Cyclopentadienyl-Amido Ligands with a Pendant "−NHR" Amino Functionality in Titanium Chemistry. Molecular Structure of [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-η-$NHCHMe_2$}Cl_2]

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The reaction of the chlorodimethylsilyl-substituted cyclopentadienyl titanium compound [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (**1**) with 1 equiv of $NH_2(CH_2)_2NHR$ (R = H, $CHMe_2$), in the presence of 2 equiv of NEt_3, afforded the mononuclear complexes [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-η-NHR}Cl_2] (R = H, **2**; $CHMe_2$, **3**) in high yield. While **2** is stable in solution, **3** slowly evolves into the strain-free complex [Ti{η^5-$C_5H_4SiMe_2NH(CH_2)_2$-η-$NCHMe_2$}Cl_2] (**4**). **1** reacts with 0.5 equiv of ethylenediamine to yield a mixture of **2** and the dinuclear titanium complex [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)$−}Cl_2]$_2$ (**5**), which contains two tethered cyclopentadienyl-silyl-amido fragments. Compound **5** is also obtained from the reaction of **2** with **1**. Treatment of **1** with 0.5 equiv of propylenediamine rendered the dinuclear compound [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_{1.5}$−}Cl_2]$_2$ (**6**), whereas a mixture of **6** and the mononuclear species [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_3NH_2$}Cl_2] (**7**) was spectroscopically observed when **1** was reacted with 1 equiv of $NH_2(CH_2)_3NH_2$ in C_6D_6. A similar reaction of **1** with *N*-methylpropylenediamine regioselectively affords the unstrained mononuclear compound [Ti{η^5-$C_5H_4SiMe_2NH(CH_2)_3$-η-NMe}Cl_2] (**8**). Dinuclear derivatives [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_x$−}Cl_2]$_2$ (x = 2 (**9**); 2.5 (**10**)) were prepared by reacting complex **1** with butylenediamine and pentylenediamine, respectively. These compounds were characterized by elemental analysis and NMR spectroscopy. The crystal structure of **3** was determined by X-ray diffraction methods.

Introduction

ansa-Monocyclopentadienyl-amido metal derivatives are receiving considerable attention[1] as alternative catalysts to the classical dicyclopentadienyl MCp_2X_2 systems[2] due to their high activity and remarkable ability to copolymerize ethene with bulkier olefins such as styrene, 1-hexene, and cyclic olefins.[3,4] Several modifications in the cyclopentadienyl-amido ligand, such as changing the substituent groups,[5] the size of the bridging chain,[6] and nature of the group attached to nitrogen atom,[7] have been introduced to achieve the desired catalytic behavior. Potential tridentate cyclopentadienyl-amido $C_5R'_4SiMe_2NCH_2CH_2X$ (R′ = H, CH_3; X = OMe, NMe_2, SMe, and PPh_2) ligands have recently been introduced by Okuda.[8] The additional two-electron-donor functionality acts as a semilabile ligand and

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allows rational modification of the electrophilicity of the metal center. The effect is to stabilize the active alkyl cationic species generated in the presence of the cocatalyst during the α-olefin polymerization process.

We have recently reported an efficient and versatile alternative strategy to prepare cyclopentadienyl-amido derivatives via reaction of primary amines[9] with the chlorosilyl-substituted cyclopentadienyl compound [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3][10] (**1**) in the presence of a base (NEt_3). Similar reactions with diamines afforded a new type of cyclopentadienyl-amido complex bearing a pendant NHR functionality.[11] The reaction of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] with $NH_2(CH_2)_2NHMe$ proceeds via aminolysis of the Ti−Cl and Si−Cl bonds with double deprotonation of the NH_2 amine group, leaving the −NHMe unit unchanged. This amine end coordinates to titanium to give the η^5-cyclopentadienylsilyl-η-amidoethylene-η-amino derivative [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-η-NHMe}Cl_2].[11]

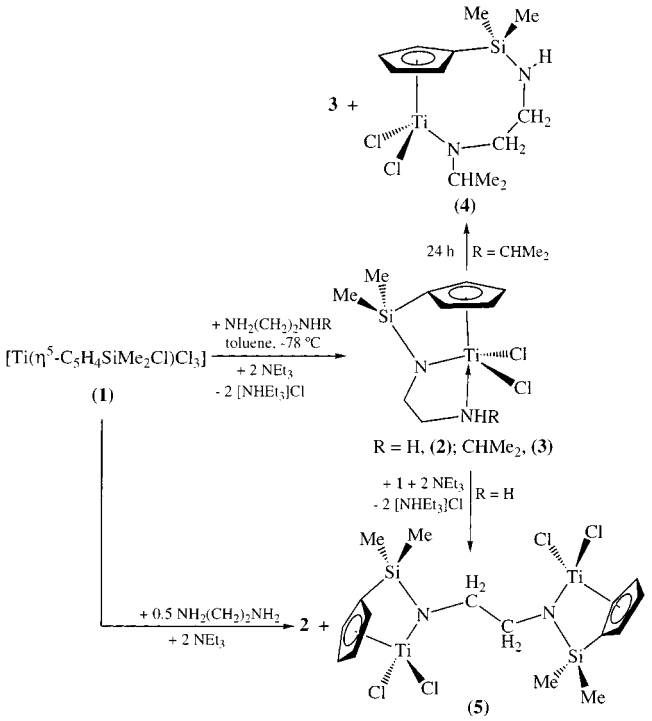
Part of our current interest is to extend this synthetic methodology to produce new types of linked cyclopentadienyl-amido compounds. We have investigated the reactions of **1** with several diamines under various working conditions. The presence of the "NHR" amino functionality results in unusual chemical behavior with important reactivity differences compared with the derivatives reported by Okuda. We report here the synthesis and characterization of an extensive group of cyclopentadienyl-amido complexes, including mononuclear and dinuclear cyclopentadienyl-amido species and mononuclear strain-free compounds.

Results

Reaction with Ethylenediamines $NH_2(CH_2)_2NHR$. Reaction of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] with 1 equiv of $NH_2(CH_2)_2NHR$ (R = H, $CHMe_2$) in toluene at −78 °C in the presence of 2 equiv of NEt_3 afforded, after removal of the ammonium salt, the cyclopentadienyl-silyl-amido derivatives [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-η-NHR}Cl_2] (R = H, **2**; $CHMe_2$, **3**) (Scheme 1). These complexes were isolated as crystalline yellow solids in excellent yields and characterized by NMR spectroscopy and elemental analysis. The molecular structure of **3**, determined by X-ray diffraction, is the first reported structure of a titanium complex with a tridentate cyclopentadienyl-amido-amino ligand.

When the reaction with *N*-isopropylethylenediamine was extended for 24 h at room temperature, the formation of a small amount of a new strain-free titanacyclic cyclopentadienyl-amido derivative [Ti{η^5-$C_5H_4SiMe_2$-$NH(CH_2)_2$-η-$NCHMe_2$}Cl_2] (**4**) (<5% by NMR) with traces of an unidentified product was observed by NMR spectroscopy. When a solution of **3** in $CDCl_3$ or C_6D_6 was monitored by ^{1}H NMR for a week, **3** slowly and cleanly transformed into **4**, with no minor product observed. Compound **4** was always formed in very low yield, even after extending the reaction time to weeks on preparative scale, preventing its isolation, and as a result it was only characterized by NMR spectroscopy.

Scheme 1



New reactivity pathways arise from the presence of the N−H bond in the terminal amino functionality in compounds **2** and **3**. The formation of **4** involves an intramolecular migration of hydrogen from the amino to the amido nitrogen with subsequent opening of the metallacycle ring, as a consequence of the presence of the bulky isopropyl group on amino nitrogen. In contrast, this behavior was not observed for **2** nor for the analogous complex [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-η-NHMe}Cl_2],[11] where less bulky hydrogen and methyl groups are bonded to the amino nitrogen, which are stable in solution under the reaction conditions.

Because the presence of the NH_2 group made [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_2NH_2$}Cl_2] capable in principle of reacting as a primary amine, compound **2** was an attractive reagent for use in the synthesis of dimetallic complexes. Consequently, we decided to study the reaction of **1** with an equimolar amount of [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_2$-η-NH_2}Cl_2] in the presence of 2 equiv of NEt_3, which afforded the dinuclear derivative [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)$−}Cl_2]$_2$ (**5**) in low yield. Direct reaction of **1** with 0.5 equiv of ethylenediamine and 2 equiv of NEt_3 also rendered compound **5**, although the reaction was slow and always gave a mixture of **2** and **5**, which were separated by using their different solubilities. To the best of our knowledge, compound **5** is the first example of a dinuclear titanium complex containing two tethered cyclopentadienyl-silyl-amido fragments.

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The ^{1}H and ^{13}C NMR spectra ($CDCl_3$ or C_6D_6 at room temperature) for compounds **2**−**5** are consistent with their C_s symmetry. The ^{1}H NMR spectra show AA′BB′ spin systems for the C_5H_4 ring protons and one signal for the SiMe_2 resonances. The spectra of **2** and **3** show AA′BB′KK′ and AA′BB′K spin systems, respectively, with two multiplets and a broad signal (see Experimental Section) for the "NCH_2CH_2NH_2" and "NCH_2CH_2N*H*" moieties. Such spectroscopic features contrast with the asymmetric structure shown by complex **3** in the solid. The downfield shift observed for amine protons indicates an interaction between the amine nitrogen and titanium.[11] This spectroscopic behavior suggests fluxional intramolecular coordination of the amine group to the titanium atom in solution, similar to that observed in [Ti{η^5-$C_5H_4SiMe_2$-η-N$(CH_2)_2$-η-NHMe}Cl_2].[11]

The ^{1}H NMR spectra of **3** and **4** are similar, showing an AA′BB′K spin system for the "NCH_2CH_2N*H*" moiety and a doublet and a septet assignable to the CHMe_2 protons. The chemical shift found for C*H*Me_2 in analogous complexes is in the range 3.8−6.2 ppm.[5b,12] However, the dissimilar nature of the backbone ligands in these complexes is confirmed by significant spectroscopic differences between them, notably the pronounced upfield shift for the N*H* proton (δ 0.55) and downfield shift for the methine proton NC*H*Me_2 (δ 6.55, septet) in **4** (C_6D_6) compared to **3** (δ 3.63 and 3.80, respectively, $CDCl_3$).

The NMR behavior of **5** is relatively simple and consistent with the proposed structure, which corresponds to a dinuclear species containing two spectroscopically equivalent C_s-symmetry metallic "Ti(η^5-C_5H_4-$SiMe_2$-η-N−)Cl_2" fragments connected by an ethylene bridge. The methylene group's resonance appears as a singlet (δ 4.22) downfield with respect to those found for complex **2** ($\delta_{average}$ 3.54), indicating the presence of a more electron-deficient titanium center in **5** and stronger pπ−dπ amido character in both nitrogen atoms.

The chemical shift of the cyclopentadienyl *ipso*-carbon atom resonances observed in the ^{13}C NMR spectra is a powerful diagnostic tool to differentiate the structure of compounds of this type.[6c,9] The significant shielding of this resonance in **2** (δ 110.2), **3** (δ 110.2), and **5** (δ 109.6) with respect to the remaining ring carbon resonances confirms the cyclopentadienyl-amido disposition of these compounds.

The structure of **3** was verified by X-ray crystallographic analysis, and the molecular structure is illustrated in Figure 1. Selected bond distances and angles are listed in Table 1. The compound is a chiral monomeric species, and the structure can be described as pseudo-trigonal-bipyramidal. The amido nitrogen and the two chlorine atoms define the equatorial plane, while the η^5-bonded cyclopentadienyl and coordinated amino ligand occupy the apical positions. Analogous structures have been reported by Okuda for zirconium species,[8c] although structural studies for cyclopentadienyl-amido titanium complexes bearing a pendant amino group coordinated to the titanium center are not known.

The Cg−Ti−N(1) and Cl(1)−Ti−Cl(2) angles are closer and more open (101.67° and 116.77(2)°), respectively, compared with unstrained cyclopentadienyl-amido complexes,[6b,11] and are comparable to those found in constrained-geometry complexes.[13] The trigonal planar geometry of the amido nitrogen atom and the short Ti−N(1) bond distance of 1.9337(13) Å suggest a N(pπ)−Ti(dπ) interaction.[14] The Ti−N(2) bond length at 2.3179(16) Å is consistent with its description as an amino-titanium linkage and is consistent with those found in a range of amino complexes.[15]

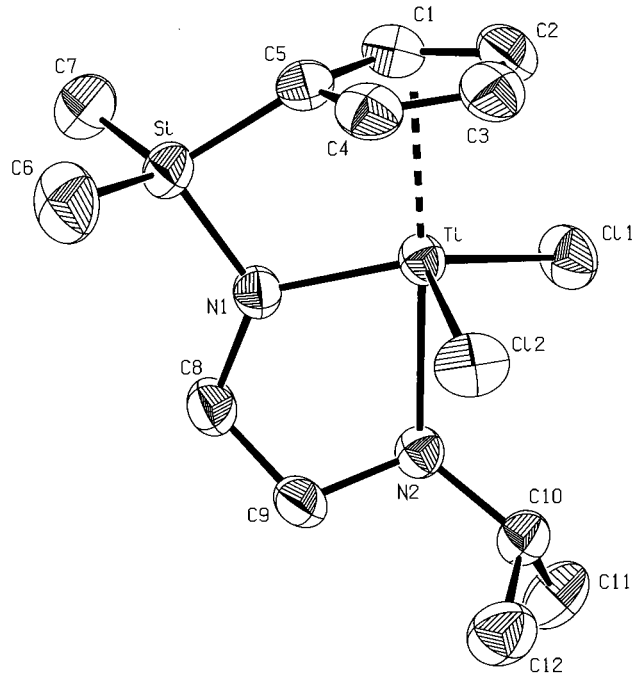

Figure 1. ORTEP[22] representation of complex **3** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Interatomic Distances (Å) and Angles(deg) for Complex 3[a]

Ti−Cl1	2.3744(6)	Ti−C5	2.3752(17)
Ti−Cl2	2.3417(6)	Ti−Cg	2.098
Ti−N1	1.9337(13)	Si−N1	1.7344(14)
Ti−N2	2.3179(16)	Si−C5	1.8534(19)
Ti−C1	2.3775(18)	N1−C8	1.462(3)
Ti−C2	2.469(2)	N2−C9	1.467(2)
Ti−C3	2.457(2)	C8−C9	1.506(3)
Ti−C4	2.386(2)		
Cl1−Ti−Cl2	116.77(2)	N1−Ti−Cg	101.67
Cl1−Ti−N1	118.38(4)	N2−Ti−Cg	174.77
Cl1−Ti−N2	75.80(4)	Ti−N2−C9	106.90(11)
Cl1−Ti−Cg	103.84	Ti−N2−C10	122.83(12)
Cl2−Ti−N1	109.44(4)	C9−N2−C10	115.64(14)
Cl2−Ti−N2	80.31(5)	C10−N2−H2	105.5(12)
Cl2−Ti−Cg	104.32	Ti−N2−H2	98.0(12)
N1−Ti−N2	74.23(5)	C9−N2−H2	105.1(12)

[a] Cg denotes the centroid of the Cp ligand.

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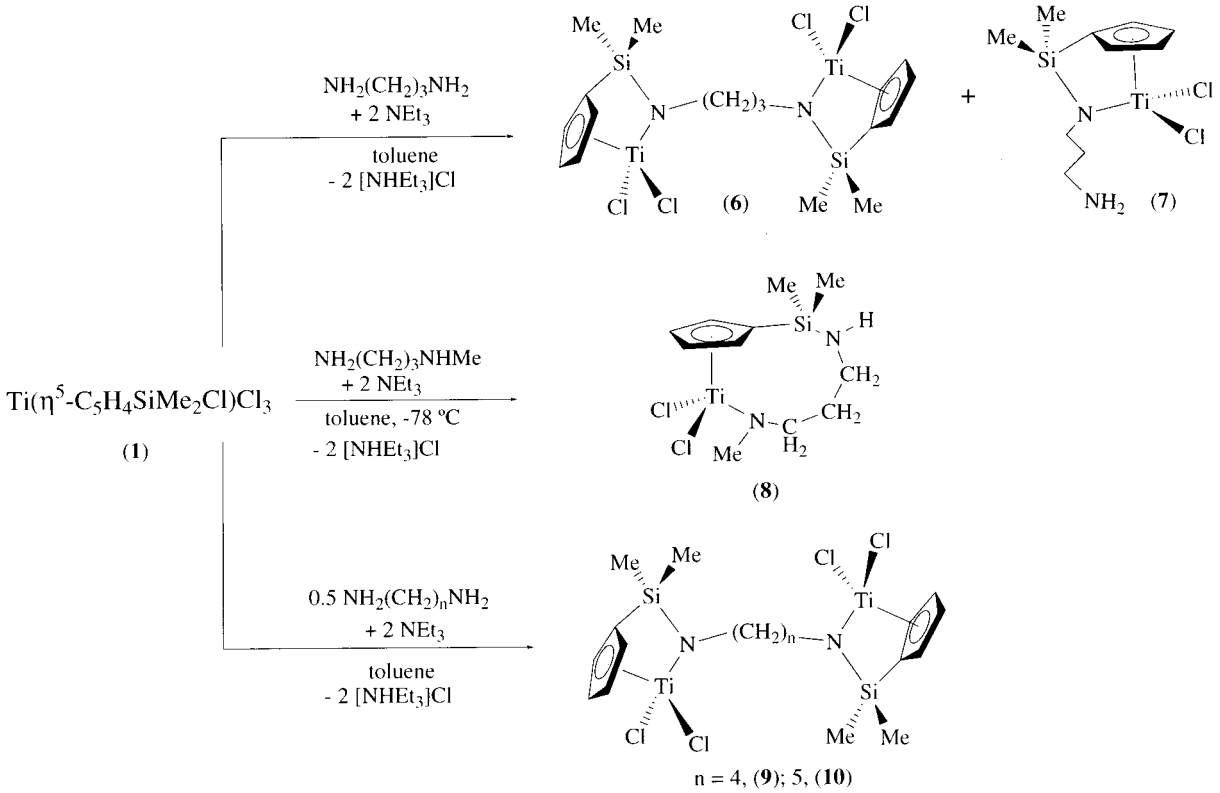
Scheme 2



The five-membered chelate ring is puckered, with the sterically demanding isopropyl substituent approximately bisecting the Cl−Ti−Cl angle, with both methyl groups turned away from the titanium center. Such a disposition minimizes the repulsion between the isopropyl and the chloro ligands and is reflected in the distorted tetrahedral geometry of amino nitrogen, as evident from the data in Table 1. The Ti−N(2)−H(2) angle is 98.0(12)°, whereas the Ti−N(2)−C(10) angle is 122.83(12)°. This disposition brings the amino hydrogen atom close to the amido nitrogen located in the equatorial plane, a significant factor in the way **3** generates **4** (see Discussion section).

Reactions with Longer Chain Diamines $NH_2(CH_2)_nNHR$ ($n \geq 3$). To evaluate the influence of the amine carbon chain length, we explored the reaction of **1** with longer chain diamines $NH_2(CH_2)_nNHR$ ($n = 3$, R = H, Me; $n = 4$, 5, R = H) (Scheme 2).

Treatment of compound **1** in toluene with 0.5 equiv of propylenediamine in the presence of 2 equiv of NEt_3 rendered the tethered dimetallic cyclopentadienyl-amido derivative $[Ti\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_{1.5}-\}Cl_2]_2$ (**6**) as an analytically pure yellow solid in excellent yield. The reaction of **1** with 1 equiv of propylenediamine and 2 equiv of NEt_3 in C_6D_6 resulted in a mixture of **6** and the expected mononuclear complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_3NH_2\}Cl_2]$ (**7**) in a 2:1 molar ratio (as evidenced by NMR spectroscopy). The rest of the diamine was recovered as the ammonium salt. This result suggests that compound **7** is initially generated as an intermediate species in the formation of **6**, with the pendant NH_2 group reacting more quickly than the free diamine, even in an excess of free diamine. Unfortunately, compound **7** could not be isolated on preparative scale due to its low stability and was only characterized by NMR spectroscopy. Compound **6** was also obtained when the reaction was carried out in the absence of NEt_3 using 2.5 equiv of the corresponding diamine.

Attempts to prepare **7** selectively using an excess of propylenediamine were not successful, and the reaction resulted in the unexpected cleavage of the Cp−amido linkage with displacement of the cyclopentadienyl ligand. When **1** was treated with an excess of propylenediamine (Ti:diamine molar ratio = 1:5), the solution became colorless and a pale orange solid was precipitated. The soluble fraction contains an equimolar mixture of cyclopentadiene and 2,2-dimethyl-1,3-diaza-2-silacyclohexane (as shown by NMR). Unfortunately, the lack of solubility of the residue along with its spectroscopic behavior (broad and featureless spectra) did not allow its full characterization.

Following an analogous procedure, $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$ reacted with an equimolar amount of *N*-methylpropylenediamine to give, regioselectively, the mononuclear strain-free complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2NH(CH_2)_3\text{-}\eta\text{-}NMe\}Cl_2]$ (**8**). This compound was isolated in high yield as a crystalline red solid, although crystals suitable for X-ray analysis could not be obtained. This result contrasts with that observed in the reaction of **1** with propylenediamine and in the previously reported reaction with *N*-methylethylenediamine.[11]

Reaction of **1** with 0.5 equiv of a longer unsubstituted diamine $NH_2(CH_2)_nNH_2$ ($n = 4$ and 5) and 2 equiv of NEt_3, or alternatively with 2.5 equiv of the diamine in the absence of NEt_3, conveniently afforded the corresponding dinuclear compounds $[Ti\{\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N(CH_2)_x-\}Cl_2]_2$ ($x = 2$, **9**; 2.5, **10**) as analytically pure substances. In contrast, in a similar reaction with propylenediamine, the mononuclear η^5-cyclopentadi-

enylsiyl-η-amido-amine derivative was never observed, regardless of the molar ratio of the diamine used.

Compounds **6** and **8**−**10** were characterized by NMR spectroscopy and elemental analysis, whereas **7** was only spectroscopically identified. The ^{1}H and ^{13}C NMR spectra are consistent with the C_s symmetry of these molecules. The ^{1}H NMR spectra ($CDCl_3$ or C_6D_6 at room temperature) show AA′BB′ spin systems for the C_5H_4 ring protons and one signal for the SiMe_2 resonances. The ^{1}H NMR spectra for **6**, **9**, and **10** show the methylene resonances due to internal CH_2 groups shifted upfield (δ 1−2), while the NCH_2 are shifted downfield (ca. 4.25 ppm) compared with the corresponding signals in the mononuclear complexes **2** and **3**. The ^{1}H NMR spectrum of compound **7** shows an AA′BB′CC′K_2 spin system for the "NCH_2CH_2CH_2NH_2" moiety with three multiplets for methylene protons and a resonance for the NH_2 protons significantly shifted upfield (δ −0.20). The upfield shift observed for the latter resonance compared with complex **2** indicates no interaction between the amine nitrogen and the titanium atom in **7**. The ^{1}H NMR spectrum of **8** shows an AA′BB′CC′K spin system for the "NCH_2CH_2CH_2NHSi" moiety, three multiplets for methylene protons, and an broad triplet for SiNH hydrogen, along with a singlet for TiNCH_3, consistent with the proposed structure. The upfield (δ 0.73) and downfield (δ 3.89) signals observed respectively for the latter two resonances confirm the amine and amido character of the nitrogen atoms.

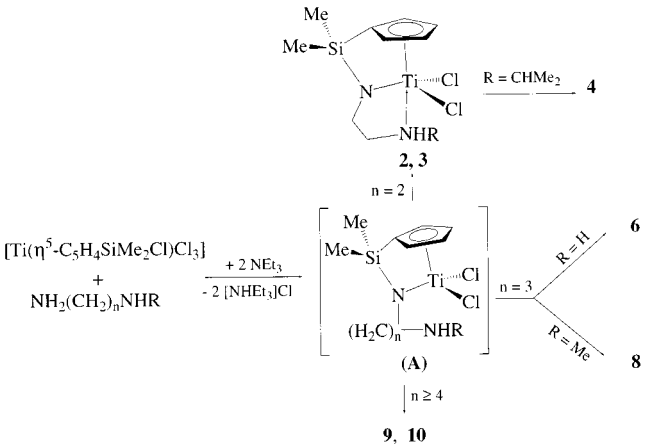
In the ^{13}C NMR spectra the *ipso*-carbon atom resonance is shifted upfield for **6**, **9**, and **10** and downfield for **8** with respect to the rest of the ring carbon resonances. This is consistent with the cyclopentadienyl-amido for the former three and the strain-free structure for the latter. The downfield shift for the "TiNCH_2" resonance in **8** with respect to **6**, **9**, and **10** is consistent with a higher π-bonding contribution from the Ti−N amido interaction in the former.[11]

Discussion

On the basis of these results, it is not possible to conclude which bond, titanium−chloro or silicon−chloro, in the compound [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] undergoes the initial aminolysis reaction. However, it seems that the reaction sequence of **1** with $NH_2(CH_2)_nNHR$ is initiated by double deprotonation of the NH_2 unit to give the constrained intermediate (**A**), which was observed in the reaction with propylenediamine (compound **7**). Then the reaction can follow different pathways depending on the number of carbon atoms and nature of the amine substituent R (Scheme 3).

Intramolecular coordination of the amine functionality is preferred when $n = 2$, stabilizing the final product [Ti{η^5-$C_5H_4SiMe_2$-η-N$(CH_2)_2$-η-NHR}Cl_2] (R = H, **2**; $CHMe_2$, **3**). In these compounds amine coordination induces a substantial increase in N−H acidity,[16] making the proton highly reactive to intramolecular NH activation. The length of the spacer along with the trigonal planar geometry of the amido nitrogen force the amine group to coordinate at the apical position, far away from the amido nitrogen. Nevertheless, the presence in **3** of the bulky demanding isopropyl substituent on nitrogen forces the amino proton to approach the amido nitrogen atom, favoring intramolecular proton transfer from the former to the latter group to afford complex **4**. The driving force for this process is the reduction to a minimum of the strain energy in the metallacycle on going from a four- to a seven-membered ring. In **2** the less sterically demanding NH_2 amino group does not force the amino group to approach the amido group, so the tricoordinated cyclopentadienyl-amido-amino ligand remains unchanged.

Scheme 3



Alternatively, the pendant amine end in complex **2** can act as a primary amine, reacting with **1** to give the tethered dinuclear cyclopentadienyl-silyl-amido complex **5**. On increasing the chain size, the reactivity of the NH_2 group increases because it can get far away, favoring contact with another metal center. Thus, reaction of **1** with $NH_2(CH_2)_nNH_2$ (n = 4 or 5) directly yielded the dinuclear complexes **9** and **10** with no mononuclear compounds observed, even in an excess of diamine.

The borderline between these two differing reactions is observed when $n = 3$. In this case, the pathway followed essentially depends on the nature of the R group attached to nitrogen. When R = H, the reaction follows the intermolecular pathway giving the dinuclear complex **6**. In contrast, when the amine substituent contains a methyl group, intramolecular amine coordination is preferred to intermolecular coordination. In this case the length of the chain allows the amino group to coordinate to the titanium atom in its preferred equatorial position,[17] bringing the NHMe group into proximity with the Ti-amido unit and favoring amino-amido hydrogen displacement to form **8**.

Concluding Remarks

Reaction of the chlorodimethylsilyl-substituted cyclopentadienyl compound **1** with diamines provides an alternative synthetic strategy for the preparation of new types of cyclopentadienyl-amido derivatives of titanium. The influence of several factors on the final product, including the nature of the groups on amine nitrogen, the size of the amine carbon chain, and the reaction's stoichiometry, has been studied. Reaction of **1** with

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ethylenediamines, in a molar ratio 1:1, proceeds yielding monomeric cyclopentadienyl-amido complexes, whereas molar ratio 1:0.5 affords the tethered dinuclear cyclopentadienyl-amido titanium complex [Ti{(η^5-$C_5H_4SiMe_2$-η-N(CH_2)−}Cl_2]$_2$ (**5**). Compound **1** reacts with longer unsubstituted diamines to give dinuclear complexes. The borderline between these different behaviors is apparent in reactions with $NH_2(CH_2)_3NHR$, where the nature of the final product essentially depends on the type of R substituent. The reaction of **1** with an excess of propylenediamine illustrates an unusual reaction for half-sandwich complexes, in which the cyclopentadienyl ligand is eliminated.

This synthetic methodology affords new complexes containing a tridentate cyclopentadienyl-amido-amine ligand, similar to those described by Okuda. However, the presence of the "−NHR" amino functionality highlights new reactivity pathways. Especially remarkable is the synthesis of, as far as we know, the first example of tethered dinuclear cyclopentadienyl-amido titanium complexes. Studies to prepare heterodinuclear complexes following this synthetic strategy are in progress.

Experimental Section

General Considerations. All manipulations were performed under argon using Schlenk and high-vacuum line techniques or in 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. Diamines (Aldrich) were purchased from commercial sources and used without further purification. [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3][10] was prepared by known procedure. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. The analytical data found for **5** deviated from expected values since **2** could not be completely separated from the mixture. NMR spectra, measured at 25 °C, were recorded on a Varian Unity FT-300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75 MHz) spectrometer, and chemical shifts are referenced to residual solvent protons.

Synthesis of [Ti{η^5-$C_5H_4SiMe_2$-η-N(CH_2)$_2$-η-NH_2}Cl_2] (2). A toluene solution (30 mL) of $NH_2(CH_2)_2NH_2$ (0.8 mL, 11.96 mmol) and NEt_3 (3.48 mL, 25 mmol) was added to a yellow solution of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (3.7 g, 11.86 mmol) in toluene (60 mL) at −78 °C. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature with stirring for 30 min. The solid formed was collected by filtration and toluene removed under vacuum. The residue was extracted into toluene (2 × 30 mL). The filtrate was dried and the solid obtained washed with pentane (2 × 30 mL). After recrystallization from toluene/hexane **2** was obtained as a yellow solid (2.31 g, 7.72 mmol, 65.2%). Anal. Calcd for $C_9H_{16}Cl_2N_2SiTi$: C, 36.14; H, 5.39; N, 9.37. Found: C, 36.13; H 5.42; N, 9.36. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.40 (s, 6H, $SiMe_2$), 3.43, 3.66, 4.30 (m, 2H, CH_2; t, J = 5.84 Hz, 2H, NCH_2; m, 2H, NH_2; AA′BB′KK′ spin system, "NCH_2CH_2-NH_2"), 6.38, 7.09 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ −3.3 ($SiMe_2$), 43.8 (t, J_{CH} = 136.0 Hz, CH_2NH_2), 57.8 ($TiNCH_2$), 110.2 (C_5H_4-*ipso*), 122.4, 128.6 (C_5H_4).

Synthesis of [Ti{η^5-$C_5H_4SiMe_2$-η-N(CH_2)$_2$-η-NHCHMe_2}Cl_2] (3). Compound **3** was obtained using 2.3 g (7.37 mmol) of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3], 0.92 mL (7.4 mmol) of $NH_2(CH_2)_2$-NHCHMe_2, and 2.09 mL (15 mmol) of NEt_3 following the method given for **2**. The product was obtained as a pale yellow solid, and recrystallization from hexane gave yellow crystals of **3** (1.81 g, 5.30 mmol, 72%). Anal. Calcd for $C_{12}H_{22}Cl_2N_2$-SiTi: C, 42.24; H, 6.5; N, 8.21. Found: C, 42.73; H, 6.9; N, 7.67. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.40 (s, 6H, $SiMe_2$), 1.30 (d, ^3J = 6.6 Hz, 6H, CHMe_2), 3.27, 3.60, 3.63 (m, 2H, CH_2; t, J = 5.64 Hz, 2H, NCH_2; m, 1H, NH; AA′BB′K spin system, "NCH_2CH_2NH"), 3.80 (sept, ^3J = 6.6 Hz, 1H, CHMe$_2$) 6.48, 6.97 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ − 3.5 ($SiMe_2$), 22.9 (CHMe_2), 46.9 (CH_2NH_2), 51.2 (CHMe$_2$), 55.7 ($TiNCH_2$), 110.2 (C_5H_4-*ipso*), 122.7, 128.2 (C_5H_4).

[Ti{η^5-$C_5H_4SiMe_2NH(CH_2)_2$-η-NCHMe_2}Cl_2] (4). When a solution of **3** was maintained in C_6D_6 for 24 h at room temperature, the formation of **4** was spectroscopically observed. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.13 (s, 6H, $SiMe_2$), 0.55, 2.38, 3.21 (br s, 1H; m, 2H; m, 2H; KAA′BB′ spin system, "NHCH_2CH_2N"), 0.98 (d, ^3J = 5.7 Hz, 6H, CHMe_2), 6.33, 6.37 (AA′BB′ spin system, 2 × 2H, C_5H_4), 6.55 (sept, ^3J = 5.7 Hz, 1H, CHMe$_2$).

Synthesis of [Ti{η^5-$C_5H_4SiMe_2$-η-N(CH_2)−}Cl_2]$_2$ (5). Method a. A toluene solution (20 mL) of [Ti{η^5-$C_5H_4SiMe_2N$-$(CH_2)_2$-η-NH_2}Cl_2] (2 g, 6.68 mmol) and NEt_3 (1.9 mL, 13.6 mmol) was added to a toluene solution (20 mL) of [Ti(η^5-C_5H_4-$SiMe_2Cl$)Cl_3] (2.08 g, 6.68 mmol) at room temperature. The reaction mixture was stirred for 48 h, filtered, and dried. The residue was extracted into toluene (3 × 10 mL) and the resulting solution cooled at −10 °C overnight to afford a yellow solid. Crystallization from toluene/hexane gave **5** as a microcrystalline yellow solid (0.57 g, 1.06 mmol, 16%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.60 (s, 2 × 6H, $SiMe_2$), 4.22 (s, 2 × 2H, $TiNCH_2$), 6.50, 6.99 (AA′BB′ spin system, 2 × 4H, C_5H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ −2.3 ($SiMe_2$), 56.2 (t, ^2J = 5.7 Hz $TiNCH_2$), 109.6 (C_5H_4-*ipso*), 123.1, 126.8 (C_5H_4).

Method b. A toluene solution (30 mL) of $NH_2(CH_2)_2NH_2$ (0.4 mL, 5.98 mmol) and NEt_3 (3.5 mL, 25.1 mmol) was added to a yellow solution of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (3.7 g, 11.86 mmol) in toluene (60 mL). The reaction mixture was stirred for 48 h. The solid formed was collected by filtration and toluene removed under vacuum. The residue was extracted into toluene (2 × 30 mL). Solvent was completely removed from the resulting solution and the solid obtained washed with pentane (2 × 30 mL). Crystallization from toluene/hexane afforded **5** in 7% yield (0.22 g, 0.41 mmol).

Synthesis of [Ti{η^5-$C_5H_4SiMe_2$-η-N(CH_2)$_{1.5}$−}Cl_2]$_2$ (6). A toluene solution (20 mL) of $NH_2(CH_2)_3NH_2$ (0.4 mL, 4.8 mmol) and NEt_3 (2.8 mL, 20 mmol) was added at room temperature to a solution of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (3 g, 9.61 mmol) in 30 mL of the same solvent. The solution was stirred for 2 h, allowed to settle down overnight, and filtered. The filtrate was dried and the residue extracted into toluene (5 × 20 mL). The solution was concentrated and cooled, yielding **6**, which was recrystallized from toluene/hexane (2.3 g, 4.16 mmol, 87%) as a yellow solid. Anal. Calcd for $C_{17}H_{26}Cl_4N_2Si_2Ti_2$: C, 36.98; H, 4.75; N, 5.07. Found: C, 37.15; H, 4.82; N, 4.96. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.52 (s, 2 × 6H, $SiMe_2$), 1.83 (m, 2H, CH_2), 4.20 (m, 2 × 2H, $TiNCH_2$), 6.48, 6.98 (AA′BB′ spin system, 2 × 4H, C_5H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ −2.5 ($SiMe_2$), 32.9 (CH_2), 56.1 ($TiNCH_2$), 109.4 (C_5H_4-*ipso*) 124.0, 126.1 (C_5H_4).

[Ti{η^5-$C_5H_4SiMe_2N(CH_2)_3NH_2$}$Cl_2$] (7). A solution (0.5 mL) of $NH_2(CH_2)_3NH_2$ (1.1 × 10^{-2} mL, 0.13 mmol) and NEt_3 (4.2 × 10^{-2} mL, 0.30 mmol) in C_6D_6 was added to a solution of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (0.04 g, 0.13 mmol) in 0.5 mL of C_6D_6 at room temperature. The solid formed was collected by filtration and the solution monitored by NMR. A mixture of **6** and **7** was detected. **7**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ −0.20 (m, 2H, NH_2), 0.13 (s, 6H, $SiMe_2$), 0.66 (m, 2H, NCH_2), 2.50 (m, 2H, CH_2), 3.46 (m, 2H, $TiNCH_2$), 6.21, 6.91 (AA′BB′ spin system, 2 × 2H, C_5H_4).

Synthesis of [Ti{η^5-$C_5H_4SiMe_2NH(CH_2)_3$-η-NMe}Cl_2] (8). A toluene solution (20 mL) of $NH_2(CH_2)_3NHMe$ (0.7 mL, 6.7 mmol) and NEt_3 (1.81 mL, 13 mmol) was added to a solution

of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (2 g, 6.41 mmol) in 30 mL of toluene at room temperature. The reaction mixture was stirred for 2 h. After filtration, the volatiles were removed under vacuum and the residue was extracted into hexane (5 × 30 mL). The resulting solution was concentrated and cooled overnight at −30 °C to give a red solid. After recrystallization from toluene/hexane **8** was obtained as a red crystalline solid (1.66 g, 5.07 mmol, 79.5%). Anal. Calcd for $C_{11}H_{20}Cl_2N_2SiTi$: C, 40.37; H, 6.17; N, 8.56. Found: C, 40.22; H, 6.18; N, 8,22. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.27 (s, 6H, $SiMe_2$), 0.73 (br t, 1H, SiNH), 1.42 (m, 2H, $SiNCH_2$), 2.56 (m, 2H, CH_2), 3.89 (s, 3H, TiNMe), 4.30 (m, 2H, $TiNCH_2$), 6.60, 6.91 (AA′BB′ spin system, 2 × 2H, C_5H_4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ −1.1 ($SiMe_2$), 31.2 ($SiNH_2$), 36.0 (CH_2), 64.5 ($TiNCH_2$), 122.3, 127.0 (C_5H_4), 129.8 (C_5H_4-*ipso*).

Synthesis of [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_2$−}Cl_2]$_2$ (9). A toluene solution (20 mL) of $NH_2(CH_2)_4NH_2$ (0.48 mL, 4.8 mmol) and NEt_3 (3 mL, 21.5 mmol) was added at room temperature to a solution of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] (3 g, 9.61 mmol) in 30 mL of the same solvent. The solution was stirred for 2 h, allowed to settle overnight, and filtered. The filtrate was dried and the residue extracted into toluene (5 × 20 mL). Concentration and cooling of the solution produced a yellow solid. After recrystallization from toluene/hexane **9** was obtained as a yellow solid (0.68 g, 1.20 mmol, 25%). Anal. Calcd for $C_{18}H_{28}Cl_4N_2Si_2Ti_2$: C, 38.19; H, 4.98; N, 4.95. Found: C, 38.54; H, 5.23; N, 4.20. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.17 (s, 2 × 6H, $SiMe_2$), 1.34 (m, 2 × 2H, CH_2), 4.24 (m, 2 × 2H, $TiNCH_2$), 6.09, 6.43 (AA′BB′ spin system, 2 × 4H, C_5H_4). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ −2.7 ($SiMe_2$), 30.2 (CH_2), 57.9 ($TiNCH_2$), 108.9 (C_5H_4-*ipso*) 123.8, 125.8 (C_5H_4).

Synthesis of [Ti{η^5-$C_5H_4SiMe_2$-η-$N(CH_2)_{2.5}$−}Cl_2]$_2$ (10). Compound **10** was prepared by reacting 9.6 mmol of **1** with the pentylenediamine by the procedure described for **9** and obtained as a yellow solid (2 g, 3.44 mmol, 71.8%). Anal. Calcd for $C_{19}H_{30}Cl_4N_2Si_2Ti_2$: C, 39.33; H, 5.21; N, 4.83. Found: C, 39.62 H, 5.81; N, 5.83. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.15 (s, 2 × 6H, $SiMe_2$), 1.13 (m, 2H, CH_2), 1.42 (m, 2 × 2H, CH_2), 4.29 (m, 2 × 2H, $TiNCH_2$), 6.07, 6.45 (AA′BB′ spin system, 2 × 4H, C_5H_4). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ −2.7 ($SiMe_2$), 24.5 (CH_2), 31.6 (CH_2), 57.8 ($TiNCH_2$), 108.9 (C_5H_4-*ipso*) 123.8, 125.8 (C_5H_4).

X-ray Structure Determination of Complex 3. Details of the X-ray experiment, data reduction, and final structure refinement calculation are summarized in Table 2. Crystals of complex **3** suitable for X-ray structure determination were grown from a saturated solution of **3** in hexane. Preliminary examination and data collection were carried out on an imaging plate diffraction system (IPDS, STOE&CIE) at the window of a rotating anode (NONIUS FR591; 50 kV; 60 mA; 3.0 kW) and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 4973 reflections. Data collection was performed at 293 K with an exposure time of 60 s per image (rotation scan modus: φ = 0° to 360° with $\Delta\varphi$ = 1.5°). A total number of 21 864 reflections were collected. Raw data were corrected for Lorentz and polarization effects. Corrections for absorption and decay effects were not applied.[18] After merging, a sum of 2866 independent reflections remained and were used for all calculations. All non-hydrogen atoms were refined anisotropically. The structure was solved by a combination of direct methods and difference Fourier syntheses.[19] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the difference Fourier map and refined freely with individual isotropic thermal displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at maximum shift/err < 0.001.[20] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[21] All other calculations (including ORTEP graphics) were carried out using the PLATON program.[22] Calculations were performed on a PC workstation (Intel Pentium II) running LINUX.

Table 2. Crystallographic Data for Complex 3

chem formula	$C_{12}H_{22}Cl_2N_2SiTi$
fw	341.18
color/shape	yellow/fragment
cryst size (mm)	0.81 × 0.36 × 0.28
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a (Å)	6.5785(4)
b (Å)	15.0383(12)
c (Å)	16.4637(14)
b (deg)	98.633(9)
V (Å$^{3)}$	1610.3(2)
Z	4
T (K)	293
ρ_{calcd} (g cm^{-3})	1.407
μ (mm^{-1})	0.923
F_{000}	712
θ-range (deg)	2.50−25.68
data collected (h,k,l)	±7, ±18, ±20
no. of reflns collected	21 864
no. of indep reflns/R_{int}	2866 (all)/0.0413
no. of obsd reflns ($I>2\sigma(I)$)	2195 (obsd)
no. of params refined	251
R1 (obsd/all)	0.0239/0.0351
wR2 (obsd/all)	0.0579/0.0602
GOF(obsd/all)	0.946/0.946
max/min $\Delta\rho$ (e Å^{-3})	+0.25/−0.16

Acknowledgment. Financial support for this research by DGICYT (Proyect PB97-0776) is gratefully acknowledged.

Supporting Information Available: Tables of crystal data, data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for complex **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0110890

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