Linked Benzylamido-Cyclopentadienyl Ligands: Synthesis and Characterization of Alkyl Titanium Complexes

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Titanium complexes of the general type $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3X_2\text{-}2,5)Cl_2$ (X = H, F), containing a linked benzylamido-cyclopentadienyl ligand, were prepared by reaction of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ with lithium amide $Li(NHCH_2C_6H_3X_2\text{-}2,5)$. A single-crystal X-ray structural analysis of $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,5)Cl_2$ revealed a conformation in the solid state in which the aryl ring is turned away from the metal center. $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_5)Cl_2$ can be alkylated with a variety of reagents to form extremely sensitive complexes of the type $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_5)R_2$ (R = Me, $CH_2C_6H_5$, CH_2SiMe_3, $CH_2CMe_2C_6H_5$). Reaction of $Li_2[C_5Me_4SiMe_2NCH_2C_6H_5]$ with $TiCl_3(THF)_3$ gave $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2C_6H_5)Cl_2$, which can also be alkylated to form dialkyl complexes of the type $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2C_6H_5)R_2$ (R = Me, $CH_2C_6H_5$, CH_2SiMe_3, C_6H_5). A single-crystal X-ray structural analysis of $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2C_6H_5)(CH_2C_6H_5)_2$ suggests the presence of α-agostic bonding of one of the titanium-bound $CH_2C_6H_5$ groups to the titanium center.

Introduction

Cyclopentadienyl ligands with an appended donor group[1] establish novel classes of d- and f-block metal complexes with coordination spheres significantly distinct from the ubiquitous bis(cyclopentadienyl)metal units. With the aim of controlling the catalytic behavior of the metal center more broadly, amido-functionalized cyclopentadienyl ligands have had a considerable impact on the design of new homogeneous catalysts for α-olefin polymerization[2]. Whilst the variation of the ring substituents and the nature of the bridge should be comparable to the situation in Brintzinger-type *ansa*-metallocenes, the modification of the amido substituent[3] will be critical as well. To date, no systematic variation of the amido substituent has appeared in the literature, although a rather significant substituent effect has been noted occasionally[4,5]. Recently a dramatic change in the copolymerization behavior toward ethylene and styrene was observed when the *tert*-butyl group on the amido function was replaced by a benzyl group[5]. We report here some synthetic and structural results for titanium complexes with an amido-cyclopentadienyl ligand bearing a benzylamido substituent.

Results and Discussion

For the successful preparation of titanium complexes with one linked amido-cyclopentadienyl ligand, the method first described by Royo et al.[6] has now been well established[3]. Thus, reaction of excess lithium amide Li(NRH) (R = *t*Bu, $CH_2CH_2NMe_2$, CH_2CH_2OMe) with $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ leads to the corresponding complex of general type $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NR)Cl_2$. In order to circumvent the use of excess amide which is required to remove hydrogen chloride, we have tested a variety of conditions under which the reaction would proceed in the desired way by employing just stoichiometric amounts of lithium amide. The use of at least one equivalent of triethylamine in addition to the stoichiometric amount of lithium amide gives satisfactory yields of the desired linked amido-cyclopentadienyl complex $Ti(\eta^5\text{-}C_5H_4SiMe_2NR)Cl_2$ in good yields after workup. This improved method applies generally to organyl groups on the amido nitrogen such as benzyl and isopropyl to give the corresponding product $Ti(\eta^5\text{-}C_5H_4SiMe_2NR)Cl_2$ **1** (R = $CH_2C_6H_5$) and **2** (R = *i*Pr), respectively. Thus, analytically pure yellow, moisture-sensitive dichloro complex $Ti(\eta^5\text{-}C_5H_4SiMe_2NCH_2C_6H_5)Cl_2$ (**1**) is isolated in 72% yield when $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ is treated with lithium benzylamide in THF in the presence of triethylamine. ^{1}H- and ^{13}C-NMR spectroscopic as well as mass spectral and analytical data confirm the structure of a mono(ligand) complex. The most peculiar spectroscopic feature is the significant deshielding of the proton signal due to the benzylic CH_2 group δ = 5.48 (Δδ > 1 ppm), which may be ascribed to the anisotropic effect caused by the titanium amido-nitrogen double bond. This phenomenon[3f] is even more pronounced in the isopropylamido derivative **2**. The methine proton of the isopropyl group in this complex is recorded as a septet at δ = 5.69. According to a single-crystal structural analysis; pertinent structure parameters of the molecule are comparable with those of similar complexes[2,3] containing the amido-cyclopentadienyl ligand (Figure 1). Thus, the amido nitrogen is planar and the short nitrogen–titanium bond length of 187.8(2) pm is due to nitrogen-to-metal π donation[7]. Similar bond parameters were found in related half-sandwich titanium amido complexes, e.g., in $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NtBu)Cl_2$[3h], $Ti(\eta^5\text{-}C_5H_5)Cl_2(NiPr_2)$[7b], and $Ti(\eta^5\text{-}C_5H_5)Cl_2(NHtBu)$[7c]. In $Ti(\eta^5\text{-}C_5H_5)Cl_2(NiPr_2)$, a β-agos-

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tic interaction with a bond length of 224 pm was detected. The corresponding value for the Ti–H distance in **2** is 279 pm, thus beyond a direct bonding situation. However, the conformation in which one β-hydrogen atom is turned to the metal center may be due to a weak interaction.

Scheme 1

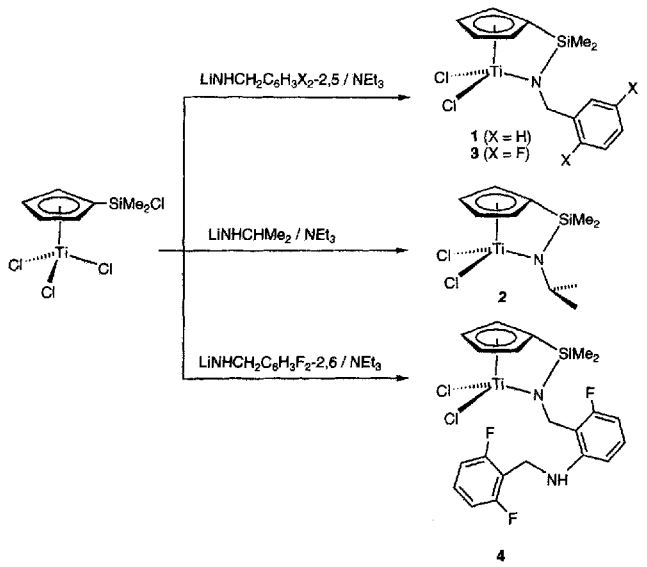
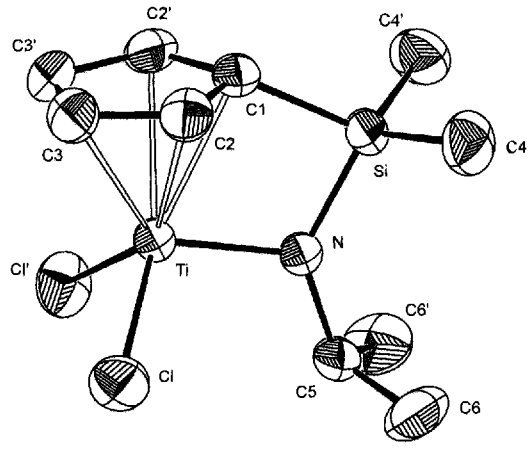
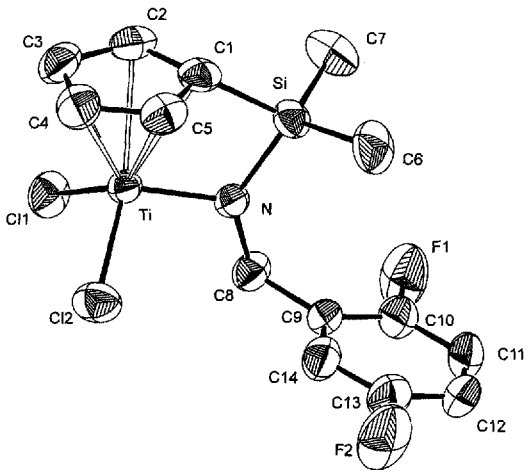


Figure 1. ORTEP diagram of the molecular structure of $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCHMe_2)Cl_2$ (**2**): thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for sake of clarity; selected bond distances (pm) and angles (°): Ti–N 187.8(2), Ti–Cl 230.2(2), Ti–C2 232.7(2), Ti–C3 238.6(2), Ti–Cl 226.59(6), Ti–N–Si 108.7(1), Ti–N–C5 117.4(1), Si–N–C5 133.9(2), N–C5–C6 110.9(1), C6–C5–C6 112.3(3), Cl–Ti–Cl 102.88(4)



In order to probe the generality of the access for ring-substituted derivatives, the synthesis of the 2,5-difluorobenzylamido along **3** was performed. Yellow crystals of **3** were obtained in moderate yield. Besides elemental, NMR spectroscopic and mass spectral analysis, a single-crystal structural analysis of **3** was performed. NMR spectra reveal the presence of a mirror plane that results from the free rotation about the benzylic carbon–aromatic carbon bond.

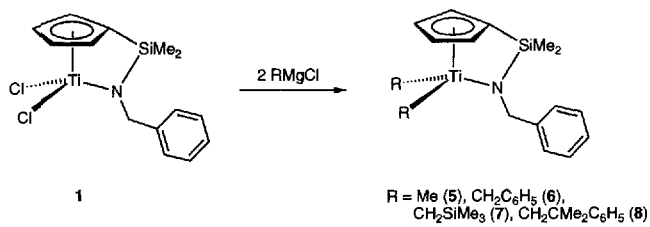
Figure 2. ORTEP diagram of the molecular structure of $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,5)Cl_2$ (**3**): thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (pm) and angles (°): Ti–N 189.0(2), Ti–Cl 231.1(2), Ti–C2 233.3(2), Ti–C3 237.5(2), Ti–C4 236.7(3), Ti–C5 232.0(2), Ti–Cl1 225.75(7), Ti–Cl2 225.86(7), N–C8–C9 111.7(2), Cl1–Ti–Cl2 105.27(3), Ti–N–Si 108.54(9), C8–N–Ti 119.7(1), Si–N–C8 131.8(2)



The most striking structural feature is the conformation of the benzyl group, which is turned away from the metal center. All other bonding parameters are comparable to those found in **2** as well as in other linked amido-cyclopentadienyl titanium complexes (vide supra).

When we attempted to prepare the 2,6-difluorobenzyl derivative by reacting $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ with $Li(NHCH_2C_6H_3F_2\text{-}2,6)$, quite surprisingly the yellow crystals isolated turned out to be complex **4**. The amido ligand in **4** was modified as a result of a nucleophilic substitution at one *ortho*-fluorine atom by another molecule of 2,6-difluorobenzylamide. The ^{1}H-NMR spectrum shows a sharp singlet at $\delta = -0.03$ for the protons of the $SiMe_2$ group and two triplet-like signals for the two sets of cyclopentadienyl ring protons at $\delta = 6.37$ and 6.50, suggesting that the molecule retains a mirror plane. In addition to two signals due to the CH_2 groups at $\delta = 4.27$ and 5.63, five multiplets are recorded due to the protons in the two phenyl rings. The signal for the NH group is observed as a triplet at 4.74 ppm. The IR spectrum clearly reveals the presence of this group through an absorption at 3400 cm^{-1}. The formation of **4** is ascribed to the fact that excess lithium 2,6-difluorobenzylamide obviously reacts more readily with the expected complex $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,6)Cl_2$ at one of the *ortho*-fluorines than with the Si–Cl function of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$. Prior coupling of the benzylamines is excluded, since the lithiation of 2,6-difluorobenzylamine with *n*-butyllithium proceeds without complications.

In view of their importance as potential precursors for α-olefin polymerization catalysts, the synthesis of alkylated derivatives of **1** was studied. Dialkyl complexes of the type $Ti(\eta^5\text{-}C_5H_4SiMe_2NCH_2C_6H_5)R_2$ were shown to form with



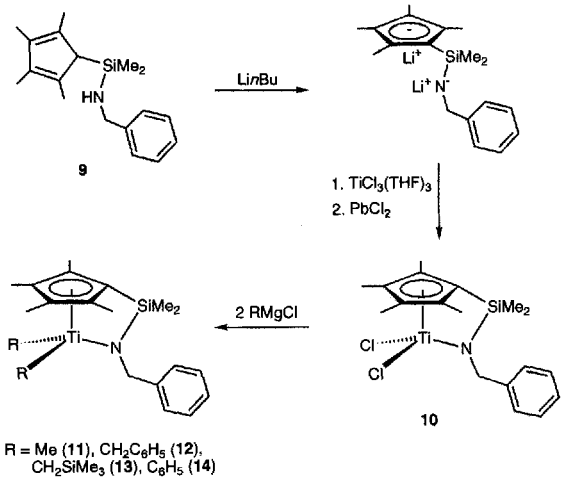
1

R = Me (5), $CH_2C_6H_5$ (6), CH_2SiMe_3 (7), $CH_2CMe_2C_6H_5$ (8)

R = Me (**5**), $CH_2C_6H_5$ (**6**), CH_2SiMe_3 (**7**), and $CH_2CMe_2C_6H_5$ (**8**) using Grignard reagents according to eq. 1. All compounds were extremely sensitive not only towards air and moisture, but also to light. In particular, the dimethyl **5** could not be stored for more than hours at ambient temperature. The high sensitivity resembles that of the "parent" $Ti(\eta^5\text{-}C_5H_5)Me_3$[8], although steric hindrance is known to impart a certain degree of thermal stability, as was shown for $Ti[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]Me_3$[9].

The synthesis of complexes in the C_5Me_4 series analogous to **1** was achieved following the well-established procedure for other complexes containing ligands of the general type $C_5Me_4SiMe_2NR$. Thus, reaction of benzylamidosilane **9** with 2 equivalents of *n*-butyllithium cleanly afforded the dilithium derivative $Li_2(C_5Me_4SiMe_2NCH_2C_6H_5)$. This compound was treated with titanium trichloride tris(tetrahydrofuran), followed by reaction with lead dichloride, to give yellow crystals of $Ti(\eta^5\text{-}C_5Me_4SiMe_2NCH_2C_6H_5)Cl_2$ (**10**) in 55% yield (Scheme 2). Elemental analysis, NMR spectroscopic and mass spectral data are fully in agreement with the expected structure. In the ^{1}H-NMR spectrum the signal for the CH_2 group at the amido-function appears at $\delta = 5.35$, slightly upfield compared to the corresponding signal in **1**.

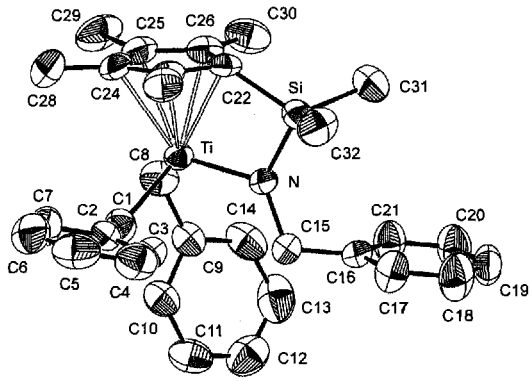
Scheme 2



R = Me (**11**), $CH_2C_6H_5$ (**12**), CH_2SiMe_3 (**13**), C_6H_5 (**14**)

Alkylations of **10** with appropriate Grignard or lithium reagents gave the corresponding dialkyl complexes $Ti(\eta^5\text{-}C_5Me_4SiMe_2NCH_2C_6H_5)R_2$ with R = Me (**11**), $CH_2C_6H_5$ (**12**), CH_2SiMe_3 (**13**) and C_6H_5 (**14**), which were characterized by spectroscopic and mass spectral analysis. As in the case of the complexes of the C_5H_4 scries, these derivatives proved to be too sensitive for elemental analysis. However, the dibenzyl complex **12** was isolated as fairly robust red crystals in good yield and was characterized completely by elemental analysis, ^{1}H- and ^{13}C-NMR and mass spectral data. The CH_2 groups give rise to an AB pattern at $\delta = 2.18$ and 2.35 in the ^{1}H-NMR spectrum, while in the ^{13}C-NMR spectrum a triplet with $J_{CH} = 125$ Hz appears at $\delta = 80.6$.

Figure 3. ORTEP diagram of the molecular structure of $Ti(\eta^5\text{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2C_6H_5)(CH_2C_6H_5)_2$ (**12**): thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (pm) and angles (°): Ti–N 191.9(3), Ti–C1 213.1(5), Ti–C8 215.7(5), Ti–C22 229.7(4), Ti–C23 236.4(4), Ti–C24 243.5(4), Ti–C25 243.2(4), Ti–C26 234.5(4), Ti–C1–C2 131.3(3), Ti–C8–C9 110.6(3), C1–Ti–C8 100.8(2), Ti–N–Si 105.3(2), C15–N–Ti 125.3(3), Si–N–C15 127.7(3), N–C15–C16 114.3(4)



However, the dibenzyl complex **12** was isolated as fairly robust red crystals in good yield and was characterized completely by elemental analysis, ^{1}H- and ^{13}C-NMR and mass spectral data. The CH_2 groups give rise to an AB pattern at $\delta = 2.18$ and 2.35 in the ^{1}H-NMR spectrum, while in the ^{13}C-NMR spectrum a triplet with $J_{CH} = 125$ Hz appears at $\delta = 80.6$.

A single-crystal X-ray structural analysis was performed on the dibenzyl complex **12** (Figure 3). The molecular structure can be described as pseudotetrahedral with the usual distortion observed at the titanium center caused by the dimethylsilane-bridged amido-cyclopentadienyl ligand. As was observed for **2**, the phenyl group at the amido function is also turned away from the metal center. The two benzyl groups adopt different conformations: One is turned away form the cyclopentadienyl ligand whereas the other is arranged in such a way that its phenyl ring is coplanar with both the C_5Me_4 ring and the amido group's phenyl. An interesting feature is that the latter benzyl group clearly exhibits an α-agostic bonding interaction of the CH_2-hydrogen atoms with the titanium center. Although not as pronounced as in $Ti(\eta^5\text{-}C_5Me_5)(CH_2C_6H_5)_3$[10], this bonding situation, which is typical for a Lewis-acidic metal center, can be deduced from comparison of the geometrical parameters of the two benzyl groups: The angle at the benzylic carbon (C1) of this benzyl group is 131.3(3)°, i.e. 20° larger than the angle at the carbon atom (C8) of the other group. The titanium–hydrogen distances for the former benzyl group (240 pm) are on average slightly shorter than those of the second benzyl group (255 pm). These values are obviously similar to those found in $Ti(\eta^5\text{-}C_5Me_5)(CH_2C_6H_5)_3$ (232 and 237 pm for the agostic CH_2 group)[10].

The dibenzyl complex **12** is thermally rather stable. NMR spectroscopic studies show that it does not appear to decompose when a hexane solution is heated to reflux for 3 h. The presence of PMe_3 does not induce any reaction either. Preliminary reactions with $B(C_6F_5)_3$ resulted in the forma-

tion of intractable mixtures. We are continuing to isolate and characterize cationic and Ti(III) species which may form under polymerization conditons.

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Experimental Section

General: All manipulations were performed under argon using standard Schlenk techniques. Solvents were purified, dried, and distilled under argon. – ^{1}H and ^{13}C NMR: Bruker AC 200 or Bruker AM 400. – Mass spectra: Finnigan 8230. – IR: Nicolet FT-5-DX. – Elemental analyses: Microanalytical laboratory of this department. – Solutions of MgMeCl, $Mg(CH_2SiMe_3)Cl$, LiC_6H_5, and Li*n*Bu were purchased from Aldrich and used as received. The following reagents were synthesized using literature procedures: $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$[6], $C_5Me_4H(SiMe_2Cl)$[2b], $TiCl_3(THF)_3$[11], $Mg(CH_2C_6H_5)_2(THF)_2$[12], and $LiCH_2CMe_2C_6H_5$[13].

Dichloro[η^5:η^1-N-(cyclopentadienyldimethylsilyl)benzylamido]titanium (**1**): To a mixture of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ (2.50 g, 8.0 mmol) and $Li(NHCH_2C_6H_5)$ (0.91 g, 8.0 mmol) was added a solution of triethylamine (1.1 ml, 8.0 mmol) in 80 ml of THF at −60 °C and the mixture was stirred for 5 h at room temp. After removal of all volatiles in vacuo, the residue was extracted with 60 ml of diethyl ether. The solvent was removed completely and the crude product recrystallized from hexane/toluene (1:2) at −30 °C to give $Ti(\eta^5\text{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_5)Cl_2$ (**1**) as yellow crystals; yield: 1.62 g (72%). – ^{1}H NMR ($CDCl_3$): δ = 0.10 (s, 6H, $SiCH_3$), 5.48 (s, 2H, CH_2), 6.48 ("t", 2H, C_5H_4), 7.00 ("t", 2H, C_5H_4), 7.24 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.3 ($SiCH_3$), 61.8 (CH_2), 110.1 (C_5H_4 at Si), 123.9, 126.3 (C_5H_4), 128.0 (*p*-C_6H_5), 128.8 (*o*-, *m*-C_6H_5), 139.8 (*ipso*-C_6H_5). – EI-MS; *m/z* (%): 345 (16) [M^+], 310 (100) [M^+ − Cl], 240 (26) [M^+ − NCH_2Ph], 205 (37) [M^+ − Cl, − NCH_2Ph], 148 (10) [$C_8H_{10}NSi^+$], 122 (11) [$C_7H_{10}Si^+$], 106 (68) [$C_7H_7NH^+$], 91 (37) [$C_7H_7^+$]. – $C_{14}H_{17}Cl_2NSiTi$ (346.2): calcd. C 48.59, H 4.95, N 4.05; found C 48.69, H 5.01, N 4.21.

Dichloro[η^5:η^1-N-(cyclopentadienyldimethylsilyl)isopropylamido]titanium (**2**): Complex **2** was obtained from $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$, lithium isopropylamide and triethylamine as yellow crystals in a manner analogous to that described for the synthesis of $Ti(\eta^5\text{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_5)Cl_2$ (**1**); yield: 42%. – ^{1}H NMR(C_6D_6): δ = 0.21 (s, 6H, $SiCH_3$), 1.04 (d, $^3J_{HH}$ = 6 Hz, 6H, CCH_3), 5.69 (sept, $^3J_{HH}$ = 6 Hz, 1H, $CHMe_2$), 6.14 ("t", 2H, C_5H_4), 6.59 ("t", 2H, C_5H_4). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = −0.9 ($SiCH_3$), 23.5 (CCH_3), 58.2 (CCH_3), 108.1 (C_5H_4 at Si), 124.0, 125.5 (C_5H_4). – EI-MS; *m/z* (%): 297 (7) [M^+], 282 (100) [M^+ − Me], 262 (4) [M^+ − Cl], 241 (57) [M^+ − $NCHMe_2$], 92 (7) [$C_5H_4Si^+$]. – $C_{10}H_{13}Cl_2NSiTi$ (298.1): calcd. C 40.29, H 5.75, N 4.70; found C 39.61, H 6.84, N 4.57.

X-ray Crystal Structure Analysis of Ti(η^5:η^1-$C_5H_4SiMe_2NCHMe_2$)Cl_2 (**2**): Yellow cubes of $Ti(\eta^5\text{:}\eta^1\text{-}C_5H_4SiMe_2NCHMe_2)Cl_2$ were obtained by slow cooling in diethyl ether. Cell dimensions and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer: $C_{10}H_{17}Cl_2NSiTi$, M = 298.15, a = 1227.4(1), b = 1209.9(2), c = 933.9(1) pm, Z = 8/2, $d_{calcd.}$ = 1.43 Mgm^{-3}, orthorhombic, *Pnma* (No. 62), Mo-K_α (λ = 71.07 pm), graphite monochromator, 0.3 × 0.3 × 0.6 mm, T = 293(2) K, 3.00° < Θ < 30.00°, F(000) = 616.0. Number of reflections measured 2800, 2316 independent reflections [R(int) = 0.016] of which 1548 were assigned observed [$I > 3\sigma(I)$], absorption coefficient 10.56 cm^{-1}. The structure was solved by direct methods (MULTAN) and difference Fourier synthesis and refined using MolEN. Hydrogen atoms were included in calculated positions, except for the hydrogen atom of the isopropyl CH group whose coordinates were refined. The refinement (78 parameters) converged with R = 0.029, Rw = 0.036, $w = 1/\sigma^2(F_o)$ for the observed F_o data, goodness of fit. 1.474. The residual electron density was 0.18 · 10^3 e m^{-3}[14].

Dichloro[η^5:η^1-N-(cyclopentadienyldimethylsilyl)-2,5-difluorobenzylamido]titanium (**3**): To a solution of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ (2.13 g, 6.8 mmol) and triethylamine (0.95 ml, 6.8 mmol) in 20 ml of THF was added dropwise a solution of lithium 2,5-difluorbenzylamide (1.02 g, 6.8 mmol) in 35 ml of THF at −60 °C. The mixture was allowed to warm to room temp. and stirred for 3 h. All volatiles were removed under vacuum and the residue was extracted with 80 ml of diethyl ether and 10 ml of hexane. Concentrating the extracts and crystallization afforded 1.15 g (44%) of **3** as yellow crystals. – ^{1}H NMR (C_6D_6): δ = 0.00 (s, 6H, $SiCH_3$), 5.40 (d, $^4J_{HF}$ = 2 Hz, 2H, CH_2), 6.08 ("t", 2H, C_5H_4), 6.50 (overlap. m, 4H, C_5H_4, $C_6H_3F_2$), 7.27 (m, 1H, $C_6H_3F_2$). – ^{13}C NMR (C_6D_6): δ = −3.5 ($SiCH_3$), 53.3 (CH_2), 109.7 (C_5H_4 at Si), 115.9 (dd, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 9 Hz, C4), 116.4 (dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 9 Hz, C3), 118.0 (dd, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 4 Hz, C6), 124.1, 126.3 (C_5H_4), 128.9 (dd, $^2J_{CF}$ = 18 Hz, $^3J_{CF}$ = 8 Hz, *ipso*-$C_6H_3F_2$), 156.5 (d, $^1J_{CF}$ = 231 Hz, C2), 158.9 (d, $^1J_{CF}$ = 232 Hz, C5). – EI-MS; *m/z* (%): 381 (22) [M^+], 346 (54) [M^+ − Cl], 327 (10) [M^+ − Cl, − F], 311 (20) [M^+ − 2 Cl], 240 (22) [M^+ − $NCH_2C_6H_3F_2$], 148 (9) [$C_8H_{10}NSi^+$], 142 (90) [$HNCH_2C_6H_3F_2^+$], 125 (100) [$C_7H_3F_2^+$], 75 (15) [$C_2H_9NSi^+$]. – $C_{14}H_{15}Cl_2F_2NSiTi$ (382.2): calcd. C 44.00, H 3.96, N 3.67; found C 44.07, H 3.96, N 3.65.

X-ray Crystal Structure Analysis of Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2C_6H_3F_2$-2,5)$Cl_2$ (**3**): Yellow cubes of $Ti(\eta^5\text{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,5)Cl_2$ were obtained by slow cooling in hexane. Cell dimensions and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer: $C_{14}H_{15}Cl_2F_2NSiTi$, M = 382.17, a = 690.5(2), b = 1121.5(5), c = 2174.0(3) pm, β = 97.21(3)°, Z = 4, $d_{calcd.}$ = 1.52 Mgm^{-3}, monoclinic, $P2_1/c$ (No. 14), Mo-K_α (λ = 71.07 pm), graphite monochromator, 0.40 × 0.50 × 0.70 mm, T = 293(2) K, 3.00° < Θ < 30.00°, F(000) = 776. Number of reflections measured 10463, 4850 independent reflections [R(int) = 0.033] of which 2688 were assigned observed [$I > 3\sigma(I)$], absorption coefficient 9.10 cm^{-1}. The structure was solved by direct methods (MULTAN) and difference Fourier synthesis and refined using MolEN. All non-hydrogen atoms were refined with anistropic temperature factors. Hydrogen atoms were refined in their positions with isotopic temperature factors. The refinement (235 parameters) converged with R = 0.030, Rw = 0.034, $w = 1/\sigma^2(F_o)$ for the observed F_o data, goodness of fit 1.071. The residual electron density was 0.28 · 10^{30} em^{-3}[14].

Dichloro[η^5:η^1-N-(cyclopentadienyldimethylsilyl)-2-(2,6-difluorobenzylamino)-6-fluorobenzylamido]titanium (**4**): $Ti\{\eta^5\text{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2[C_6H_3F\text{-}6\text{-}(NHCH_2C_6H_3F_2\text{-}2,6)\text{-}2]\}Cl_2$ was obtained from the reaction of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ with lithium 2,6-difluorobenzylamide in the presence of triethylamine as yellow crystals in a manner analogous to that described for the synthesis of $Ti(\eta^5\text{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,6)Cl_2$ (**3**); yield: 32%. – ^{1}H NMR (C_6D_6): δ = 0.09 (s, 6H, $SiCH_3$), 4.27 (d, $^3J_{HH}$ = 5 Hz, 2H, $NHCH_2$), 4.74 (t, $^3J_{HH}$ = 5 Hz, 1H, NH), 5.63 (d, $^4J_{HF}$ = 2 Hz, 2H, NCH_2), 6.37 ("t", 2H, C_5H_4), 6.41 (m, 1H, C_6H_3F), 6.50 (overlap. m, 2H, C_5H_4; 1H, C_6H_3F), 6.63 (m, 2H, C_6H_3F), 6.74 (m, 1H, C_6H_3F), 6.95 (m, 1H, C_6H_3F). – $^{13}C\{^1H\}$ NMR (C_6D_6):

δ = −3.7 ($SiCH_3$), 35.8 ($NHCH_2$), 50.6 (d, $^3J_{CF}$ = 7 Hz, NCH_2), 103.7 (d, $^2J_{CF}$ = 23 Hz, C_6H_3F), 105.9 (C_5H_4 at Si), 111.2 (m, C_6H_3F), 114.8 (t, $^2J_{CF}$ = 19 Hz, C_6H_3F), 123.6, 126.3 (C_5H_4), 127.9 (C_6H_3F), 129.7 (t, $^2J_{CF}$ = 10 Hz, C_6H_3F), 130.2 (d, $^2J_{CF}$ = 10 Hz, C_6H_3F), 148.8 (d, $^3J_{CF}$ = 6 Hz, C_6H_3F), 161.3 (d, $^1J_{CF}$ = 243 Hz, C_6H_3F), 162.2 (dd, $^1J_{CF}$ = 243 Hz, $^3J_{CF}$ = 8 Hz, C_6H_3F). – IR: $\tilde{\nu}$ = 3400 cm^{-1} (NH). – EI-MS; *m/z* (%): 504 (3) [M^+], 341 (4) [$C_{15}H_{15}Cl_2SiTi^+$], 266 (20) [$C_8H_{10}Cl_2NSiTi^+$], 249 (100) [$CHC_6H_3F - NHCH_2C_6H_3F_2^+$], 201 (11) [$C_8H_{15}NSiTi^+$], 136 (36) [$C_7H_{10}NSi^+$], 127 (32) [$C_7H_5F_2^+$], 109 (8) [$C_7H_6F^+$]. – $C_{21}H_{21}Cl_2F_3NSiTi$ (505.3): calcd. C 49.92, H 4.19, N 5.54; found C 48.41, H 4.65, N 5.40.

[η⁵:η¹-N-(Cyclopentadienyldimethylsilyl)benzylamido]dimethyltitanium (**5**): A solution of **1** (0.40 g, 1.20 mmol) in 40 ml of THF was cooled to −60°C and methylmagnesium chloride (0.83 ml, 3 M solution in THF) was slowly added. The mixture was allowed to warm up to room temp. and stirred for 4 h. Removal of the solvent in vacuo afforded a brown oil which was dissolved in 30 ml of hexane and filtered. Cooling the filtrate to −60°C gave **5** as extremely sensitive, waxy white solid; yield: 0.23 g (65%). – ^{1}H NMR (C_6D_6): δ = 0.06 (s, 6H, $SiCH_3$), 0.77 (s, 6H, $TiCH_3$), 5.00 (s, 2H, CH_2), 5.99 ("t", 2H, C_5H_4), 6.83 ("t", 2H, C_5H_4), 7.27 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 0.13 ($SiCH_3$), 51.18 ($TiCH_3$), 56.33 (CH_2), 103.17 (C_5H_4 at Si), 118.82, 122.65 (C_5H_4), 127.23 (*p*-C_6H_5), 128.61 (*o*-C_6H_5), 128.66 (*m*-C_6H_5), 142.89 (*ipso*-C_6H_5). – EI-MS; *m/z* (%): 305 (100) [M^+], 290 (46) [M^+ − Me], 275 (58) [M^+ − 2 Me], 195 (21) [M^+ − 2 Me, − C_6H_8], 186 (37) [MH_2^+ − 2 Me, − CH_2Ph], 169 (16) [M^+ − 2 Me, − $NHCH_2Ph$], 153 (12) [M^+ − 3 Me, − NH_2CH_2Ph], 140 (5) [M^+ − $C_{11}H_{19}N$], 113 (6) [MH^+ − $C_{11}H_{19}NSi$], 106 (5) [$C_7H_7NH^+$], 91 (63) [$C_7H_7^+$]. – $C_{16}H_{23}NSiTi$ (305.4): calcd. C 62.94, H 7.59, N 4.59; found C 56.44, H 6.58, N 6.87.

Dibenzyl[η⁵:η¹-N-(cyclopentadienyldimethylsilyl)benzylamido]titanium (**6**): To a mixture of **1** (1.02 g, 2.94 mmol) and dibenzylmagnesiumbis(tetrahydrofuran) (1.03 g, 2.94 mmol) was added 60 ml of hexane, cooled to −78°C. The suspension was warmed to room temp. and stirred for 20 h to give a deep red mixture with a white precipitate. All volatiles were removed under vacuum, the oily red residue was extracted with 60 ml of hexane and filtered. Recrystallization at −20°C gave 1.07 g of **6** as red crystals; yield: 80%. – ^{1}H NMR (C_6D_6): δ = −0.13 (s, 6H, $SiCH_3$), 2.32 (d, $^2J_{HH}$ = 10 Hz, 2H, $TiCH_2$), 2.68 (d, $^2J_{HH}$ = 10 Hz, 2H, $TiCH_2$), 5.15 (s, 2H, NCH_2), 5.51 ("t", 2H, C_5H_4), 6.43 ("t", 2H, C_5H_4), 6.87 (m, 5H, $NCH_2C_6H_5$), 7.17 (m, 10H, $TiCH_2C_6H_5$). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 0.3 ($SiCH_3$), 57.6 (NCH_2), 80.8 ($TiCH_2$), 105.6 (C_5H_4 at Si), 122.2, 122.3, 125.1, 126.1, 128.3, 128.7, 129.1 (C_5H_4, *p*-, *o*-, *m*-$NCH_2C_6H_5$, *p*-, *o*-, *m*-$TiCH_2C_6H_5$), 142.1 (*ipso*-$NCH_2C_6H_5$), 148.3 (*ipso*-$TiCH_2C_6H_5$). – EI-MS; *m/z* (%): 367 (32) [M^+ − CH_2Ph], 276 (100) [M^+ − 2 CH_2Ph], 196 (4) [MH^+ − 2 CH_2Ph, − Ph], 170 (10) [M^+ − 2 CH_2Ph, − NCH_2Ph], 140 (3) [M^+ − $C_{23}H_{27}N$], 91 (100) [$C_7H_7^+$]. – $C_{28}H_{31}NSiTi$ (457.5): calcd. C 73.51, H 6.83, N 3.06; found C 73.21, H 6.93, N 3.15.

[η⁵:η¹-N-(Cyclopentadienyldimethylsilyl)benzylamido]-bis(trimethylsilylmethyl)titanium (**7**): A solution of trimethylsilylmethylmagnesium chloride (4.80 ml, 1 M in diethyl ether) was added to a solution of **1** (0.80 g, 2.3 mmol) in 60 ml of hexane at −50°C. After the addition was complete, the reaction mixture was allowed to warm up to room temp. and left stirring for 5 h. The solvent was removed under vacuum and extraction of the residue with hexane (60 ml), followed by filtration and crystallization at −78°C, afforded 0.54 g of **7** as extremely sensitive, colorless crystals; yield: 52%. – ^{1}H NMR (C_6D_6): δ = 0.17 (s, 6H, $SiCH_3$), 0.27 (s, 18H, CH_2SiCH_3), 1.17 (d, $^2J_{HH}$ = 11 Hz, 2H, $TiCH_2$), 1.60 (d, $^2J_{HH}$ = 11 Hz, 2H, $TiCH_2$), 5.38 (s, 2H, NCH_2), 6.25 ("t", 2H, C_5H_4), 7.00 ("t", 2H, C_5H_4), 7.32 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = −0.37 ($SiCH_3$), 2.7 (CH_2SiCH_3), 58.7 (NCH_2), 103.2 (C_5H_4 at Si), 117.4, 122.7 (C_5H_4), 128.3 (*p*-C_6H_5), 128.7 (*o*-C_6H_5), 129.3 (*m*-C_6H_5), 142.3 (*ipso*-C_6H_5). – EI-MS: *m/z* (%): 434 (2) [M^+ − Me], 362 (38) [M^+ − CH_2SiMe_3], 275 (100) [M^+ − 2 CH_2SiMe_3], 184 (4) [M^+ − 2 CH_2SiMe_3, − CH_2Ph], 169 (6) [M^+ − 2 CH_2SiMe_3, − NCH_2Ph], 153 (3) [M^+ − $C_{16}H_{34}NSi_2^+$], 106 (3) [$PhCH_2NH^+$]. – $C_{22}H_{39}NSi_3Ti$ (449.7): calcd. C 58.76, H 8.74, S 3.11; found C 59.82, H 9.16, N 3.45.

[η⁵:η¹-N-(Cyclopentadienyldimethylsilyl)benzylamido]-dineophyltitanium (**8**): Following a procedure analogous to that described for the preparation of **7**, **1** (0.82 g, 2.34 mmol) was reacted with $LiCH_2CMe_2Ph$ (0.66 g, 4.74 mmol) to give **8** as yellow crystals in 38% yield. – ^{1}H NMR (C_6D_6): δ = −0.04 (s, 6H, $SiCH_3$), 1.26 (s, 6H, CCH_3), 1.29 (s, 6H, CCH_3), 1.55 (d, $^2J_{HH}$ = 11 Hz, 2H, $TiCH_2$), 2.21 (d, $^2J_{HH}$ = 11 Hz, 2H, $TiCH_2$), 5.27 (s, 2H, NCH_2), 5.73 ("t", 2H, C_5H_4), 6.01 ("t", 2H, C_5H_4), 7.21 (m, 15H, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = −1.6 ($SiCH_3$), 32.7, 34.8 (CCH_3), 44.0 (CCH_3), 59.3 (NCH_2), 97.1 ($TiCH_2$), 102.2 (C_5H_4 at Si), 117.5, 123.9 (C_5H_4), 125.6, 125.7, 126.7, 128.3, 128.7, 129.4 (*p*-, *o*-, *m*-$CH_2C_6H_5$, *p*-, *o*-, *m*-$TiCH_2CMe_2Ph$), 142.4 (*ipso*-$CH_2C_6H_5$), 152.5 (*ipso*-$CMe_2C_6H_5$). – EI-MS; *m/z* (%): 266 (7) [(2 CH_2CMePh)$^+$], 195 (3) [M^+ − $C_{26}H_{34}$], 134 (19) [$PhCMe_3^+$], 119 (100) [$PhCMe_2^+$], 106 (37) [$PhCH_2NH^+$], 91 (52) [$C_7H_7^+$]. – $C_{34}H_{43}NSiTi$ (541.7): calcd. C 75.39, H 8.00, N 2.59; found C 68.99, H 9.98, N 3.14.

N-[Dimethyl(tetramethylcyclopentadienyl)silyl]benzylamine (**9**): (C_5Me_4H)($SiMe_2Cl$) (4.1 g, 19.0 mmol) was added to a suspension of $LiNHCH_2Ph$ (2.2 g, 19.0 mmol) in 30 ml of hexane at −78°C. The reaction mixture was allowed to room temp. and stirred for 14 h. Filtration of the resulting solution and removal of the solvent in vacuo gave crude (C_5Me_4H)$SiMe_2NHCH_2Ph$ as a yellow oil which was distilled at 105°C and $8 \cdot 10^{-3}$ mbar; yield: 4.6 g (84%). – ^{1}H NMR (C_6D_6): δ = −0.05 (s, 6H, $SiCH_3$), 1.75 (s, 6H, CCH_3), 1.91 (s, 6H, CCH_3), 2.91 (s, 1H, C_5H), 3.85 (d, $^2J_{HH}$ = 8 Hz, 2H, CH_2), 7.23 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = −0.3 ($SiCH_3$), 11.2, 14.4 (CCH_3), 46.1 (CH_2), 56.8 (C_5Me_4 at Si), 126.4, 126.9, 128.2 (*p*-, *o*-, *m*-C_6H_5), 132.9, 135.7 (CCH_3), 144.1 (*ipso*-C_6H_5). – EI-MS; *m/z* (%): 285 (15) [M^+], 196 (9) [MH^+ − CH_2Ph], 180 (7) [$C_{11}H_{20}Si^+$], 164 (100) [$PhCH_2NHSiMe_2^+$], 148 (7) [$C_8H_{10}NSi^+$], 135 (62) [$C_7H_9NSi^+$], 107 (65) [$C_9H_{13}^+$], 91 (44) [$C_7H_7^+$], 75 (69) [$C_2H_9NSi^+$]. – $C_{18}H_{27}NSi$ (285.5): calcd. C 75.72, H 9.53, N 4.91; found C 74.50, H 9.82, N 4.99.

Dichloro{η⁵:η¹-N-[dimethyl(tetramethylcyclopentadienyl)silyl]-benzylamido}titanium (**10**): Crude $Li_2(C_5Me_4SiMe_2NCH_2Ph)$ (3.84 g, 12.9 mmol), obtained by double deprotonation of (C_5Me_4H)$SiMe_2NHCH_2Ph$ with *n*-butyllithium in hexane, was dissolved in 80 ml of THF and added dropwise to a suspension of $TiCl_3(THF)_3$ (4.78 g, 12.9 mmol) in 20 ml of THF at −60°C. After warming up to room temp., the green reaction mixture was stirred for 2 h and treated with $PbCl_2$ (3.59 g, 12.9 mmol). After stirring for 2 h, the solvent was removed under vacuum and the residue was extracted with 60 ml of a dichloromethane/hexane mixture (2:1). Filtering, concentrating the extracts and crystallization at −20°C afforded 2.86 g of **10** as yellow microcrystals; yield: 55%. – ^{1}H NMR ($CDCl_3$): δ = 0.23 (s, 6H,$SiCH_3$), 2.12 (s, 6H, CCH_3), 2.25 (s, 6H, CCH_3), 5.35 (s, 2H, CH_2), 7.26 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 2.2 ($SiCH_3$), 13.0, 16.0, (CCH_3), 59.2 (CH_2), 104.0 (C_5Me_4 at Si), 127.6 (*p*-C_6H_5), 128.6 (*o*-C_6H_5), 128.7 (*m*-C_6H_5), 136.0, 140.8 (CCH_3), 141.3 (*ipso*-C_6H_5). – EI-MS; *m/z* (%):

401 (38) [M^+], 366 (100) [$M^+ - Cl$], 296 (44) [$M^+ - NCH_2Ph$], 177 (5) [$C_{11}H_{17}Si^+$], 163 (4) [$C_9H_{13}NSi^+$], 119 (6) [$C_9H_{11}^+$], 106 (45) [$PhCH_2NH^+$], 91 (45) [$C_7H_7^+$], 77 (8) [$C_6H_5^+$]. – $C_{18}H_{25}Cl_2NSiTi$ (402.3): calcd. C 53.74, H 6.26, N 3.48; found C 53.92, H 6.08, N 2.93.

{η^5:η^1-N-[Dimethyl(tetramethylcyclopentadienyl)silyl]-benzylamido}dimethyltitanium (**11**): To a solution of **10** (0.99 g, 2.46 mmol) in 80 ml of THF cooled to −60 °C, was added methylmagnesium chloride (1.70 ml, 3 M solution in THF). Upon warming up to room temp. a yellow mixture with a white precipitate formed. Removal of the solvent in vacuo afforded a brown oil which was dissolved in 30 ml of hexane and filtered. Cooling the filtrate to −60 °C gave **11** as extremely sensitive, white solid; yield: 0.61 g (69%). – ^1H NMR (C_6D_6): δ = 0.12 (s, 6H, $SiCH_3$), 0.52 (s, 6H, $TiCH_3$), 1.86 (s, 6H, CCH_3), 1.97 (s, 6H, CCH_3), 5.28 (s, 2H, CH_2), 7.18 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 2.8 ($SiCH_3$), 11.9, 15.1 (CCH_3), 50.7 ($TiCH_3$), 55.3 (CH_2), 97.2 (C_5Me_4 at Si), 127.1, 128.2, 128.7, 134.4 (*p*-, *o*-, *m*-C_6H_5, CCH_3), 143.8 (*ipso*-C_6H_5). – EI-MS; *m/z* (%): 331 (17) [M^+ − 2 Me], 195 (9) [$C_5Me_4SiMe_2NH_3^+$], 106 (100) [$PhCH_2NH^+$], 91 (66) [$C_7H_7^+$], 77 (31) [$C_6H_6^+$]. – $C_{20}H_{31}NSiTi$ (361.4): calcd. C 66.46, H 8.64, N 3.88; found C 64.80, H 8.95, N 3.91.

Dibenzyl{η^5:η^1-N-[dimethyl(tetramethylcyclopentadienyl)-silyl]benzylamido}titanium (**12**): Compound **12** was obtained from the reaction of **10** with dibenzylmagnesiumbis(tetrahydrofuran) as red crystals in a manner analogous to that described for the synthesis of **5**; yield: 72%. – ^1H NMR (C_6D_6): δ = 0.01 (s, 6H, $SiCH_3$), 1.77 (s, 6H, CCH_3), 1.82 (s, 6H, CCH_3), 2.18 (d, $^2J_{HH}$ = 10 Hz, 2H, $TiCH_2$), 2.35 (d, $^2J_{HH}$ = 10 Hz, 2H, $TiCH_2$), 4.77 (s, 2H, NCH_2), 7.04 (m, 10H, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 3.1 ($SiCH_3$), 11.4, 14.9 (CCH_3), 56.7 (NCH_2), 80.6 ($TiCH_2$), 90.0 (C_5Me_4 at Si), 122.2, 127.0, 127.1, 128.4, 128.7, 129.3, 129.6, 135.1 (*p*-, *o*-, *m*-$NCH_2C_6H_5$, *p*-, *o*-, *m*-$TiCH_2C_6H_5$), CCH_3), 142.6 (*ipso*-$NCH_2C_6H_5$), 148.0 (*ipso*-$TiCH_2C_6H_5$). – EI-MS; *m/z* (%): 422 (56) [$M^+ - CH_2Ph$], 331 (100) [$M^+ - 2\ CH_2Ph$], 250 (14) [$M^+ - C_{20}H_{23}$], 224 (10) [$M^+ - C_{21}H_{23}N$], 208 (6) [$C_{12}H_{22}NSi^+$], 193 (2) [$C_{11}H_{19}NSi^+$], 163 (6) [$C_{10}H_{15}Si^+$], 91 (34) [$C_7H_7^+$]. – $C_{32}H_{39}NSiTi$ (513.6): calcd. C 74.83, H 7.65, N 2.73; found C 73.86, H 7.68, N 3.95.

X-ray Crystal Structure Analysis of Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2C_6H_5$)($CH_2C_6H_5$)$_2$ (**12**): Red cubes of **12** were obtained by slow cooling in hexane. Cell dimensions and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer: $C_{32}H_{39}NSiTi$, M = 513.65, a = 1060.0(1), b = 1049.9(2), c = 1525.4(3) pm, α = 95.34(2), β = 97.72(1)°, γ = 114.76(1), Z = 2, $d_{calcd.}$ = 1.19 Mgm^{-3}, triclinic, $P\bar{1}$ (No. 2), Mo-K_α (λ = 71.07 pm), graphite monochromator, 0.10 × 0.50 × 0.50 mm, T = 293(2) K, 3.00° < Θ < 29.00°, F(000) = 548.0. Number of reflections measured 12045, 7561 independent reflections [R(int) = 0.053] of which 2930 were assigned observed [$I > 2\sigma(I)$], absorption coefficient 9.10 cm^{-1}. The structure was solved by direct methods (MULTAN) and difference Fourier synthesis and refined using MolEN. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included in idealized positions except for the hydrogen atoms of the benzylic CH_2 groups, whose coordinates were refined. The refinement (334 parameters) converged with R = 0.055, Rw = 0.046, $w = 1/\sigma^2(F_o)$ for the observed F_o data, goodness of fit 1.235. The residual electron density was 0.30 · 10^{30} e m^{-3}[14].

{η^5:η^1-N-[Dimethyl(tetramethylcyclopentadienyl)silyl]-benzylamido}bis(trimethylsilylmethyl)titanium (**13**): To a solution of **10** (0.74 g, 1.84 mmol) in 40 ml of diethyl ether and 30 ml of toluene was added dropwise a solution of trimethylsilylmethylmagnesium chloride (4.00 ml, 1 M in diethyl ether) at −50 °C. The mixture was stirred at −50 °C for 30 min and was allowed to warm up to room temp. After stirring for 3 h at room temp. all volatiles were removed under vacuum. Extraction of the residue with 50 ml of *n*-pentane and 20 ml of hexane, followed by filtration, concentrating and crystallization at −78 °C yielded **13** as a yellow, glassy solid; yield: 0.54 g (58%). – ^1H NMR (C_6D_6): δ = 0.04 (s, 6H, $SiCH_3$), 0.18 (s, 18H, CH_2SiCH_3), 0.61 (d, $^2J_{HH}$ = 11 Hz, 2H, $TiCH_2$), 0.98 (d, $^2J_{HH}$ = 11 Hz, 2H, $TiCH_2$), 1.89 (s, 6H, CCH_3), 1.95 (s, 6H, CCH_3), 5.38 (s, 2H, NCH_2), 7.11 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 2.6 ($SiCH_3$), 3.2 (CH_2SiCH_3), 13.0, 16.1 (CCH_3), 58.1 (NCH_2), 71.0 ($TiCH_2$), 99.0 (C_5Me_4 at Si), 127.3, 128.3, 129.1, 129.0, 133.7 (CCH_3, *o*-, *m*-, *p*-C_6H_5), 143.0 (*ipso*-C_6H_5). – EI-MS; *m/z* (%): 418 (11) [$M^+ - CH_2SiMe_3$], 366 (100) [$M^+ - C_8H_{15}Si$], 331 (45) [$M^+ - 2\ CH_2SiMe_3$], 195 (2) [$C_{11}H_{21}NSi^+$], 163 (3) [$C_{10}H_{15}Si^+$], 106 (78) [$PhCH_2NH^+$], 91 (23) [$C_7H_7^+$].

{η^5:η^1-N-[Dimethyl(tetramethylcyclopentadienyl)silyl]-benzylamido}diphenyltitanium (**14**): A suspension of **10** (0.64 g, 1.59 mmol) in 35 ml of diethyl ether was cooled to −60 °C and a solution of phenyllithium [1.76 ml, 1.8 M in cyclohexane/diethyl ether (70:30)], diluted with 20 ml of diethyl ether, was added within 10 min with stirring. After stirring at this temp. for 30 min all volatiles were removed under vacuum at 0 °C. The residue was extracted with 30 ml of hexane and 5 ml of diethyl ether. Upon cooling to −30 °C, **14** precipiated as an extremely sensitive, pale yellow solid; yield: 0.35 g (45%). – ^1H NMR (C_6D_6): δ = 0.24 (s, 6H, $SiCH_3$), 1.84 (s, 6H, CCH_3), 1.93 (s, 6H, CCH_3), 5.32 (s, 2H, CH_2), 7.13 (overlap. m, 11H, $CH_2C_6H_5$; *p*, *o*-TiC_6H_5), 7.65 (overlap. m, 4H, *m*-TiC_6H_5). – $^{13}C\{^1H\}$NMR (C_6D_6): δ = 3.0 ($SiCH_3$), 12.7, 16.0 (CCH_3), 56.4 (CH_2), 99.5 (C_5Me_4 at Si), 126.7, 127.2, 127.9, 128.6, 129.5, 134.6 (*p*-, *o*-, *m*-$CH_2C_6H_5$; *o*-, *p*-, *m*-TiC_6H_5), 131.1, 137.1 (CCH_3), 142.3 (*ipso*-$CH_2C_6H_5$), 195.9 (*ipso*-TiC_6H_5). – EI-MS; *m/z* (%): 407 (3) [M^+ − PhH], 331 (9) [M^+ − 2 Ph], 241 (2) [MH^+ − 2 Ph, − CH_2Ph], 78 (100) [$C_6H_6^+$].

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[14] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-406120 for **2**, -406121 for **3**, and -406122 for **12**, the names of the authors and the journal citation.

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