave a mixture of two different amido derivatives, $[Ti\{\eta^5\text{-}C_5H_4SiMe_2NMe(CH_2)_2\text{-}\eta\text{-}NMe\}Cl_2]$ (**1**) and $[Ti\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_2\text{-}\eta\text{-}NHMe\}Cl_2]$ (**2**), in a spectroscopic molar ratio of ca. 3:1 with elimination of $[NEt_3H]Cl$ and CH_3Cl (Scheme 1). The reaction mixture was separated by repeated extractions into *n*-hexane, and compounds **1** and **2** were obtained as red (53% yield) and yellow (5% yield) pure solids, respectively. Complex **2** is fairly insoluble in hexane, whereas compound **1** is slightly soluble.

In an effort to find the working conditions that would cause the process to be regiospecific, an extensive series of experiments using various reaction conditions were carried out, but the attempts were unsuccessful. However, when the reaction was performed using a second equivalent of the diamine, instead of NEt_3, its lower basicity made the ratio of final products change to 1:1.

Alternatively, compound **2** could be prepared in good yield (83%) as an analytically pure product by treatment of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ with an equimolar amount of the diamine $NH_2(CH_2)_2NHMe$ in the presence of 2 equiv of NEt_3 in toluene at room temperature (Scheme 1).

These results do not distinguish which bond, Ti−Cl or Si−Cl, reacts preferentially in the aminolysis reaction, which has been reported[12a,c] to be unselective for reactions of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ with monoamines NH_2R. Two different pathways may be used to explain the behavior observed for the reactions with diamines (Scheme 1). Preferential aminolysis of one of the Ti−Cl bonds (pathway i) would give an amido compound, A, which would then be transformed either into compound **2** by aminolysis of the Si−Cl bond with elimination of X−Cl (X = H, Me) and coordination of the terminal amino group to the titanium center or into compound **1** by aminolysis of the Si−Cl bond by reaction with the terminal amino group. Alternatively, preferential aminolysis of the Si−Cl bond (pathway ii) would give compound B, which may then be converted either into **2** by aminolysis of the Ti−Cl bond and elimination of X−Cl and coordination of the terminal amino group or into **1** by further aminolysis of the Ti−Cl bond by reaction with the terminal amino group.

For either of these two pathways, regiospecific double deprotonation of the NH_2 group when *N*-methylethylenediamine is used is confirmed by the regiospecific formation of compound **2**. Formation of **2** in the reaction

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Scheme 1
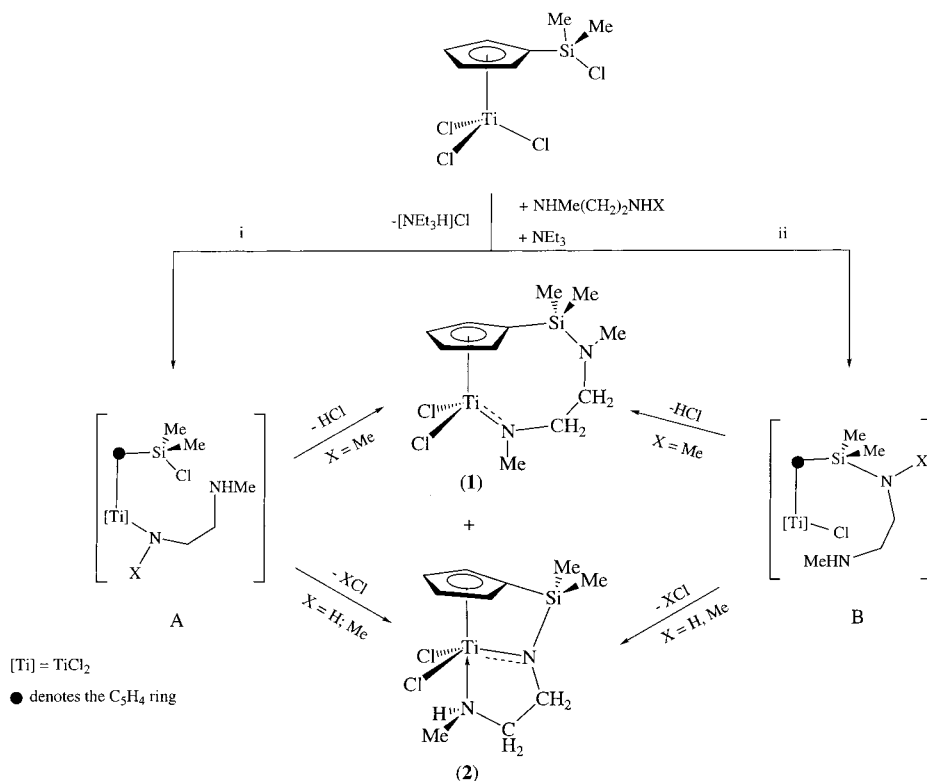
with *N,N*-dimethylethylenediamine involves an unexpected dehalomethylation with elimination of MeCl, which is much more unfavorable and leads to a very low yield of compound **2**. The aminolysis of the terminal amino group is the most favorable process in this case. However, when X = H, preferential aminolysis takes place at the central N, leading to the η^5-cyclopentadienylsilyl-η-amidoethylen-η-amino compound **2**.

A few examples of CH$_3$Cl elimination have been reported to give Cp–alkoxo derivatives, always in the presence of an activator or under thermal conditions.[15] However, in our case the elimination of methyl chloride occurred at room temperature.

Compounds **1** and **2** are very air sensitive but thermally stable. Both complexes are soluble in aromatic and chlorinated solvents but poorly soluble in aliphatic hydrocarbons. Spectroscopic and analytical data (see the Experimental Section) are in agreement with the proposed structures. The IR spectrum of compound **2** shows a ν(N–H) sharp absorption band of medium intensity at 3228 cm^{-1}.[8a] The molecular structure of **1** was determined by X-ray diffraction methods.

The ^{1}H NMR spectra (CDCl$_3$) of complexes **1** and **2** at 25 °C are consistent with C_s symmetry, and show AA'BB' spin systems for the C$_5$H$_4$ ring protons and one signal for the SiMe$_2$ resonances. However, the spectrum of **1** shows two singlets (δ 3.97 and 2.55) for the two nonequivalent methyl groups attached to the two different nitrogen atoms and one AA'BB' spin system for

the methylene protons of the "N(CH_2)$_2$N" fragment, while that of compound **2** shows an AA'BB'K spin system, two multiplets (δ 3.29 and 3.62) and a broad signal (δ 3.94), for the "NCH_2CH_2NH" moiety, and one doublet (δ 2.92, 3H, ^3J = 6.1 Hz) for the unique methyl group, NH*Me*, coupled with N–H. The chemical shifts of N*H*Me protons differ significantly from those found for the free diamine (δ 2.40 NMe, 1.80–1.90 NH), indicating some interaction between the titanium atom and the amino nitrogen.

The ^{13}C{^{1}H} NMR spectrum (CD$_2$Cl$_2$) at room temperature of **1** shows two signals at δ 71.0 and 51.3 assigned to the C(1) and C(2) atoms, respectively, for the "SiMe$_2$NC(1)H$_2$$C$(2)H$_2$NMeTi" bridged unit. However, in the ^{13}C{^{1}H} NMR spectrum (CD$_2$Cl$_2$) of **2** the resonances for the CH$_3$ and the C(1) (δ 39.1 and 56.1) of the "NC(1)H$_2$C(2)H$_2$NH*Me*" moiety have values similar to those found for the free diamine MeNHCH$_2$CH$_2$-NHMe (δ 36.4 and 52.0).[16] The pronounced deshielding for the "TiNCH$_2$" resonance ($\Delta\delta$ 14.9 ppm) in **1** with respect to **2** is in agreement with a larger π-donor character of the Ti–N amido interaction in **1** than in **2**.[17] This feature is also confirmed by the solid-state structure studied by X-ray diffraction methods for complex **1**. Other important spectroscopic differences between **1** and **2** are the cyclopentadienyl *ipso*-carbon atom resonance, the methyl silyl carbon atom signals, and the ^{29}Si resonance, which are significantly shielded in **2** (δ 111.2, −3.2, and −13.2, respectively) with respect to **1** (δ 127.4, −1.6, and −4.5, respectively). These data demonstrate a cyclopentadienyl electron density distribution in complex **1** different from that in **2**, resulting

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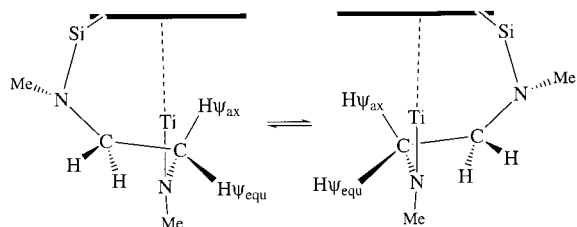
Figure 1. Interconversion between the two enantiomeric conformations observed for compound **1** in solution.

from a different coordination mode of the C_5H_4 ring to the metal center and two different $p\pi-d\pi$ interactions between nitrogen and titanium. Complex **1** exhibits a strain-free Cp−amido chelating disposition with η^5-C_5H_4 coordination, whereas a certain contribution from η^3:η^2-C_5H_4 coordination could be proposed for **2**.

The asymmetric solid-state structure of **1** (see the X-ray study) contrasts with the C_s symmetry observed in solution at room temperature and suggests that this compound exhibits dynamic behavior in solution. At 158 K the ^1H NMR spectrum of **1** in CD_2Cl_2 shows two signals (δ 0.23 and 0.42) for the SiMe_2, four resonances [δ 2.76, 2.87, 3.00, 5.04 (1H each)] for the methylene groups, and three signals [δ 6.60 (2H), 6.64 (1H), 6.73 (1H)] for the cyclopentadienyl protons. The difference of the chemical shifts between the two TiNCH_2 protons ($\Delta\delta \approx 2$) may be explained by a respective "pseudoaxial" and "pseudoequatorial" disposition.[18] The observed fluxional behavior of **1** involves interconversion between the two enantiomeric conformations shown in Figure 1.

The kinetic parameters of this process [log A = 13.1 ± 0.4, E_a =8.3 ± 0.35 kcal/mol (r = 0.996, $F_{6.2.4}$ = 524.8), $\Delta H^{\ddagger}$ = 7.94 ± 0.35 kcal/mol, $\Delta S^{\ddagger}$ = 0.4 ± 2.0 eu (r = 0.996, $F_{6.2.4}$ = 483.9), $\Delta G^{\ddagger,298K}$ = 7.8 kcal/mol], calculated by full line shape analysis for the mutual exchange of the SiMe_2 resonances, are in agreement with an intramolecular process and indicate the same polarization in the ground and transition states of **1**.

The ^1H NMR spectrum of **2** at 25 °C shows some broad signals (CH_2NH and BB′ part of C_5H_4), indicating possible fluxional behavior with the relative rate within the NMR time scale. At 195 K the ^1H NMR spectrum indicates the loss of the C_s symmetry, as deduced by the presence of two signals for the SiMe_2, one AA′BC spin system for the cyclopentadienyl protons, and one ABCD spin system for the methylene protons of the backbone ligand. The value of the "BC" proton−proton coupling constant (J = 3.2 Hz) is consistent with the "W" disposition of the α-protons in planar fragments and corresponds to $^3J_{HH}$.[19] The observed AA′BC spin system results from very fast exchange, on the NMR time scale, between AA′ positions and slow exchange of the BC nucleus.

This process may be described as an exchange between two enantiomeric C_1 ground states (Figure 2). The dissociation of the terminal amino group takes place in the transition state. The observed C_1 symmetry of **2** at low temperature may be explained by coordination of
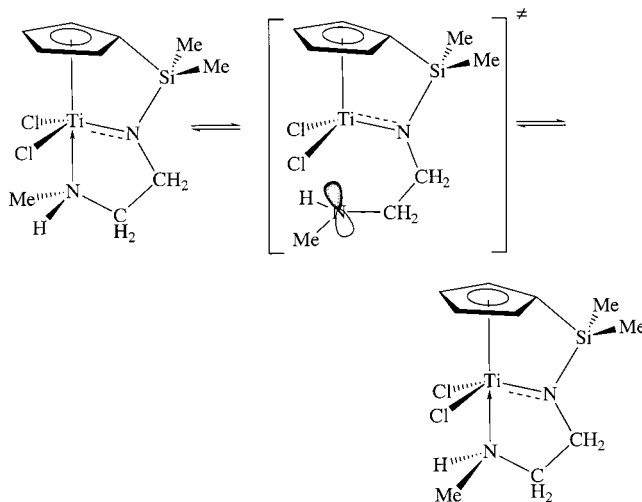
Figure 2. Exchange between the two enantiomeric C_1 ground states observed for compound **2** in solution.
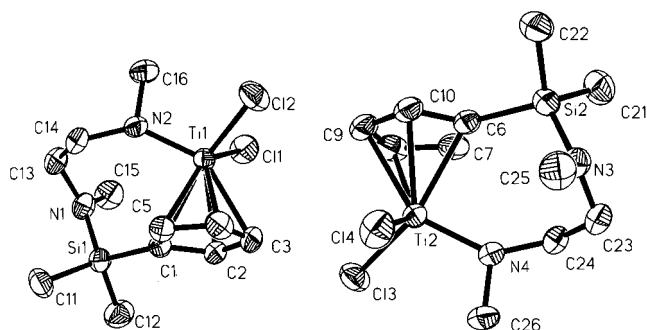
Figure 3. ORTEP drawing of the molecular structure of compound **1** together with the atomic labeling scheme.

the lone electron pair of the amino nitrogen to the titanium center, which prevents inversion of the lone electron pair. Similar dispositions have been reported for half-sandwich zirconium complexes, derived from X-ray crystallographic and spectroscopic data.[6g] However, this is one of the few cases of titanium half-sandwich complexes for which an intramolecular coordinating amino function is present.[20]

The kinetic parameters of this process [log A = 13.6 ± 0.3, E_a = 14.0 ± 0.3 kcal/mol (r = 0.999, $F_{7.2.5}$ = 1811.4), $\Delta H^{\ddagger}$ = 13.6 ± 0.3 kcal/mol, $\Delta S^{\ddagger}$ = 2.2 ± 1.3 eu (r = 0.999, $F_{7.2.5}$ = 1747.9), $\Delta G^{\ddagger,298K}$ = 12.9 kcal/mol, $\Delta G^{\ddagger,267K}_{calcd}$ = 13.0 kcal/mol, $\Delta G^{\ddagger,267K}_{exptl}$ = 12.1 kcal/mol], calculated for the exchange of an AB spin system, are in accord with an intramolecular process and nonpolarized transition state. The free Gibbs energy value ($\Delta G^{\ddagger,298K}$ = 12.9 kcal/mol) is in agreement with the "activation barrier" ($\Delta G^{\ddagger,280K}$ = 13.1 kcal/mol) found for similar zirconium complexes.[6g]

Crystal Structure of [Ti{η^5-C_5H_4SiMe$_2$NMe(CH$_2$)$_2$-η-NMe}Cl$_2$] (1). The structure of complex **1** was confirmed by a single-crystal X-ray diffraction study. Figure 3 shows an ORTEP view of the structure along with the atom-labeling scheme. Selected bond distances and bond angles with their standard deviations are listed in Table 1. The unit cell contains two independent crystal-

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Table 1. Bond Lengths (Å) and Angles (deg) for 1[a]

molecule 1		molecule 2	
Ti(1)−N(2)	1.870(3)	Ti(2)−N(4)	1.864(3)
Ti(1)−Cl(1)	2.2734(12)	Ti(2)−Cl(4)	2.2855(13)
Ti(1)−Cl(2)	2.3001(13)	Ti(2)−Cl(3)	2.2926(13)
Ti(1)−C(3)	2.343(4)	Ti(2)−C(7)	2.339(4)
Ti(1)−C(2)	2.347(4)	Ti(2)−C(9)	2.350(4)
Ti(1)−C(5)	2.362(4)	Ti(2)−C(10)	2.351(4)
Ti(1)−C(4)	2.368(4)	Ti(2)−C(8)	2.359(4)
Ti(1)−C(1)	2.369(4)	Ti(2)−C(6)	2.367(4)
Si(1)−N(1)	1.714(3)	Si(2)−N(3)	1.718(3)
Si(1)−C(12)	1.849(4)	Si(2)−C(22)	1.853(4)
Si(1)−C(11)	1.859(4)	Si(2)−C(21)	1.873(4)
Si(1)−C(1)	1.886(4)	Si(2)−C(6)	1.888(4)
N(1)−C(15)	1.454(5)	N(3)−C(25)	1.450(5)
N(1)−C(13)	1.456(5)	N(3)−C(23)	1.462(5)
N(2)−C(14)	1.468(5)	N(4)−C(24)	1.460(5)
N(2)−C(16)	1.487(5)	N(4)−C(26)	1.480(5)
C(1)−C(5)	1.421(5)	C(6)−C(7)	1.415(5)
C(1)−C(2)	1.425(5)	C(6)−C(10)	1.428(5)
C(2)−C(3)	1.400(5)	C(7)−C(8)	1.411(6)
C(3)−C(4)	1.394(6)	C(8)−C(9)	1.382(6)
C(4)−C(5)	1.404(5)	C(9)−C(10)	1.399(5)
C(13)−C(14)	1.522(5)	C(23)−C(24)	1.529(6)
Ti(1)−Cp(1)	2.030	Ti(2)−Cp(2)	2.026
N(2)−Ti(1)−Cl(1)	105.27(10)	N(4)−Ti(2)−Cl(4)	104.59(10)
N(2)−Ti(1)−Cl(2)	103.66(10)	N(4)−Ti(2)−Cl(3)	104.48(10)
Cl(1)−Ti(1)−Cl(2)	101.47(5)	Cl(4)−Ti(2)−Cl(3)	102.34(5)
N(1)−Si(1)−C(12)	109.7(2)	N(3)−Si(2)−C(22)	110.97(19)
N(1)−Si(1)−C(11)	110.63(19)	N(3)−Si(2)−C(21)	110.1(2)
N(1)−Si(1)−C(1)	111.98(16)	N(3)−Si(2)−C(6)	111.62(16)
C(15)−N(1)−C(13)	114.0(3)	C(25)−N(3)−C(23)	115.8(4)
C(15)−N(1)−Si(1)	122.9(3)	C(25)−N(3)−Si(2)	120.8(3)
C(13)−N(1)−Si(1)	120.1(3)	C(23)−N(3)−Si(2)	119.4(3)
C(14)−N(2)−C(16)	111.7(3)	C(24)−N(4)−C(26)	112.2(3)
C(14)−N(2)−Ti(1)	139.4(2)	C(24)−N(4)−Ti(2)	139.9(3)
C(16)−N(2)−Ti(1)	108.6(3)	C(26)−N(4)−Ti(2)	107.7(2)
N(2)−Ti(1)−Cp(1)	114.2	Cl(3)−Ti(2)−Cp(2)	113.9
Cl(1)−Ti(1)−Cp(1)	115.4	Cl(4)−Ti(2)−Cp(2)	116.2
Cl(2)−Ti(1)−Cp(1)	115.2	N(4)−Ti(2)−Cp(2)	113.8

[a] Cp(1) is the centroid of C(1),C(2),C(3),C(4),C(5), and Cp(2) is the centroid of C(6),C(7),C(8),C(9),C(10).

4A　　**4B**　　**4C**

The dotted line depicts the plane bisecting the Cl-Ti-Cl angle

Figure 4. Effect of spacer length on the dispositions found for the titanium−silicon backbone.

spacer and the sp^2 hybridization of the N(1) atom make this metallacycle exhibit a conformation different from those shown for the bidentate Cp−amido complexes reported to date (Figure 4). In constrained geometry compounds (one member spacer) the *ipso*-carbon of the cyclopentadienyl ligand and the atoms of the metallacycle are in the plane bisecting the Cl−Ti−Cl angle (Figure 4A). In {Ti[η^5-C_5H_4(CH_2)$_3$NPr^i]Cl_2}[10] and {Ti-[η^5-C_5H_4(CH_2)$_3$O]Cl_2}[8a] (three member spacers) the atoms of the side chain displayed a zigzag pattern with respect to this plane (Figure 4B). In contrast, for **1** the linkage (four members) between the cyclopentadienyl and amido functions adopts a helical conformation around the Cp−Ti bond, locating the SiMe$_2$ moiety 1.946(1) Å [1.946(1) Å] away from the plane defined by Cp−Ti−N (Figure 4C) to minimize the strain in the metallacycle.

The C−C distances in the cyclopentadienyl ring (1.393(6)−1.424(5) Å) and the Cp−Ti distance 2.03 Å [2.026 Å] are similar to those found for the series of unconstrained complexes [Ti(C_5H_4X)(NRR′)Cl_2] (X = H, R = R′ = *i*-Pr; X = H, R = H, R′ = *t*-Bu; X = Me, R = H, R′ = *t*-Bu).[21c,d] These features reflect that the length of the backbone leaves sufficient flexibility in the system to convey η^5-bonding character to the C_5H_4 ring.

The short Ti−N(2) bond distance 1.870(3) Å [1.864(2) Å], in the range 1.80−1.90 Å,[21c,d,22] suggests the pπ−dπ bonding between Ti and the amido ligands, and the planar geometry of the nitrogen atom indicates sp^2 hybridization of the N(2) atom with the out-of-plane lone pair, giving an N(pπ)−Ti(dπ) interaction. The strain-free chelated ligand allows optimal overlap between the nitrogen pπ orbital and the vacant titanium dπ orbital, increasing the Ti−N double-bond character with respect to the "constrained geometry" systems.

The silicon atom is slightly pushed, 0.06 Å [0.10 Å] out of the Cp ring plane, away from the metal center, in contrast to the location observed in constrained geometry compounds in which the chelating ligand causes the Si atom to be displaced toward the metal center (0.85−0.95 Å).[6g] The Si−N distance of 1.714(3) Å [1.717(3) Å] and the essentially trigonal-planar environment (sum of the angles about the nitrogen atom ca. 355°) at the nitrogen atom indicate an important degree of double-bond character in the Si−N bond. The distance is comparable to those reported for different

lographic units. Since both molecules show practically identical structural features, only one is described in detail (data for the second are given in square brackets). In the solid state **1** is a chiral compound for which two independent enantiomers are present.

The compound is monomeric with a pseudo-three-legged piano-stool coordination geometry around the titanium atom, as expected for complexes of the type TiCp(X)Cl_2.[21] The Cp−Ti−N(2) angle, where Cp represents the centroid of the C_5H_4 ring, at 114.2° [113.9°] is significantly larger, ca. 10°, than the corresponding angle in the constrained *ansa*-monocyclopentadienyl−silyl−amido complexes [Ti{(η^5-C_5R_4SiMe$_2$-η-NR′}Cl_2].[6h] This result suggests that increasing the length of the spacer leaves a less open metal center as reflected in the Cl−Ti−Cl angle value 101.4° [102.34(5)°], which is in the normal range of the values observed for unconstrained monocyclopentadienyl−amido derivatives.[21c,d]

If the centroid of the cyclopentadienyl ring is considered as a single coordination site, the central core of **1** appears as a seven-membered (Cp−Si−N−C−C−N−Ti) metallacycle. The length of the "Si−N(1)−CH$_2$–CH$_2$"

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Scheme 2

R = Me (**3**), CH₂Ph (**4**), NMe₂ (**5**)
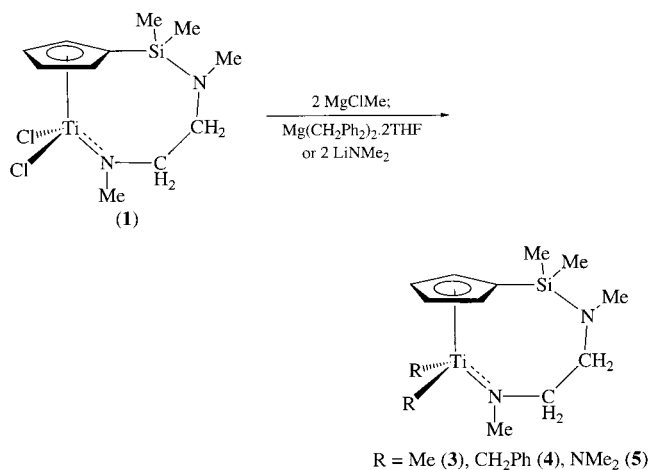
silylamines[23] and for the niobium complex [Nb(η^5-C₅H₄-SiMe₂NH^{t}Bu)Cl₂(N^{t}Bu)].[12b]

All of these structural results lead to the conclusion that the length and flexibility of the chain provide considerable "freedom", more akin to unlinked monocyclopentadienyl complexes than to cyclopentadienyl−silyl−amido constrained geometry complexes.

Synthesis of Alkyl and Amido Complexes. The dichloride derivative **1** was readily converted to the alkyl compounds [Ti{η^5-C₅H₄SiMe₂NMe(CH₂)₂-η-NMe}R₂], R = Me (**3**), R = CH₂Ph (**4**), or the diamido complex [Ti-{η^5-C₅H₄SiMe₂NMe(CH₂)₂-η-NMe}(NMe₂)₂] (**5**) by a salt metathesis route. Complex **1** reacted with a stoichiometric amount of the appropriate Grignard reagent, MgClMe or Mg(CH₂Ph)₂·2THF, or the lithium salt LiNMe₂ in toluene at −78 °C to give the corresponding dialkyl or diamido derivatives, which have been fully characterized (Scheme 2). Attempts to prepare the monoalkyl complexes by reaction of **1** with 1 equiv of the alkylating agent were unsuccessful, always leading to mixtures of compounds with various degrees of substitution. Reactions of **2** with the same alkylating agents were not straightforward and afforded a mixture of unidentified products.

Compounds **3**−**5** are air and moisture sensitive and very soluble in the usual hydrocarbon solvents. However, **4** and **5** are thermally more stable than **3** and can be stored for weeks at ambient conditions without appreciable decomposition. By contrast, the methyl derivative is light sensitive even in the solid state; hence, it had to be stored in the dark at low temperature.

The ^{1}H NMR spectra (C₆D₆ or CDCl₃) at room temperature of **3**−**5** show one signal for the Si*Me₂* and one AA′BB′ spin system for the C₅*H₄* ring protons along with the expected resonances for the R groups. One AA′BB′ spin system for the methylene and two singlets for the methyl protons of the "N(Me)CH₂CH₂N(Me)" moiety are also observed. The methylene protons of the benzyl groups in complex **4** exhibit an AB spin system ($^2J = 11.4$ Hz) due to the prochiral character of the metal center, whereas the observation of four equivalent NMe groups for the amido ligands in **5** is consistent with fast rotation around the Ti−N bond. A more important

Scheme 3
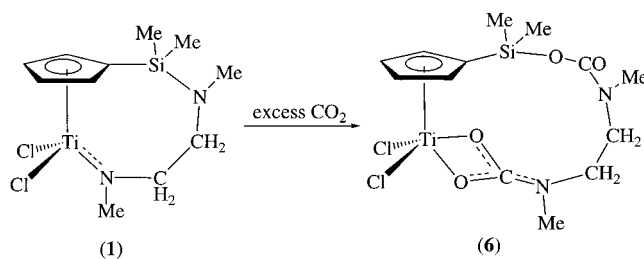
feature in the ^{13}C NMR spectra of these derivatives is shielding of the "TiN*CH₂*" resonances with respect to that observed for **1** [$\Delta\delta = \delta(\mathbf{1}) - \delta(\mathbf{4,5,6}) \approx 10$], depending on the electron properties of the R groups.

Reaction of [Ti{η^5-C₅H₄SiMe₂NMe(CH₂)₂-η-NMe}-Cl₂] (1) with CO₂. A solution of [Ti{η^5-C₅H₄SiMe₂NMe-(CH₂)₂-η-NMe}Cl₂] in chloroform at −78 °C was saturated with CO₂. When the reaction mixture was warmed to room temperature, the insertion of carbon dioxide into the Si−N and Ti−N bonds took place to give the corresponding dicarbamate derivative [Ti{η^5-C₅H₄Si-Me₂OC(O)NMe(CH₂)₂NMe-η^2-OCO}Cl₂] (**6**) (Scheme 3), which was isolated and analytically and spectroscopically characterized.

Compound **6** is stable at room temperature. However, when a solution of **6** in benzene-d_6 was heated at 70 °C for 2 days, elimination of 1,3-dimethyl-2-imidazolidinone and CO₂ was observed with formation of a mixture containing the two well-known dinuclear oxo derivatives [Ti{μ-(SiMe₂O-η^5-C₅H₄)Cl₂}]₂[13] and [(TiCl₂)₂(μ-O){μ-(η^5-C₅H₄)₂−SiMe₂O}][24] as the major and minor components, respectively. Analogous reactions with CO₂ have been reported for amide derivatives of titanium,[12a] zirconium,[25] germanium, and tin compounds.[26] However, although the insertion of CO₂ into the M−N bond has been proposed as the first step in this process, such carbamate intermediates have not been observed.

Under these conditions the isomerization process of [Ti{μ-(SiMe₂O-η^5-C₅H₄)Cl₂}]₂ into [(TiCl₂)₂(μ-O){μ-(η^5-C₅H₄)₂SiMe₂O}] has to be ruled out since this transformation requires heating at temperatures higher than 130 °C. A possible explanation for this process is proposed in Scheme 4.

Thermolysis of **6** results in the elimination of the "−C(O)−NMe−CH₂−CH₂−NMe−C(O)−O−", which rearranges to give 1,3-dimethyl-2-imidazolidinone, identified by comparison with a commercial sample, with evolution of CO₂. This elimination may take place by an intermolecular reaction, with the possible formation of three different types of intermediates, A, B, and C, depending on the relative orientation of the two approaching molecular units. Similar dinuclear species containing bridging siloxy groups are known as stable compounds characterized by X-ray diffraction methods for zirconium.[12a,25] Elimination of CO₂ and the organic substance takes place for A by cleavage and formation of two Ti−O bonds, whereas from B two Si−O bonds are cleaved and

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(26) (a) Sita, L. R.; Babcock, J. R.; Xi, R. *J. Am. Chem. Soc.* **1996**, *118*, 10912. (b) Babcock, J. R.; Liable-Sands, L.; Rheingold, A. L.; Sita, L. R. *Organometallics* **1999**, *18*, 4437. (c) Babcock, J. R.; Incarvito, Ch.; Rheingold, A. L.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 5729.

Scheme 4
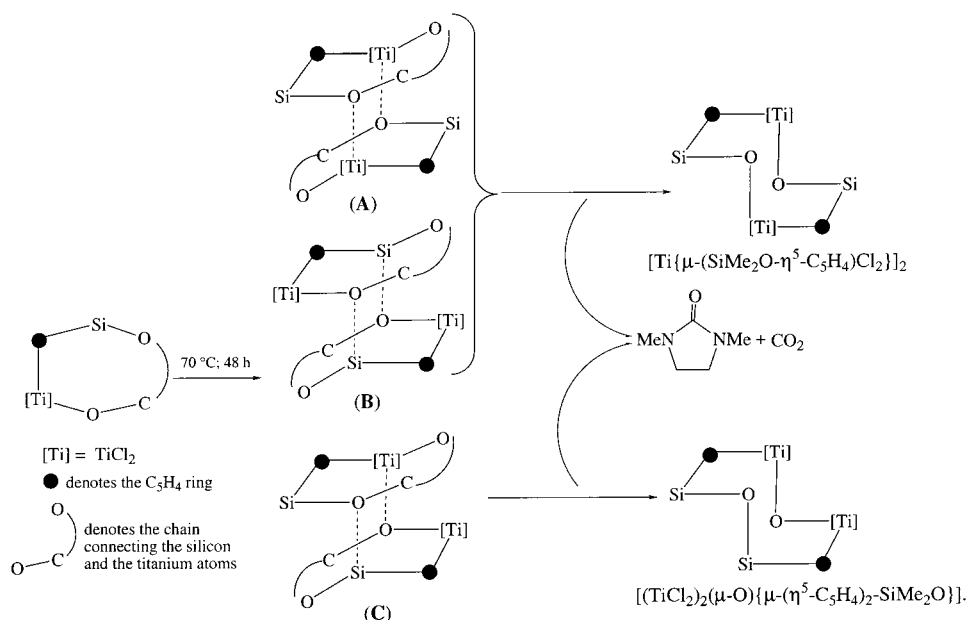
two Si−O bonds are formed to give the same final oxo compound with two Si−O−Ti bridges [Ti{μ-(SiMe$_2$O-η^5-C$_5$H$_4$)Cl$_2$}]$_2$. However, when the orientation is that represented by C, elimination occurs by cleavage and formation of one Si−O and one Ti−O bond, leading in this case to the final oxo compound, which contains one Si−O−Si and one Ti−O−Ti bridge [(TiCl$_2$)$_2$(μ-O){μ-(η^5-C$_5$H$_4$)$_2$SiMe$_2$O}]. Formation of [Ti{μ-(SiMe$_2$O-η^5-C$_5$H$_4$)-Cl$_2$}]$_2$ as the major component may result from the kinetic control based on the steric hindrance of the bridging system.

The ^{1}H NMR spectrum of compound **6** (CDCl$_3$) at 25 °C exhibits one singlet for the Si*Me$_2$* (δ 0.54), one AA′BB′ spin system for the C$_5$H$_4$ protons (δ 6.98, 7.39), two narrow singlets for the N*Me* groups (δ 2.96, 2.98), and two very broad signals for the methylene protons. The most notable feature in the ^{13}C{^{1}H} NMR spectrum is the presence of two resonances at δ 163.9 and 154.6, corresponding to an η^2-carbamate TiO$_2$*C*N moiety and a monocoordinated carbamate SiO*C*(O)N ligand, respectively.[27] The pronounced deshielding of the Si*Me$_2$*−OC-(O)−N*Me* (0.14 and 0.43 ppm) and the shielding of Ti−O$_2$C−N*Me* (0.99 ppm) resonances with respect to those found in **1** and the small difference between the chemical shifts for the two N*Me* groups in **6** ($\Delta\delta$ = 0.02) compared with that observed for **1** ($\Delta\delta$ = 1.42) are consistent with our proposal.

The infrared spectrum shows two strong absorptions (1569 and 1668 cm^{-1}) in the 1560−1685 cm^{-1} region assigned to the O$_2$CN moiety, which also indicates the presence of both bidentate and monodentate carbamato ligands.[27,28]

Compound **6** shows dynamic behavior in solution. At 213 K the ^{1}H NMR spectrum displays two signals (δ

0.40 and 0.70) for Si*Me$_2$* and two ABCD spin systems for the C$_5$H$_4$ ring (δ 7.00, 7.02, 7.19, and 7.67) and for the "NC*H$_2$*C*H$_2$*N" protons (δ 2.95, 3.05, 3.87 and 4.53), indicating the loss of the C_s symmetry observed at room temperature. We propose that the fluxional behavior of **6** is similar to that observed in **1** and entails enantiomeric conformational metallacycle interconversion. The larger values of the activation parameters displayed for **6** in comparison with **1** are related to the increasing size of the cycle.[29]

The kinetic parameters calculated for the mutual exchange of Si*Me$_2$* resonances between 233 and 263 K [log A = 12.6 ± 0.25, E_a = 11.5 ± 0.3 kcal/mol (r = 0.9986, N = 6), $\Delta H^\ddagger$ = 11.05 ± 0.3 kcal/mol, $\Delta S^\ddagger$ = −2.4 ± 1.2 eu (r = 0.9986, N = 6), $\Delta G^\ddagger$ = 11.7 kcal/mol] are consistent with the intramolecular nature of the process, and the $\Delta S^\ddagger$ value is consistent with the same polarization in the ground- and transition-state species.

Concluding Remarks

The reaction of diamines with the chlorosilyl-substituted cyclopentadienyl compound [Ti(η^5-C$_5$H$_4$SiMe$_2$Cl)-Cl$_3$] in the presence of a base offers a versatile and convenient synthetic route for the preparation of different types of linked Cp−amido derivatives of titanium, the final compound depending on the nature of the groups on the nitrogen and the length of the carbonated chain bridging the two nitrogen atoms in the amine reagents.[30] The reaction of [Ti(η^5-C$_5$H$_4$SiMe$_2$Cl)Cl$_3$] with *N,N*′-dimethylethylenediamine yields a mixture containing mainly [Ti{η^5-C$_5$H$_4$SiMe$_2$NMe(CH$_2$)$_2$-η-NMe}-Cl$_2$] (**1**) with a substantial amount of [Ti{η^5:η-C$_5$H$_4$-SiMe$_2$N(CH$_2$)$_2$-η-NHMe}Cl$_2$] (**2**). In contrast, the corresponding reaction of [Ti(η^5-C$_5$H$_4$SiMe$_2$Cl)Cl$_3$] with *N*-methylethylenediamine specifically affords **2**. It is noteworthy that **1** is the compound with the longest spacer chelating Cp−amido ligand reported to date for titanium

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derivatives. We report here the first case of the formation of a titanamidacycle via elimination of CH_3Cl in very mild conditions.

The reaction of **1** with dried CO_2 allowed us to isolate the dicarbamate complex [Ti{η^5-$C_5H_4SiMe_2OC(O)NMe$-$(CH_2)_2NMe$-η^2-OCO}Cl_2] (**6**) in a high yield as an intermediate of the metathesis reaction between CO_2 and the nitrogen–group 4 metal bond. This compound decomposes thermally with elimination of carbon dioxide and 1,3-dimethyl-2-imidazolidinone, to give a mixture of two known oxo derivatives. We have been able to evaluate the kinetic parameters and study the dynamic behavior in solution for several of these complexes. Examples of such fluxional behavior for chelating cyclopentadienyl–amido group 4 derivatives have just been suggested.[6g]

Experimental Section

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox, model HE-63. The solvents were purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. NEt_3 (Aldrich) was distilled before use and stored over 4 Å molecular sieves. $NHMe(CH_2)_2NHMe$ (Aldrich), $NH_2(CH_2)_2$-$NHMe$ (Aldrich), $MgClMe$ (Aldrich), $LiNMe_2$ (Aldrich), and CO_2 (SEO) were purchased from commercial sources and used without further purification. [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3][13] and $Mg(CH_2Ph)_2$·$2THF$[31] were prepared by known procedures. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. The analytical values found deviated (>1% (C)) due to their air sensitivity and difficulties in the manipulation of samples. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrophotometer using CsI pellets; only selected IR data are reported. NMR spectra, measured at +25 or −60 °C, were recorded on a Varian Unity 500 Plus spectrometer, and chemical shifts are referenced to the residual proton and carbon signals of the solvent. The NMR data were calculated using gNMR and SPSS 9.0 programs.

Synthesis of [Ti{η^5-$C_5H_4SiMe_2NMe(CH_2)_2$-η-NMe}Cl_2] (1). A solution of $NHMe(CH_2)_2NHMe$ (0.35 mL, 3.2 mmol) and NEt_3 (0.9 mL, 6.5 mmol) in 20 mL of toluene was added at ambient temperature to a solution of Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (1 g, 3.2 mmol) in 30 mL of the same solvent. The reaction mixture was stirred for 2 h. The color changed instantaneously from yellow to dark red, and a large quantity of white solid precipitated, which was collected by filtration. After toluene removal, the residue was extracted with hexane (5 × 30 mL) and cooled overnight at −30 °C to give a small amount (5 × 10^{-2}, 5%) of yellow crystalline solid characterized as **2**. Concentration and cooling to −30 °C of the resultant solution affords **1** as a red solid (0.55 g, 53%). Recrystallization from toluene/hexane gave **1** as a red crystalline substance. Anal. Calcd for $C_{11}H_{20}Cl_2N_2SiTi$: C, 40.38; H, 6.16; N, 8.56. Found: C, 39.16; H, 6.50; N, 7.61. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.40 (s, 6H, $SiMe_2$), 2.55 (s, 3H, $SiNMe$), 2.87, 4.04 (m, 2 × 2H, CH_2), 3.97 (s, 3H, $TiNMe$), 6.60, 6.65 (m, 2 × 2H, C_5H_4). ^{13}C–{^1H} NMR (125 MHz, CD_2Cl_2, 25 °C): δ −1.4 ($SiMe_2$), 38.6 ($SiNMe$), 45.2 ($TiNMe$), 51.3 ($SiNCH_2$), 71.0 ($TiNCH_2$), 122.2, 126.7 (C_5H_4), 127.4 (C_5H_4-$ipso$). ^{29}Si NMR (99.3 MHz, $CDCl_3$, 25 °C): δ = −4.5.

Synthesis of [Ti{η^5:η^1-$C_5H_4SiMe_2N(CH_2)_2$-η-$NHMe$}Cl_2] (2). A solution of $NH_2(CH_2)_2NHMe$ (0.5 mL, 5.7 mmol) and NEt_3 (1.6 mL, 11.4 mmol) in toluene (30 mL) was added to a

(31) Schrock, R. *J. Organomet. Chem.* **1976**, *122*, 209.

yellow solution of Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (1.77 g, 5.7 mmol) in toluene (60 mL) at −78 °C. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature and stirred for 2 h, during which time the mixture turned red and a white solid precipitated. After filtration and removal of the solvent, the resultant residue was washed with hexane (2 × 30 mL) and dried under vacuum to afford **2** as a yellow solid (1.3 g). Concentration and cooling to −30 °C of the solution gave a second crop (0.2 g), yielding a total 1.5 g (4,79 mmol, 84%) of product. Anal. Calcd for $C_{10}H_{18}Cl_2N_2SiTi$: C, 38.35; H, 5.8; N, 8.94. Found: C, 39.20; H, 5.67; N, 8.93. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.39 (s, 6H, $SiMe_2$), 2.92 (d, 3H, $^3J_{H-H}$ = 6.1 Hz, NH*Me*), 3.29, 3.62 (m, 2 × 2H, CH_2), 3.94 (br s, 1H, NH), 6.38 (m, 2H, C_5H_4), 7.0 (m, 2H, C_5H_4).^{13}C–{^1H} NMR (125 MHz, CD_2Cl_2, 25 °C): δ −3.2 ($SiMe_2$), 39.1 (NMe), 53.4 ($NHMeCH_2$), 56.1 ($TiNCH_2$), 111.2 (C_5H_4-$ipso$), 122.2, 129.1 (C_5H_4). ^{29}Si NMR (99.3 MHz, $CDCl_3$, 25 °C): δ = −13.2. IR (cm^{-1}): ν (N–H) 3228.

Synthesis of [Ti{η^5-$C_5H_4SiMe_2NMe(CH_2)_2$-η-NMe}$(CH_3)_2$] (3). A 2.1 mL sample of a 3 M solution of $MgClMe$ (6.3 mmol) in THF was added to a solution of Ti[(η^5-C_5H_4)$SiMe_2NMe$-$(CH_2)_2NMe$]Cl_2 (1.0 g, 3.0 mmol) in toluene (30 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 5 h. The toluene was removed under reduced pressure and the resultant residue extracted with 60 mL of hexane and reduced to 10 mL. Cooling at −30 °C overnight gave a yellow solid which was dried under vacuum, recrystallized from cold hexane, and characterized as **3** (0.49 g, 1.71 mmol, 56% yield). Anal. Calcd for $C_{13}H_{26}N_2SiTi$: C, 54.51; H, 9.17; N 9.77. Found: C, 53.61; H, 8.21; N, 8.85. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 0.14 (s, 6H, $SiMe_2$), 0.70 (s, 6H, $TiMe_2$), 2.30 (s, 3H, $SiNMe$), 2.51, 3.40 (m, 2 × 2H, CH_2), 3.17 (s, 3H, $TiNMe$), 5.79, 6.51 (m, 2 × 2H, C_5H_4). ^{13}C–{^1H} NMR (125 MHz, C_6D_6, 25 °C): δ −1.1 ($SiMe_2$), 37.5 ($SiNMe$), 45.5 ($TiNMe$), 50.6 ($SiNCH_2$), 60.3 ($TiNCH_2$), 50.4 ($TiMe_2$), 113.2, 113.8 (C_5H_4), 116.5 (C_5H_4-$ipso$).

Synthesis of [Ti{η^5-$C_5H_4SiMe_2NMe(CH_2)_2$-η-NMe}$(CH_2$-$Ph)_2$] (4). A solution of $Mg(CH_2Ph)_2$·$2THF$ (1.08 g, 3.0 mmol) in toluene (20 mL) was added to a solution of Ti[(η^5-C_5H_4)$SiMe_2$-$NMe(CH_2)_2NMe$]Cl_2 (1.0 g, 3.0 mmol) in toluene (20 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was completely removed and the residue extracted into *n*-hexane (50 mL). The resultant solution was concentrated (10 mL) and cooled at −30 °C to give a dark red solid which was dried under reduced pressure, recrystallized from cold hexane, and characterized as **4** (0.9 g, 2 mmol, 67% yield). Anal. Calcd for $C_{25}H_{34}N_2SiTi$: C, 68.46; H, 7.83; N, 6.38. Found: C, 67.23; H, 7.96; N, 6.90. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 0.05 (s, 6H, $SiMe_2$), 2.28 (s, 3H, $SiNMe$), 2.42, 2.47 (d, 2 × 2H, $^2J_{HH}$ = 11.4 Hz, C*H₂*-Ph), 2.51, 3.18 (m, 2 × 2H, CH_2), 3.20 (s, 3H, $TiNMe$), 5.56, 6.26 (m, 2 × 2H, C_5H_4), 6.90, 7.22 (m, 6H and 4H, Ph). ^{13}C–{^1H} NMR (125 MHz, C_6D_6, 25 °C): δ −1.6 ($SiMe_2$), 36.9 ($SiNMe$), 40.2 ($TiNMe$), 49.5 ($SiNCH_2$), 60.9 ($TiNCH_2$), 80.1 (*C*H_2Ph), 120.7, 121.7 (C_5H_4), 121.8 (C_5H_4-$ipso$), 125.9, 128.2, 128.9 (Ph), 150.8 (C_6H_5-$ipso$).

Synthesis of [Ti{η^5-$C_5H_4SiMe_2NMe(CH_2)_2$-η-NMe}(N-Me_2)$_2$] (5). A 0.28 g sample of $LiNMe_2$ (6.0 mmol) was added to a solution of Ti[(η^5-C_5H_4)$SiMe_2NMe(CH_2)_2NMe$]Cl_2 (1.0 g, 3.0 mmol) in hexane (100 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 6 h. The solution was filtered, concentrated (10 mL), and cooled at −30 °C to give a brown solid which was dried under reduced pressure, recrystallized from cold *n*-hexane, and characterized as **5** (0.67 g, 1.95 mmol, 64% yield). Anal. Calcd for $C_{15}H_{32}N_4$-SiTi: C, 52.27; H, 9.38; N 16.26. Found: C, 52.80; H, 9.60; N, 17.01. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.29 (s, 6H, $SiMe_2$), 2.66 (s, 3H, $SiNMe$), 2.80, 3.31 (m, 2 × 2H, CH_2), 3.00 (s, 12H, $TiNMe_2$), 3.10 (s, 3H, $TiNMe$), 6.04, 6.19 (m, 2 × 2H, C_5H_4). ^{13}C–{^1H} NMR (125 MHz, $CDCl_3$, 25 °C): δ −1.7 ($SiMe_2$), 36.9

(SiNMe), 45.0 (SiNCH$_2$), 59.3 (TiNCH$_2$), 49.6 (TiNMe), 50.0 (TiNMe$_2$), 113.6, 116.0 (C$_5$H$_4$), 118.5 (C$_5$H$_4$-*ipso*).

Synthesis of [Ti{(η^5-C$_5$H$_4$SiMe$_2$(OCO)NMe(CH$_2$)$_2$N-Me(η^2-OCO)}Cl$_2$] (6). A Schlenk flask containing chloroform (50 mL) was charged with Ti[(η^5-C$_5$H$_4$)SiMe$_2$NMe(CH$_2$)$_2$NMe]-Cl$_2$ (1.0 g, 3.0 mmol). After the solution had been cooled to −78 °C the argon atmosphere was replaced by CO$_2$. The reaction mixture was stirred in the dark for 2 h and then slowly warmed to room temperature. The color of the solution changed from red to yellow. The solvent was removed, and **6** was obtained as a yellow microcrystalline solid. Recrystallization from dichloromethane/*n*-hexane gave 0.63 g (50%) of **6**. Anal. Calcd for C$_{13}$H$_{20}$Cl$_2$N$_2$O$_4$SiTi: C, 37.6; H, 4.86; N, 6.74. Found: C, 38.2; H, 5.20; N, 7.56. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ 0.54 (s, 6H, SiMe), 2.96, 2.98 (s, 2 × 3H, NMe), 3.4, 3.6 (m, 2 × 2H, −CH$_2$−CH$_2$−), 6.98, 7.39 (m, 2 × 2H, C$_5$H$_4$). ^{1}H NMR (500 MHz, CDCl$_3$, −60 °C): δ 0.40, 0.70 (s, 2 × 3H, SiMe), 2.95, 3.05, 3.87, 4.53 (m, 4 × 1H, −CH$_2$−CH$_2$−), 2.98, 3.0 (s, 2 × 3H, NMe), 7.00, 7.02, 7.19, 7.67 (m, 4 × 1H, C$_5$H$_4$). ^{13}C−{^{1}H} NMR (125 MHz, CDCl$_3$, −60 °C): δ −2.8, 1.0 (SiMe), 34.1 (SiOCON), 36.0 (TiO$_2$CN), 45.9 (SiNCH$_2$), 46.8 (TiNCH$_2$), 124.3, 124.9, 128.1, 128.6 (C$_5$H$_4$), 132.2 (C$_5$H$_4$-*ipso*), 154.6 (SiO*C*O), 163.9 (TiO$_2$*C*). IR (KBr, cm^{-1}): ν $_{str}$(O$_2$CN) 1569 and 1668.

Reaction of [Ti{η^5-C$_5$H$_4$SiMe$_2$NMe(CH$_2$)$_2$-η-NMe}Cl$_2$] (1) with CO$_2$ at 70 °C. An NMR tube containing chloroform-*d*$_1$ (1.5 mL) was charged with 30 × 10^{-3} g of Ti[(η^5-C$_5$H$_4$)SiMe$_2$-NMe(CH$_2$)$_2$NMe]Cl$_2$ (9 × 10^{-2} mmol). After the solution had been cooled to −196 °C the argon atmosphere was replaced by CO$_2$. The reaction mixture was warmed to −60 °C, and the formation of **3** was confirmed. After the solution was warmed at 70 °C for 48 h, it was directly subjected to spectroscopic measurements, and the formation of the compounds [Ti{μ-(η^5-C$_5$H$_4$SiMe$_2$-η-O)}Cl$_2$]$_2$, (TiCl$_2$)$_2$(μ-O)-[μ-{(η^5-C$_5$H$_4$SiMe$_2$)$_2$(μ-O)}], and 1,3-dimethylimidazolidione was observed.

Crystal Structure Determination of [Ti{η^5-C$_5$H$_4$SiMe$_2$N-Me(CH$_2$)$_2$-η-NMe}Cl$_2$] (1). Red crystals of compound **1** were obtained by crystallization from hexane, and a suitably sized crystal was sealed, under argon, in a Lindemann tube and mounted in an Enraf-Nonius CAD 4 automatic four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystallographic and experimental details are summarized in Table 2. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction correction was made. The structure was solved by direct methods (SHELXL 97)[32] and refined by least-squares against F^2 (SHELXL 97).[32] All non-hydrogen atoms were

(32) Sheldrick, G. M. SHELX-97: *Programs for Crystal Structure Analysis* (Release 97-2), University of Göttingen, Germany, 1998.

Table 2. Crystal Data and Structure Refinement Procedures for Compound 1

empirical formula	C$_{11}$H$_{20}$Cl$_2$N$_2$SiTi
fw	327.18
cryst size (mm)	0.20 × 0.22 × 0.28
cryst syst	monoclinic
space group	P2$_1$/n
unit cell dimens	
a, b, c (Å)	8.101(1), 14.464(1), 26.601(1)
β (deg)	93.22(1)
V (Å^3)	3112.0(5)
Z	8
density(calcd) (g cm^{-3})	1.397
F(000)	1360
μ (cm^{-1})	9.52
scan mode	ω/2θ, 2.08 < θ < 24.97
no. of reflns collected	5870
no. of obsd reflns ($I > 2\sigma(I)$)	3543
index ranges	0 < h < +9, 0 < k < +17, −31 < l < +31
no. of std reflns	3 every 200 reflns
refinement method	full-matrix least-squares on F^2
final R indices ($I > 2\sigma(I)$)^a	R1 = 0.0412, wR2 = 0.0919
weighting scheme	$w_{calcd} = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 2.6572P]$ where $P = (F_o^2 + 2F_c^2)/3$
largest diff peak and hole (e/Å^3)	+0.570, −0.242
goodness of fit on F^2	1.001

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

refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with fixed thermal parameters (U = 0.08 Å^2). The final R values and other interesting X-ray structural analysis data are present in Table 2. Calculations were carried out on an ALPHA AXP (Digital) workstation.

Supporting Information Available: Final crystallographic atomic coordinates, equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, a complete list of bond distances and angles, an ORTEP diagram for **1,** and figures giving low-temperature ^{1}H NMR spectra for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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