Titanium Complexes with a Linked Amido−Cyclopentadienyl Ligand and a Bidentate Organyl Group: Synthesis, Structure, and Ethene Polymerization Activity☆

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Titanium complexes containing a linked isopropyl- or benzylamido(tetramethylcyclopentadienyl) ligand $C_5Me_4SiMe_2NR$ (R = *i*Pr, CH_2Ph,) and one bidentate organyl group $C_6H_4(CH_2NMe_2)$-2, $CH_2C_6H_4(NMe_2)$-2, and $\{\eta^5$-$C_5H_3(CH_2NMe_2)$-2$\}Fe(\eta^5$-$C_5H_5)$ were prepared by salt metathesis of the corresponding dichloro complex $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2NR)Cl_2$ with the lithium organyl. Single crystal X-ray structural analysis of $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2NCH_2Ph)\{C_6H_4(CH_2NMe_2)-2\}Cl$ and of $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2N$*i*Pr)$\{CH_2C_6H_4(NMe_2)$-2$\}Cl$ revealed the presence of intramolecular coordination with square pyramidal geometry around titanium. In the ferrocenyl derivative $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2NCH_2Ph)[\{\eta^5$-$C_5H_3(CH_2NMe_2)-2\}Fe(\eta^5$-$C_5H_5)]Cl$ the NMe_2 group is not bonded at the titanium atom. Ethene polymerization catalyzed by these complexes upon activation with methylaluminoxane was examined.

Introduction

Homogeneous polymerization catalysts based on titanium complexes with the linked amido−cyclopentadienyl ligand $C_5Me_4SiMe_2N$*t*Bu[1a][1b][1c] have recently gained enormous technological importance for the efficient synthesis of novel copolymers of ethene with α-olefins such as 1-octene and styrene[2]. The initial design of this ligand system by Bercaw and Shapiro[1a][1b][1c] was guided by the increased Lewis acidity of the metal complexes that would accommodate the bulkier comonomers more easily, compared to *ansa*-metallocenes containing a linked bis(cyclopentadienyl) ligand. Because of the great industrial interest not many detailed studies on structure−activity relationships of this class of complexes have so far appeared in the open literature[3]. In particular the influence of each of the ligand moieties on the polymerization performance remains unknown. We have synthesized and characterized several titanium complexes containing a linked amido−cyclopentadienyl ligand with different amido and cyclopentadienyl substituents[1d][1h][1i][1j][4a]. More recently, the influence of a donor-functionalized amido side chain on the Lewis acidity of the titanium center has been investigated in some detail[4]. In continuation of these studies we describe here the synthesis and characterization of some new titanium complexes with this ligand system and assess their activity towards ethene polymerization. In particular we focus on those systems that contain a bidentate organyl group, since they may give a clue to the possible polymerization of functionalized monomers.

Results and Discussion

The established synthetic route to titanium dichloro complexes containing a linked amido−cyclopentadienyl ligand $C_5Me_4SiMe_2NR$ is the metathesis of $TiCl_3(THF)_3$ with the dimetallated ligand $[C_5Me_4SiMe_2NR]^{2-}$, followed by chlorination with $PbCl_2$[1h][1i][1j]. However, in the case of the prototypical ligand system $C_5Me_4SiMe_2N$*t*Bu, the yield of the isolated crystalline product $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2N$*t*Bu)Cl_2 (**1**)[5] was invariably low in our hands, never exceeding 40%. Obviously, the nature of the amido substituent R in the ligand $C_5Me_4SiMe_2NR$ critically influences the yield of $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2NR)Cl_2$ and we suspected that a tertiary amido substituent causes significant steric hindrance during coordination of the bidentate ligand to the titanium center. Thus, the reaction of the doubly deprotonated ligand $Li_2[C_5Me_4SiMe_2NAd]$ (Ad = 1-adamantyl) resulted only in a yield of 30% for the titanium dichloro complex $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2NAd)Cl_2$ (**2**). Low yield was also encountered during the preparation of $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2NCMe_2$-CH_2*t*Bu)Cl_2 (**3**), derived from the inexpensive 1,1,3,3,-tetramethylbutylamine. However, the analogous reaction with $Li_2[C_5Me_4SiMe_2N$*i*Pr] gave the yellow crystalline isopropylamido derivative $Ti(\eta^5{:}\eta^1$-$C_5Me_4SiMe_2N$*i*Pr)Cl_2 (**4**) in excess of 70% yield (Scheme 1). Analytical and spectroscopic characterizations of **1**−**4** are straightforward. In the ^1H-NMR spectrum of **4**, a low field shift of the methine proton (δ = 5.55) is observed which is typical for all related complexes with secondary amido groups [$Ti(\eta^5{:}\eta^1$-$C_5H_4SiMe_2N$-*i*Pr)Cl_2: δ = 5.69[1j]; $Ti\{\eta^5{:}\eta^1$-$C_5Me_4(CH_2)_nSiMe_2N$*i*Pr$\}Cl_2$: δ = 5.92 (*n* = 2), δ = 6.57 (*n* = 3)[6]].

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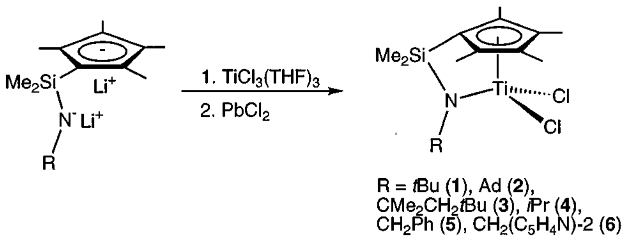
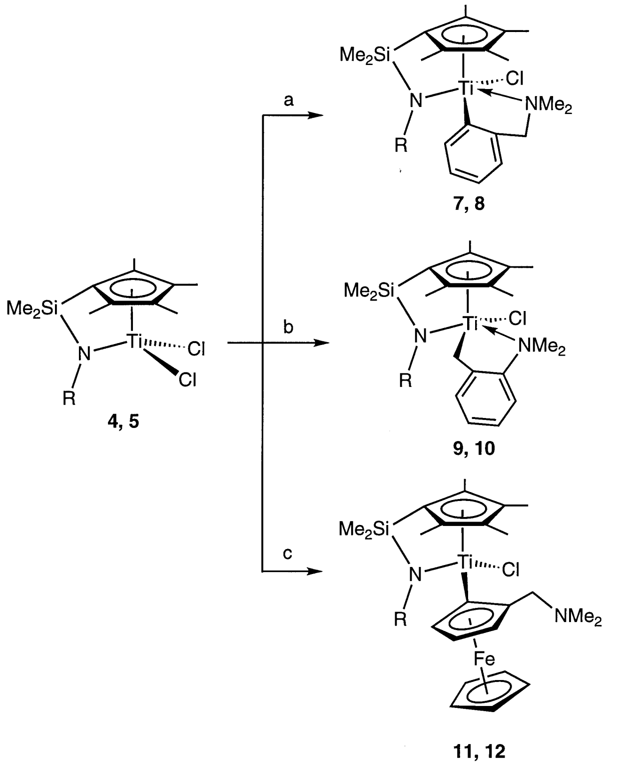
Scheme 1



Scheme 2



a) Li{$C_6H_4(CH_2NMe_2)$-2}; b) Li{$CH_2C_6H_4NMe_2$)-2}; c) Li[{η^5-$C_5H_3(CH_2NMe_2)$-2}Fe(η^5-C_5H_5)]

Yet another limitation to the complexation of the $C_5Me_4SiMe_2NR$ ligand was noted, when (2-pyridyl)methyl-amido as a "hetero-benzylamido" ligand was introduced. Previously we had synthesized the benzylamido complex Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2Ph$)Cl_2 (**5**) without any difficulty[1j]. However, after tedious workup, Ti{η^5:η^1-$C_5Me_4SiMe_2NCH_2(C_5H_4N)$-2}$Cl_2$ (**6**) was recovered only in 30% yield as orange crystals. The NMR data indicate the existence of a mirror plane and do not allow the distinction between a rigid intramolecular interaction of the pyridyl group at the titanium center and a fluxional complexation. However, in the the ^{1}H-NMR spectrum of **6** the *ortho* proton of the pyridyl group at $\delta = 9.40$ is remarkably shifted to low field compared to that in the ligand precursor (C_5Me_4H)$SiMe_2NHCH_2(C_5H_4N)$-2 ($\delta = 8.59$).

We successfully introduced each of the organyl ligands with an appended *N*,*N*-dimethylamino donor group 2-(*N*,*N*-dimethylaminomethyl)phenyl, 2-(*N*,*N*-dimethylamino)benzyl and {2-(*N*,*N*-dimethylamino)methyl}ferrocenyl by substituting one chloro ligand in **4** and **5** through salt metathesis. This type of bidentate organyl ligands were reported to be capable of stabilizing extremely sensitive monomeric, paramagnetic bis(cyclopentadienyl)titanium(III) derivatives[7]. Attempts to obtain compounds with two organyl groups failed so far, presumably due to the steric repulsion ot these bulky groups. As summarized in Scheme 2, the complexes **7**−**10** were obtained in good yields by the reaction in toluene of the dichloro precursors **4** and **5** with one equivalent of lithium{2-(*N*,*N*-dimethylaminomethyl)phenyl} and lithium{2-(*N*,*N*-dimethylamino)benzyl}, respectively. The complexes **7** and **8** were isolated as yellow, **9** and **10** as red crystals, sensitive to air and moisture. They were fully characterized by NMR spectroscopy, mass spectral and elemental analysis.

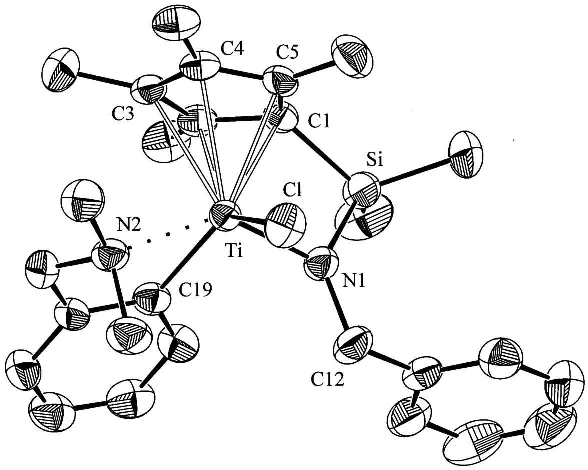
Complexes **7**−**10** are soluble in toluene and THF, but only slightly soluble in aliphatic hydrocarbons. In contrast to the dichloro complexes **4** and **5**, the ^{1}H-NMR spectra reveal four signals for the methyl groups at the cyclopentadienyl ring as well as two for the methyl groups at the silicon due to the asymmetric titanium metal center. All methylene protons of the various CH_2 groups in **7**−**10** are diastereotopic, each giving rise to an AB spin pattern. The chemical shift differences between the two doublets for the CH_2NMe_2 group in **7** and **8** with $\Delta\delta > 1.1$ ppm are unusually large[8]. In **9** and **10**, the resonances due to the CH_2 group at titanium are centered around $\delta = 2.3$.

At room temperature, a single resonance is observed for the methyl groups of the *N*,*N*-dimethylamino group for **7**−**10** in both the ^{1}H- and ^{13}C-NMR spectra. The diastereotopic methyl groups are rendered equivalent through the fast inversion at the nitrogen atom. This finding suggests that the *N*,*N*-dimethylamino function in these complexes is either not coordinated at the titanium or undergoes a rapid association−dissociation equilibration process on the NMR time scale. Temperature dependent ^{1}H-NMR measurements of **9** down to −50°C in $CDCl_3$ only resulted in slight changes in the chemical shifts and no decoalescence of the NMe_2 signal was observed. Based on what we have learned from the titanium complexes with the potentially tridentate ligand system $[C_5R'_4SiMe_2NCH_2CH_2NMe_2]^{2-}$ ($C_5R'_4$ = C_5H_4, C_5H_3tBu, C_5Me_4)[4a][4b], the latter scenario appears to be more probable, in particular in view of the crystal structures of **8** and **9** (vide infra). Likewise, a similar bonding situation can be found for the trichloro complexes of the type Ti(η^5-$C_5H_4CH_2CH_2NRR'$)Cl_3[9a][9b].

According to single crystal X-ray structural analysis, the structures of **8** and **9** in the solid state unequivocally reveal the presence of a Ti−NMe_2 interaction (Figure 1 and 2). In the 2-(*N*,*N*-dimethylaminomethyl)phenyl derivative **8** the titanium−amino nitrogen bond length is 240.1(3) pm, whereas in the benzyl derivative **9** the corresponding bond distance is 254.0(1) pm. Nitrogen−titanium bond lengths in tetravalent titanium complexes range from 226 to 245 pm[9], estimated titanium−amine distances are in the range of 196 to 197 pm[10]. The bond distances observed in **8** and

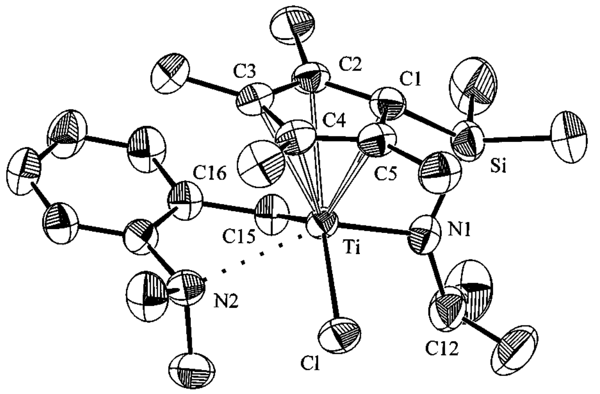
9 are clearly longer than average. In Ti(η^5:η^1:η^1-$C_5H_4SiMe_2NCH_2CH_2NMe_2$)$Cl_2$ a bond length of 241.8(7) pm was observed[4b]. Interestingly, the titanium(III) complex (η^5-C_5H_5)Ti{($C_6H_4(CH_2NMe_2)$-2} shows Ti−N bond distances of 298.9(4) pm[11]. The coordination geometry for each complex **8** and **9** can be best described as square pyramidal, where the atoms N1, N2, Cl, and C15(C19) define a plane and the cyclopentadienyl ring resides perpendicular to this plane. In both **8** and **9**, the *N*,*N*-dimethylamino group adopts the coordination site trans to the amido ligand. This coordination avoids the amido and the benzyl/phenyl ligand from competing for the same metal-derived orbitals. The amido nitrogen atoms have almost planar geometry in agreement with all structurally characterized Ti(IV) complexes containing the linked amido−cyclopentadienyl ligand[12]. There is no α-agostic interaction for the benzyl group in **9**, as was observed in the crystal structure of Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2Ph$)$(CH_2Ph)_2$[1j]. Both the Ti−C15 of 217.1(2) pm and Ti−C15−C16 of 112.83(9)° are within the expected range.

Figure 1. ORTEP diagram of the molecular structure of Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2Ph$){$C_6H_4(CH_2NMe_2)$-2}Cl (**8**); thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for the sake of clarity[a]



[a] Selected bond distances [pm] and angle [°]; Cp denotes the cyclopentadienyl centroid: Ti−N1 194.1(3), Ti−Cl 238.40(11), Ti−N2 240.1(3), Ti−Cp 209.9(4), Ti−C1 229.9(4), Ti−C2 239.5(4), Ti−C3 253.1(4), Ti−C4 250.4(4), Ti−C5 237.3(4), Ti−C19 219.5(4), Cp−Ti−N1 105.5, Ti−N1−Si 106.3(2), Ti−N1−C12 123.5(3), Si−N1−C12 130.1(3), Cl−Ti−N1 90.3(1), Cl−Ti−N2 79.42(9), N1−Ti−N2 139.7(1).

Figure 2. ORTEP diagram of the molecular structure of Ti(η^5:η^1-$C_5Me_4SiMe_2N$*i*Pr){$CH_2C_6H_4(NMe_2)$-2}Cl (**9**); thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for the sake of clarity[a]



[a] Selected bond distances (pm) and angle (°); Cp denotes the cyclopentadienyl centroid: Ti−N1 192.57(12), Ti−Cl 237.27(7), Ti−N2 254.03(13), Ti−Cp 208.4(2), Ti−C1 229.5(2), Ti−C2 241.4(2), Ti−C3 251.9(2), Ti−C4 247.5(2), Ti−C5 233.8(2), Ti−C15 217.2(2), Cp−Ti−N1 105.6, Ti−N1−Si 105.81(6), Ti−N1−C12 122.2(1), Si−N1−C12 131.3(1), Cl−Ti−N1 93.66(4), Cl−Ti−N2 78.39(3), N1−Ti−N2 139.35(5), Ti−C15−C16 112.83(9).

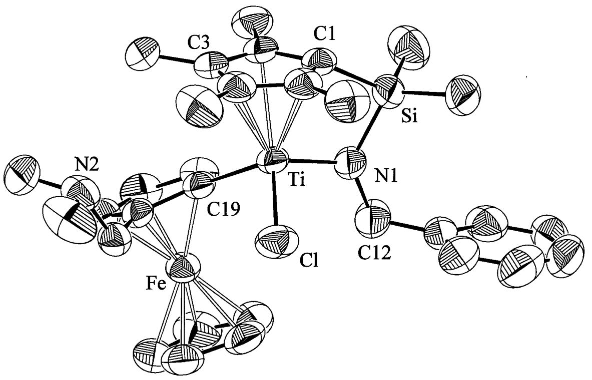
The reaction of the dichloro complexes **4** and **5** with Li[{η^5-$C_5H_3(CH_2NMe_2)$-2}Fe(η^5-C_5H_5)], generated in situ by lithiation of {2-(*N*,*N*-dimethylamino)methyl}ferrocene with *n*-butyllithium, gave the mono(ferrocenyl) derivative **11** and **12** as hydrocarbon-soluble, violet crystals in yields of 43 and 48%, respectively (Scheme 2). In the ^1H- and ^{13}C-NMR spectra of **11** and **12**, the asymmetry of the molecule can be easily detected by the occurence of diastereotopic resonances. The presence of the ferrocenyl moiety is obvious from the sharp singlet due to the η^5-C_5H_5 group at δ = 4.46 and 4.39 for **11** and **12**, respectively, as well as a set of three resonances around δ = 4.0 for the η^5-$C_5H_3(CH_2NMe_2)$-2 part. As in the case of **7**−**10**, only one signal for the *N*,*N*-dimethylamino group is recorded in the ^1H- and ^{13}C-NMR spectra, excluding a rigid coordination of the *N*,*N*-dimethylamino group at the titanium center in solution.

The single crystal X-ray structure analysis of **12** (Figure 3) reveals a monodentate 2-(*N*,*N*-dimethylamino)ferrocenyl ligand in which the *N*,*N*-dimethylamino group is directed away from the titanium atom. Somewhat shorter Ti−N1, Ti−Cp and Ti−Cl distances as compared to **8** were found. The Ti−C19 distance of 210.5(3) pm is shorter. The bonding mode of **12** does not differ from that found in the titanocenes Ti(η^5-C_5H_5)$_2Cl_{(2-n)}$[{η^5-$C_5H_3(CH_2NMe_2)$-2}Fe(η^5-C_5H_5)]$_n$ (n = 1, 2)[13], whereas in the half-sandwich complex Ti(η^5-C_5H_5)Cl_2[{η^5-$C_5H_3(CH_2NMe_2)$-2}Fe(η^5-C_5H_5)][9c] a bidentate ferrocenyl ligand was observed. The well-known significantly stronger inductive effect of the ferrocenyl group in comparison to the phenyl group may be responsible for the bonding mode observed in **12**[14].

The intense color the ferrocenyl derivatives **11** and **12** exhibit are due to the presence of low-energy charge-transfer bands. For instance, the UV/Vis spectrum of a hexane solution of **12** exhibits absorptions at λ = 525 nm (ε = 340) and 406 nm (ε = 1270) besides a strong band at 225 nm ($\varepsilon = 2.9 \cdot 10^4$). According to cyclovoltammetric studies in 1,2-dimethoxyethane solutions, these complexes show a rather complicated electrochemical behavior: One reversible oxidation wave at an electrode potential (E_p = 0.485 V for **11**, 0.524 V for **12**) can be attributed to the oxidation of the ferrocenyl moiety. Other oxidation waves observed are irreversible. Furthermore, the complexes **11** and **12** exhibited only irreversible reduction waves, with no reversible reduction of the titanium(IV) center being detectable.

Ethene polymerizations catalyzed by the complexes using methylaluminoxane (MAO) as cocatalyst were examined in

Figure 3. ORTEP diagram of the molecular structure of $Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2Ph)[\{\eta^5-C_5H_3(CH_2NMe_2)-2\}Fe(\eta^5-C_5H_5)]Cl$ (**12**); thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for the sake of clarity[a]



[a] Selected bond distances [pm] and angle [°]; Cp denotes the cyclopentadienyl centroid: Ti−N1 191.3(3), Ti−Cl 227.61(11), Ti−Cp 204.4(3), Ti−C1 230.8(3), Ti−C2 236.9(3), Ti−C3 243.7(3), Ti−C4 240.6(3), Ti−C5 234.0(3), Ti−C19 210.5(3), Cp−Ti−N1 105.5, Ti−N1−Si 107.2(1), Ti−N1−C12 124.1(2), Si−N1−C12 128.7(2), Cl−Ti−N1 105.7(9).

a preliminary manner, as summarized in Table 1. Compared to the activity of the prototypical catalyst **1** with a *tert*-butylamido or **2** with the adamantyl, the isopropylamido substituent complex **4** is less active, whereas the benzylamido complex **5** exhibits the highest activity. The substitution of one chloro ligand by a bidentate organyl group influenced the activity in a different manner. **8** shows only moderately decreased activity, suggesting that the cationic active species formed by the action of MAO from both **5** and **8** are identical. However, the introduction of the ferrocenyl group as in **12** results in a catalyst that produces low yields of polyethene under the same conditions. The melting temperatures of the isolated polyethenes, as determined by DSC, range between 134 and 142°C.

Table 1[a]

Complex	Yield[g]	Activity[b]	T_m[°C][c]	ΔH[J/g][c]
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2N\textit{t}Bu)Cl_2$ (**1**)	4.11	950	141.6	128.4
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NAd)Cl_2$ (**2**)	2.01	460	133.5	108.5
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2N\textit{i}Pr)Cl_2$ (**4**)	0.43	100	142.2	103.9
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2Ph)Cl_2$ (**5**)	13.34	3090	135.6	138.2
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2Ph)-\{C_6H_4(CH_2NMe_2)-2\}Cl$ (**8**)	8 .89	2060	140.0	151.5
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2Ph)-[\{\eta^5-C_5H_3(CH_2NMe_2)-2\}Fe(\eta^5-C_5H_5)]Cl$ (**12**)	0.35	80	138.6	121.9

[a] Polymerization conditions: titanium complex 5 µmol, methylaluminoxane 2500 µmol in toluene at 23°C, constant ethene pressure 3 bar, reaction time 2 h. − [b] Activity in kg(PE)/molTi·h·c_{ethene}. − [c] Determined by DSC.

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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. − ^1H and ^{13}C NMR: Bruker AC 200 or Bruker AM 400. − Mass spectra: Finnigan 8230. − UV/Vis: Zeiss spectrophotometer DM4. − Elemental analyses: Microanalytical laboratory of the university. − The following reagents were synthesized using literature procedures: $C_5Me_4H(SiMe_2Cl)$[1c], $TiCl_3(THF)_3$[15], $Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2Ph)Cl_2$[7], {2-[(*N*,*N*-dimethylamino)methyl]phenyl}lithium[16], [2-(*N*,*N*-dimethylamino)benzyl]lithium[17], {2-[(*N*,*N*-dimethylamino)methyl)]ferrocenyl}lithium[17].

N-[Dimethyl(tetramethylcyclopentadienyl)silyl](1-adamantyl)amine: $(C_5Me_4H)SiMe_2Cl$ (2.38 g, 11.1 mmol) was added to a suspension of Li(NHAd) (1.74 g, 11.1 mmol) in 70 ml of hexane at −78°C. The reaction mixture was allowed to warm to room temp. and stirred for 14 h. Filtration of the resulting suspension and removal of all volatiles in vacuo gave $(C_5Me_4H)SiMe_2NHAd$ as a yellow oil, yield 2.01 g (55%). − ^1H NMR (C_6D_6): δ = 0.27 (s, 6 H, $SiCH_3$), 1.06 (s, 1 H, NH), 1.66 (s, 6H, CCH_3), 1.74 (br d, 3 H, CH_2, Ad), 1.83 (s, 6H, CCH_3), 1.99 (br s, 3 H, CH, Ad), 2.04 (br d, 6 H, CH_2, Ad), 2.17 (br s, 3 H, CH, Ad), 2.92 (s, 1 H, $C_5Me_4\textit{H}$). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 4.0 ($SiCH_3$), 11.4, 15.0 ($C\textit{C}H_3$), 30.5 (3-Ad), 36.7 (4-Ad), 47.6 (2-Ad), 53.9, 57.2 (*ipso*-Ad, C_5Me_4H at Si), 133.3, 135.4 ($\textit{C}_5Me_4$).

Dichloro{η⁵:η¹-N-dimethyl(tetramethylcyclopentadienyl)silyl](1-adamantyl)amido}titanium (**2**)**:** Crude $Li_2(C_5Me_4SiMe_2NAd)$ (1.41 g, 4.1 mmol), obtained by deprotonation of $(C_5Me_4H)SiMe_2NHAd$ with 2 equiv. of Li*n*Bu in hexane, was dissolved in 20 ml of THF and added dropwise to a suspension of $TiCl_3(THF)_3$ (1.53 g, 4.1 mmol) in 40 ml of toluene at −60°C. After warming to room temp., the green reaction mixture was stirred for 2 h and treated with $PbCl_2$ (1.15 g, 4.1 mmol). After stirring for 12 h, the solvent was removed under vacuum and the residue was extracted with 50 ml of a toluene/hexane mixture (2:1). Filtration of the extracts, followed by concentrating the filtrate and cooling to −20°C afforded in several crops $Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NAd)Cl_2$ as yellow crystals, yield 0.57 g (31%); by-product: $Ti(\eta^5:\eta^1-C_5Me_4H)Cl_3$. − ^1H NMR (C_6D_6): δ = 0.61 (s, 6 H, $SiCH_3$), 1.64 (br dd, 6 H, CH_2, 4-Ad), 2.09 (br s, 3 H, CH, 3-Ad), 2.14, 2.16 (s, 6H, CCH_3), 2.22 (br d, 6 H, CH_2, 2-Ad). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 5.9 ($SiCH_3$), 13.1, 16.2 ($C\textit{C}H_3$), 30.7 (3-Ad), 36.3 (4-Ad), 45.6 (2-Ad), 63.8 (*ipso*-Ad), 104.1 (C_5Me_4 at Si), 137.9, 140.6 ($\textit{C}CH_3$). − EI MS; *m/z* (%): 445 (88) [M^+], 414 (31) [M^+ − Me], 390 (33) [$M^+ - C_4H_7$], 356 (100) [$M^+ - C_4H_9Cl$], 324 (27) [$M^+ - C_6H_6Cl_2$], 297 (21) [$C_{11}H_{19}Cl_2SiTi^+$], 237 (27) [$C_5H_{17}Cl_2Ti^+$], 197 (35) [$C_{11}H_{23}NSi^+$], 159 (33) [$C_{10}H_{11}Si^+$], 149 [$C_9H_{13}Si^+$]. − $C_{21}H_{33}Cl_2NSiTi$ (446.4): calcd. C 56.51, H 7.45, N 3.14; found C 55.29, H 7.55, N 4.38.

N-[Dimethyl(tetramethylcyclopentadienyl)silyl](1,1,3,3-tetramethylbutyl)amine: $(C_5Me_4H)SiMe_2Cl$ (3.00 g, 14.0 mmol) was added to a suspension of $Li(NHCMe_2CH_2\textit{t}Bu)$ (1.89 g, 14.0 mmol) in 60 ml of hexane at −78°C. The reaction mixture was allowed to warm to room temp. and stirred for 14 h. Filtration of the resulting suspension and removal of all volatiles in vacuo gave crude $(C_5Me_4H)SiMe_2NHCMe_2CH_2\textit{t}Bu$ which was distilled at 95°C and $8 \cdot 10^{-3}$ mbar to give a yellow oil, yield 2.15 g (50%). − ^1H NMR (C_6D_6): δ = 0.34 (s, 6 H, $SiCH_3$), 0.51 (s, 1 H, NH), 1.08 [s, 9 H, $C(CH_3)_3$], 1.24 [s, 6 H, $C(CH_3)_2$], 1.42 (s, 2 H, CH_2), 1.81 (s, 6 H, CCH_3), 1.94 (s, 6 H, CCH_3), 2.80 (s, 1 H, $C_5Me_4\textit{H}$). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 2.9 ($SiCH_3$), 11.4, 14.9 ($C\textit{C}H_3$), 31.9 [$C(\textit{C}H_3)_3$,

$\mathit{C}(CH_3)_3$], 33.6 [C($\mathit{C}H_3$)$_2$], 53.2, 56.8 [C(CH$_3$)$_2$, C$_5$Me$_4$H at Si], 58.9 (CH$_2$), 133.4, 135.3 (CCH$_3$). − EI MS; *m/z* (%): 307 (27) [M$^+$], 236 (15) [$C_{14}H_{26}NSi^+$], 186 (100) [$C_{10}H_{24}NSi^+$], 121 (10) [$C_9H_{13}{}^+$], 114 (13) [$C_8H_{18}{}^+$], 105 (11) [$C_6H_9{}^+$], 74 (42) [$C_2H_8NSi^+$], 59 (10) [$C_2H_7Si^+$], 55 (5) [$C_2H_3Si^+$]. − $C_{19}H_{37}NSi$ (307.6): calcd. C 74.19, H 12.12, N 4.55; found C 73.72, H 12.12, N 5.03.

Dichloro{η^5:η^1-N-dimethyl(tetramethylcyclopentadienyl)silyl](1,1,3,3-tetramethylbutyl)amido}titanium (**3**): Crude Li$_2$(C$_5$Me$_4$SiMe$_2$NCMe$_2$CH$_2$*t*Bu) (1.86 g, 5.8 mmol), obtained by deprotonation of (C$_5$Me$_4$H)SiMe$_2$NHCMe$_2$CH$_2$*t*Bu with 2 equiv. of Li*n*Bu in hexane, was dissolved in 40 ml of THF and added dropwise to a suspension of TiCl$_3$(THF)$_3$ (2.16 g, 5.8 mmol) in 30 ml of toluene at −60 °C. After warming to room temp., the green reaction mixture was stirred for 2 h and treated with PbCl$_2$ (1.61 g, 5.8 mmol). After stirring for 12 h, the solvent was removed under vacuum and the residue was extracted with 80 ml of a toluene/hexane mixture (2:1). Filtration of the extracts, followed by concentrating the filtrate and cooling to −20 °C afforded Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_2$CH$_2$*t*Bu)Cl$_2$ as yellow crystals; yield 0.47 g (19%). − ^{1}H NMR (C$_6$D$_6$): δ = 0.62 (s, 6 H, SiCH$_3$), 1.10 [s, 9 H, C(CH$_3$)$_3$], 1.75 [s, 6 H, C(CH$_3$)$_2$], 1.87 (s , 2 H, CH$_2$), 2.13 (s, 6 H, CCH$_3$), 2.14 (s, 6 H, CCH$_3$). − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 6.0 (SiCH$_3$), 13.0, 16.2 (CCH$_3$), 31.7 [C(CH$_3$)$_3$], 31.7 [C(CH$_3$)$_2$], 31.8 [C(CH$_3$)$_3$], 57.3 (CH$_2$), 67.0 [C(CH$_3$)$_2$], 104.1 (C$_5$Me$_4$ at Si), 138.2, 140.5 (CCH$_3$). − EI MS; *m/z* (%): 408 (7) [M$^+$ − Me], 352 (100) [M$^+$ − CH$_2$CMe$_3$], 296 (17) [M$^+$ − NCMe$_2$CH$_2$CMe$_3$], 261 (4) [M$^+$ − NCMe$_2$CH$_2$CMe$_3$, − Cl], 243 (3) [$C_{15}H_{21}NSi^+$], 203 (2) [$C_{12}H_{17}NSi^+$], 177 (9) [$C_{11}H_{17}Si^+$], 161 (6) [$C_{10}H_{13}Si^+$], 148 (4) [$C_8H_{12}Si^+$], 119 (2) [$C_9H_{11}{}^+$], 57 (16) [$C_2H_5Si^+$]. − $C_{19}H_{35}Cl_2NSiTi$ (424.4): calcd. C 53.78, H 8.31, N 3.30; found C 52.76, H 8.40, N 5.06.

N-[Dimethyl(tetramethylcyclopentadienyl)silyl]isopropylamine: (C$_5$Me$_4$H)SiMe$_2$Cl (4.83 g, 22.5 mmol) was added to a suspension of Li(NH*i*Pr) (1.46 g, 22.5 mmol) in 60 ml of hexane at −78 °C. The reaction mixture was allowed to warm to room temp. and stirred for 14 h. Filtration of the resulting suspension and removal of all volatiles in vacuo gave crude (C$_5$Me$_4$H)SiMe$_2$NH*i*Pr which was distilled at 70 °C and $8 \cdot 10^{-3}$ mbar to give a yellow oil; yield 4.30 g (80%). − ^{1}H NMR (CDCl$_3$): δ = 0.01 (s, 6 H, SiCH$_3$), 0.30 (s, 1 H, NH), 1.05 (d, $^3J_{HH}$ = 7 Hz, 6 H, CHCH_3), 1.83 (s, 6 H, CCH$_3$), 1.98 (s, 6 H, CCH$_3$), 2.88 (s, 1 H, C$_5$Me$_4$$\mathit{H}$), 3.04 (sept, $^3J_{HH}$ = 7 Hz, 1 H, CHCH$_3$). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = -1.6 (SiCH$_3$), 11.1, 14.5 (CCH$_3$), 27.9 (CHCH$_3$), 43.2 (CHCH$_3$), 56.9 (C$_5$Me$_4$H at Si), 133.0, 135.5, (CCH$_3$). − EI MS; *m/z* (%): 237 (16) [M$^+$], 196 (3) [MH$_2{}^+$ − C$_3$H$_7$], 179 (2) [$C_{11}H_{20}Si^+$], 164 (100) [$C_5H_{15}NSi^+$], 73 (9) [$C_2H_7NSi^+$]. − $C_{14}H_{27}NSi$ (237.5): calcd C 70.81, H 11.46, N 5.90; found C 70.77, H 11.33, N 6.04.

Dichloro{η^5:η^1-N-dimethyl(tetamethylcyclopentadienyl)silyl]isopropylamido}titanium (**4**): Crude Li$_2$(C$_5$Me$_4$SiMe$_2$N*i*Pr) (3.75 g, 15.0 mmol), obtained by deprotonation of (C$_5$Me$_4$H)SiMe$_2$NH*i*Pr with 2 equiv. of Li*n*Bu in hexane, was dissolved in 40 ml of THF and added dropwise to a suspension of TiCl$_3$(THF)$_3$ (5.57 g, 15.0 mmol) in 80 ml of toluene at −60 °C. After warming to room temp., the green reaction mixture was stirred for 2 h and treated with PbCl$_2$ (4.18 g, 15.0 mmol). After stirring for 12 h, the solvent was removed under vacuum and the residue was extracted with 100 ml of a toluene/hexane mixture (2:1). Filtration of the extracts, followed by concentrating the filtrate and cooling to −20 °C afforded Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$N*i*Pr)Cl$_2$ as yellow crystals, yield 3.75 g (70%). − ^{1}H NMR (C$_6$D$_6$): δ = 0.47 (s, 6 H, SiCH$_3$), 1.13 (d, $^3J_{HH}$ = 6 Hz, 6 H, CHCH_3), 2.09 (s, 6 H, CCH$_3$), 2.10 (s, 6 H, CCH$_3$), 5.45 (sept, $^3J_{HH}$ = 6 Hz, 1 H , CHCH$_3$). − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 4.7 (SiCH$_3$), 12.9, 16.0 (CCH$_3$), 24.0 (CHCH$_3$), 55.6 (CHCH$_3$), 102.0 (C$_5$Me$_4$ at Si), 135.8, 140.1 (CCH$_3$). − EI MS; *m/z* (%): 353 (10) [M$^+$], 338 (100) [M$^+$ − Me], 318 (2) [M$^+$ − Cl], 296 (36) [M$^+$ − N*i*Pr], 283 (5) [M$^+$ − 2Cl], 204 (4) [$C_{12}H_{18}NSi^+$], 177 (10) [$C_{11}H_{17}Si^+$], 163 (4) [$C_{10}H_{15}Si^+$], 119 (3) [$C_9H_{11}{}^+$], 97 (2) [$C_4H_7NSi^+$], 73 (2) [$C_2H_7NSi^+$]. − $C_{14}H_{25}Cl_2NSiTi$ (354.2): calcd. C 47.47, H 7.11, N 3.95; found C 47.67, H 7.20, N 3.85.

N-[Dimethyl(tetramethylcyclopentadienyl)silyl](2-pyridyl)-methylamine: (C$_5$Me$_4$H)SiMe$_2$Cl (2.82 g, 13.2 mmol) was added to a suspension of Li{NHCH$_2$(C$_5$H$_4$N)-2} (1.50 g, 13.2 mmol) in 60 ml of hexane at −78 °C. The reaction mixture was allowed to warm to room temp. and stirred for 14 h. Filtration of the resulting solution and removal of the solvent in vacuo gave crude (C$_5$Me$_4$H)SiMe$_2$NHCH$_2$(C$_5$H$_4$N)-2 which was distilled at 135 °C and $8 \cdot 10^{-3}$ mbar to give a yellow oil, yield 2.56 g (68%). − ^{1}H NMR (C$_6$D$_6$): δ = 0.14 (s, 6 H, SiCH$_3$), 1.46 (s, 1 H, NH), 1.94 (s, 6 H, CCH$_3$), 2.19 (s, 6 H, CCH$_3$), 2.98 (s, 1 H, C$_5$Me$_4$$\mathit{H}$), 4.17 (d, $^3J_{HH}$ = 8 Hz, 2 H, CH$_2$), 6.76 (m, 1 H, 4-C$_5$H$_4$N), 7.11 (d, $^3J_{HH}$ = 8 Hz, 1 H, 6-C$_5$H$_4$N), 7.23 (m, 1 H, 5-C$_5$H$_4$N), 8.59 (d, $^3J_{HH}$ = 5 Hz, 1 H, 3-C$_5$H$_4$N). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = -2.6 (SiCH$_3$), 11.1, 14.3 (CCH$_3$), 47.7 (CH$_2$), 56.6 (C$_5$Me$_4$H at Si), 120.8 (5-C$_5$H$_4$N), 121.3 (6-C$_5$H$_4$N), 132.7, 135.6 (C_5Me$_4$), 136.3 (5-C$_5$H$_4$N), 148.8 (3-C$_5$H$_4$N), 162.9 (*ipso*-C$_5$H$_4$N). − EI MS; *m/z* (%): 252 (8) [M$^+$ − C$_2$H$_{10}$], 196 (100) [MH$^+$ − C$_6$H$_5$N], 181 (12) [$C_{11}H_{21}Si^+$], 163 (6) [$C_8H_{11}N_2Si^+$], 131 (13) [$C_6H_3N_2Si^+$], 120 (39) [$C_9H_{12}{}^+$], 105 (25) [$C_6H_5N_2{}^+$], 91 (6) [$C_6H_5N^+$], 75 (39) [$C_2H_9NSi^+$], 58 (2) [$C_2H_6Si^+$]. − $C_{17}H_{26}N_2Si$ (286.5): calcd. C 71.27, H 9.15, N 9.78; found C 68.16, H 9.88, N 11.44.

Dichloro{η^5:η^1-N-dimethyl(tetamethylcyclopentadienyl)silyl](2-pyridylmethyl)amido}titanium (**6**): Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$-2-C$_5$H$_4$N)Cl$_2$ was obtained from the reaction of Li$_2$(C$_5$Me$_4$SiMe$_2$NCH$_2$-2-C$_5$H$_4$N) (2.02 g, 6.78 mmol) with TiCl$_3$(THF)$_3$ (2.51 g, 6.78 mmol) and PbCl$_2$ (1.89 g, 6.78 mmol) in THF as an orange solid in a manner analogous to that described for the synthesis of **4**; yield 0.85 g (31%). − ^{1}H NMR (C$_6$D$_6$): δ = 0.46 (s, 6 H, SiCH$_3$), 2.31 (s, 6 H, CCH$_3$), 2.45 (s, 6 H, CCH$_3$), 4.46 (s, 2 H, CH$_2$), 6.57 (d, $^3J_{HH}$ = 8 Hz, 1 H, 6-C$_5$H$_4$N), 6.68 (t, $^3J_{HH}$ = 6 Hz, 1 H, 4-C$_5$H$_4$N), 6.94 (dt, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1 H, 5-C$_5$H$_4$N), 9.40 (d, $^3J_{HH}$ = 6 Hz, 1 H, 3-C$_5$H$_4$N). − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 1.8 (SiCH$_3$), 13.4, 15.9 (CCH$_3$), 63.5 (CH$_2$), 102.6 (C$_5$Me$_4$ at Si), 119.0 (4-C$_5$H$_4$N), 121.1 (6-C$_5$H$_4$N), 134.8, 136.2 (CCH$_3$), 138.7 (5-C$_5$H$_4$N), 152.7 (3-C$_5$H$_4$N), 161.9 (*ipso*-C$_5$H$_4$N). − EI MS; *m/z* (%): 402 (5) [M$^+$], 387 (7) [M$^+$ − Me), 372 (14) [M$^+$ − C$_2$H$_6$], 238 (7) [M$^+$ − C$_6$H$_8$NCl$_2$], 178 (14) [$C_{11}H_{18}Si^+$], 163 (100) [$C_8H_{11}N_2Si^+$], 133 (7) [$C_6H_5N_2Si^+$], 121 (27) [$C_9H_{13}{}^+$], 105 (27) [$C_6H_5N_2{}^+$], 93 (30) [$C_6H_7N^+$], 79 (17) [$C_5H_5N^+$], 73 (27) [$C_2H_7NSi^+$], 59 (32) [$C_2H_7Si^+$], 52 (11) [C_2Si^+]. − $C_{17}H_{24}Cl_2N_2SiTi$ (403.3): calcd. 50.63 H, 6.00 N, 6.95; found C 49.61, H 6.16, N 7.10.

Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$NiPr){C$_6$H$_4$(CH$_2$NMe$_2$)-2}Cl (**7**): A mixture of **4** (0.60 g, 1.69 mmol) and Li{C$_6$H$_4$(CH$_2$NMe$_2$)-2} (0.24 g, 1.69 mmol) was treated dropwise with 65 ml of toluene at −60 °C and stirred for 12 h at room temp. After removal of the solvent, the residue was extracted with 60 ml of CH$_2$Cl$_2$. Removal of CH$_2$Cl$_2$ and crystallization from toluene at −50 °C afforded yellow crystals, yield 0.55 g (72%). − ^{1}H NMR (C$_6$D$_6$): δ = 0.75 (s, 3 H, SiCH$_3$), 0.81 (s, 3 H, SiCH$_3$), 1,46 (d, $^3J_{HH}$ = 6 Hz, 3 H, CHCH_3), 1.58 (d, $^3J_{HH}$ = 6 Hz, 3 H, CHCH_3), 1.63 (s, 3 H, CCH$_3$), 1.80 (s, 3 H, CCH$_3$), 1.91 (s, 3 H, CCH$_3$), 2.47 (s, 6 H, NCH$_3$), 2.57 (s, 3 H, CCH$_3$), 2.84 (d, $^2J_{HH}$ = 14 Hz, 1 H, NCH$_2$), 3.95 (d, $^2J_{HH}$ = 14 Hz, 1 H, NCH$_2$), 4.87 (sept, $^3J_{HH}$ = 6 Hz, 1 H, CHCH$_3$), 6.92 (m, 1 H, C$_6$H$_4$), 7.17 (m, 2 H, C$_6$H$_4$), 7.83 (m, 1 H, C$_6$H$_4$). −

$^{13}C\{^1H\}$ NMR (C_6D_6): δ = 5.3, 5.8 ($SiCH_3$), 12,8, 17.1, 18.0 (CCH_3), 24.1, 25,8 ($CHCH_3$), 49.3 (NCH_3), 55.9 ($CHCH_3$), 70.8 (CH_2NMe_2), 103.0 (C_5Me_4 at Si), 122.5, 125.6, 126.3 (C_6H_4), 131.4, 131.1, 134.0, 138.2, 144.27 (CCH_3, C_6H_4), 145.5 (2-C_6H_4), 195.1 (1-C_6H_4). − EI MS; *m/z* (%): 452 (5) [M^+], 437 (6) [M^+ − Me], 410 (3) [M^+ − C_3H_6], 318 (19) [M^+ − $C_6H_4CH_2NMe_2$, − C_3H_6], 134 (100) [$C_6H_4CH_2NMe_2^+$]. − $C_{23}H_{37}ClNSiTi$ (453.0): calcd. C 60.99, H 8.23, N 6.18; found C 60.88, H 8.16, N 6.30.

Ti(η⁵:η¹-C₅Me₄SiMe₂NCH₂Ph){C₆H₄(CH₂NMe₂)-2}Cl (**8**): A mixture of **5** (1.27 g, 3.16 mmol) and Li$\{C_6H_4(CH_2NMe_2)$-2$\}$ (0.45 g, 3.19 mmol) was treated dropwise with 65 ml of toluene at −60°C and stirred for 12 h at room temp. After removal of the solvent, the residue was extracted with 60 ml of CH_2Cl_2. Removal of CH_2Cl_2 and crystallization from toluene at −50°C afforded yellow crystals, yield 1.08 g (68%). − ^1H NMR (C_6D_6): δ = 0.18 (s, 3 H, $SiCH_3$), 0.44 (s, 3 H, $SiCH_3$), 1.51 (s, 3 H, CCH_3), 1.70 (s, 3 H, CCH_3), 1.78 (s, 3 H, CCH_3), 2.38 (s, 6 H, NCH_3), 2.49 (s, 3 H, CCH_3), 2.73 (d, $^2J_{HH}$ = 14 Hz, 1 H, C_6H_4-2-CH_2), 3.85 (d, $^2J_{HH}$ = 14 Hz, 1 H, C_6H_4-2-CH_2), 5.12 (d, $^2J_{HH}$ = 14 Hz, 1 H, NCH_2Ph), 5.70 (d, $^2J_{HH}$ = 14 Hz, 1 H, NCH_2Ph), 6.83 (d, $^3J_{HH}$ = 7 Hz, 1 H, C_6H_4), 7.14 (m, 5 H, C_6H_5), 7.54 (m, 2 H, C_6H_4), 7.67 (d, $^3J_{HH}$ = 7 Hz, 1 H, C_6H_4). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 3.4, 3.7 ($SiCH_3$), 12.6, 12.7, 17.1, 17.9 (CCH_3), 49.4 (NCH_2Ph), 59.91 ($SiMe_2NCH_2$), 70.9 (CH_2NMe_2), 104.0 (C_5Me_4 at Si), 122.6, 126.5, 127.1, 127.4, 128.6, 129.1, 129.3, 130.4, 130.8, 142.3, 143.0, 145.7 (C_6H_5, C_6H_4, CCH_3, *ipso*-C_6H_5), 195.94 (1-C_6H_4). − EI MS; *m/z* (%): 500 (8) [M^+], 485 (6) [M^+ − Me], 410 (11) [M^+ − $C_6H_4CH_2$], 134 (100) [$Me_2NCH_2C_6H_4^+$], 106 (23) [$PhCH_2NH^+$], 91 (59) [$PhCH_2^+$], 78 (8) [$C_6H_6^+$]. − $C_{27}H_{37}ClN_2SiTi$ (501.0): calcd. C 64.78, H 7.46, N 5.60; found C 65.05, H 7.83, N 6.22.

Ti(η⁵:η¹-C₅Me₄SiMe₂NiPr){CH₂C₆H₄(NMe₂)-2}Cl (**9**): A mixture of **4** (0.62 g, 1.74 mmol) and $LiCH_2C_6H_4(NMe_2)$-2 (0.25 g, 1.74 mmol) was treated with 50 ml of toluene at −50°C and stirred for 14 h at room temp. After removal of the solvent, the residue was extracted with 50 ml of a toluene/hexane mixture (1:1). Filtration and cooling to −50°C afforded red crystals, yield 0.51 g (65%). − ^1H NMR (C_6D_6): δ = 0.58 (s, 3 H, $SiCH_3$), 0.64 (s, 3 H, $SiCH_3$), 1.14 (s, 3 H, CCH_3), 1.16 (d, $^3J_{HH}$ = 7 Hz, 3 H, $CHCH_3$), 1.44 (d, $^3J_{HH}$ = 6 Hz, 3 H, $CHCH_3$), 1.99 (s, 3 H, CCH_3), 2.14 (s, 3 H, CCH_3), 2.29 (d, $^2J_{HH}$ = 12 Hz, 1 H, $TiCH_2$), 2.39 (overlap. d, $^2J_{HH}$ = 10 Hz, 1 H, $TiCH_2$), 2.40 (s, 3 H, CCH_3), 2.69 (s, 6 H, NCH_3), 5.19 (sept, $^3J_{HH}$ = 6 Hz, 1 H, $CHCH_3$), 6.86 (d, $^3J_{HH}$ = 8 Hz, 1 H, 3-C_6H_4), 6.93 (m, 1 H, 4-C_6H_4,), 7.05 (dt, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1 H, 5-C_6H_4), 7.12 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, 6-C_6H_4). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 4.5, 6.1 ($SiCH_3$), 10.4, 12.5, 14.5, 16.8 (CCH_3), 24.2, 24.5 ($CHCH_3$), 46.9 (NCH_3), 55.0 ($CHCH_3$), 72.2 ($TiCH_2$), 102.7 (C_5Me_4 at Si), 118.7, 123.4, 124.9 (C_6H_4), 130.3, 130.9, 132.0, 135.8 (CCH_3), 144.7 (1-C_6H_4), 152.5 (2-C_6H_4). − EI MS; *m/z* (%): 318 (100) [M^+ − $CH_2C_6H_4NMe_2$], 274 (5) [M^+ − $CH_2C_6H_4NMe_2$, − C_3H_8], 260 (53) [M^+ − $CH_2C_6H_4NMe_2$, − C_3H_8N], 243 (11) [M^+ − $CH_2C_6H_4NMe_2$, − $C_4H_{13}N$], 230 (3) [M^+ − $CH_2C_6H_4NMe_2$, − $C_5H_{14}N$], 224 (6) [M^+ − $CH_2C_6H_4NMe_2$, − C_3H_9N, − Cl], 202 (4) [$C_{12}H_{16}NSi^+$], 166 (4) [$C_{10}H_{18}Si^+$], 118 (16) [$C_9H_{10}^+$]. − $C_{23}H_{37}ClNSiTi$ (453.0): calcd. C 60.99, H 8.23, N 6.18; found C 60.83, H 8.43, N 6.22.

Ti(η⁵:η¹-C₅Me₄SiMe₂NCH₂Ph){CH₂C₆H₄(NMe₂)-2}Cl (**10**): A mixture of **5** (0.85 g, 2.11 mmol) and $LiCH_2C_6H_4(NMe_2)$-2 (0.30 g 2.11 mmol) was treated with 50 ml of toluene at −50°C and stirred for 14 h at room temp. After removal of the solvent, the residue was extracted with 50 ml of a toluene/hexane mixture (1:1). Filtration and cooling to −50°C afforded red crystals; yield 0.65 g (61%). − ^1H NMR (C_6D_6): δ = 0.13 (s, 3 H, $SiCH_3$), 0.41 (s, 3 H, $SiCH_3$), 1.06 (s, 3 H, CCH_3), 1.99 (s, 3 H, CCH_3), 2.11 (s, 3 H, CCH_3), 2.23 (d, $^2J_{HH}$ = 12 Hz, 1 H, $TiCH_2$), 2.34 (d, $^2J_{HH}$ = 12 Hz, 1 H, $TiCH_2$), 2.49 (s, 3 H, CCH_3), 2.73 (s, 6 H, NCH_3), 4.69 (d, $^2J_{HH}$ = 14 Hz, 1 H, NCH_2), 5.88 (d, $^2J_{HH}$ = 14 Hz, 1 H, NCH_2), 7.08 (m, 7 H, Ph, C_6H_4), 7.62 (m, 2 H, Ph, C_6H_4). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 1.0, 3.6 ($SiCH_3$), 10.3, 12.4, 14.3, 17.1 (CCH_3), 47.7 (NCH_3), 59.3 (NCH_2), 73.7 ($TiCH_2$), 104.7 (C_5Me_4 at Si), 118.4, 123.4, 125.3 (C_6H_4), 127.3, 128.3, 128.6 (C_6H_5), 129.5, 130.5, 131.5, 135.5, 143.0 (CCH_3, *ipso*-C_6H_5), 144.9 (1-C_6H_4), 153.1 (2-C_6H_4). − EI MS; *m/z* (%): 500 (9) [M^+], 366 (45) [M^+ − $CH_2C_6H_4NMe_2$], 261 (13) [M^+ − $CH_2C_6H_4NMe_2$, − NCH_2Ph], 163 (8) [$C_9H_{13}NSi^+$], 134 (100) [$CH_2C_6H_4NMe_2^+$], 118 (6) [$C_9H_{10}^+$], 91 (3) [$PhCH_2^+$], 58 (4) [$SiMe_2^+$]. − $C_{27}H_{37}ClN_2SiTi$ (501.0): calcd. C 64.73, H 7.44, N 5.59; found C 64.49, H 7.49, N 5.83.

Ti(η⁵:η¹-C₅Me₄SiMe₂NiPr)[{η⁵-C₅H₃(CH₂NMe₂)-2}Fe(η⁵-C₅H₅)]Cl (**11**): To a solution of **4** (0.97 g, 2.74 mmol) in 90 ml of toluene cooled to −78°C was slowly added Li[{η⁵-$C_5H_3(CH_2NMe_2)$-2}Fe(η⁵-C_5H_5)] (0.68 g, 2.74 mmol), dissolved in 5 ml of diethyl ether. The mixture was allowed to warm up to room temperature and stirred for additional 17 h. The solvent was evaporated and the residue was extracted with 70 ml of hexane. Concentrating and cooling of the solution to −20°C afforded of violet crystals, yield 0.66 g (43%). − ^1H NMR (C_6D_6): δ = 0.64 (s, 3 H, $SiCH_3$), 0.74 (s, 3 H, $SiCH_3$), 1.36 (d, $^3J_{HH}$ = 7 Hz, 3 H, $CHCH_3$), 1.56 (d, $^3J_{HH}$ = 7 Hz, 3 H, $CHCH_3$), 1.81 (s, 3 H, CCH_3), 2.19 (s, 3 H, CCH_3), 2.21 (s, 3 H, CCH_3), 2.23 (s, 6 H, NCH_3), 2.26 (s, 3 H, CCH_3), 3.13 (d, $^2J_{HH}$ = 12 Hz, 1 H, NCH_2), 3.43 (d, $^2J_{HH}$ = 12 Hz, 1 H, NCH_2), 3.85 (m, 1 H, C_5H_3), 4.28 (m, 1 H, C_5H_3), 4.38 (m, 1 H, C_5H_3), 4.46 (s, 5 H, C_5H_5), 5.91 (sept, $^3J_{HH}$ = 7 Hz, 1 H, $CHCH_3$). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 5.6, 5.8 ($SiCH_3$), 12.8, 13.3, 15.6, 15.9 (CCH_3), 25.8, 26.8 ($CHCH_3$), 45.7 (NCH_3), 52.9 ($CHCH_3$), 62.2 (NCH_2), 68.8 (4-C_5H_3), 71.4 (C_5H_5), 71.9, 74.2, (C_5H_3), 89.6 (2-C_5H_3), 100.0 (C_5Me_4 at Si), 127.2, 133.1, 136.6, 137.2, 138.4 (CCH_3, 1-C_5H_3). − EI MS; *m/z* (%): 560 (100) [M^+], 516 (5) [M^+ − C_3H_8], 360 (10) [M^+ − $C_{11}H_{12}Fe$], 317 (11) [$C_{14}H_{24}NClSiTi^+$], 281 (5) [$C_{14}H_{23}NSiTi^+$], 242 (35) [$C_{13}H_{16}NFe^+$], 199 (13) [$C_{11}H_{11}Fe^+$], 186 (2) [$C_{11}H_{26}Si^+$], 121 (4) [$C_5H_4Fe^+$]. − $C_{27}H_{41}N_2ClFeSiTi$ (560.9): calcd. C 57.82, H 7.37, N 4.99; found C 57.61, H 7.24, N 5.10.

Ti(η⁵:η¹-C₅Me₄SiMe₂NCH₂Ph)[{η⁵-C₅H₃(CH₂NMe₂)-2}Fe(η⁵-C₅H₅)]Cl (**12**): To a solution of **5** (1.27 g, 3.16 mmol) in 90 ml of toluene cooled to −78°C was slowly added 0.78 g (3.16 mmol) of Li[{η⁵-$C_5H_3(CH_2NMe_2)$-2}Fe(η⁵-C_5H_5)], dissolved in 5 ml of diethyl ether. The mixture was allowed to warm up to room temperature and stirred for additional 17 h. The solvent was evaporated and the residue was extracted with 70 ml of hexane. Concentrating and cooling of the solution to −20°C afforded violet crystals, yield 0.92 g (48%). − ^1H NMR (C_6D_6): δ = 0.28 (s, 3 H, $SiCH_3$), 0.30 (s, 3 H, $SiCH_3$), 1.98 (s, 3 H, CCH_3), 2.07 (s, 3 H, CCH_3), 2.27 (s, 3 H, CCH_3), 2.34 (s, 6 H, NCH_3), 2.39 (s, 3 H, CCH_3), 3.05 (d, $^2J_{HH}$ = 13 Hz, 1 H, CH_2NCH_3), 3.87 (d, $^3J_{HH}$ = 1 Hz, 1 H, C_5H_3), 4.08 (d. $^2J_{HH}$ = 13 Hz, 1 H, CH_2NCH_3), 4.21 (m, 1 H, C_5H_3), 4.36 (d, $^3J_{HH}$ = 1 Hz, 1 H, C_5H_3), 4.39 (s, 5 H, C_5H_5), 5.80 (d, $^2J_{HH}$ = 15 Hz, 1 H, NCH_2Ph), 5.98 (d, $^2J_{HH}$ = 15 Hz, 1 H, NCH_2Ph), 7.26 (m, 3 H, C_6H_5), 7.55 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-C_6H_5). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 2.2, 3.5 ($SiCH_3$), 12.3, 12.6, 16.0, 16.4 (CCH_3), 46.0 (NCH_3), 58.4 (CH_2Ph), 62.4 (CH_2NCH_3), 68.6 (4-C_5H_3), 71.1 (C_5H_5), 72.5 (3-C_5H_3), 75.2 (5-C_5H_3), 88.2 (2-C_5H_3), 102.0 (C_5Me_4 at Si), 127.5, 127.9, 128.9, 129.1, 133.1, 134.3, 136.5, 138.4, 139.6 (CCH_3, C_5H_3, C_6H_5), 142.8 (*ipso*-C_6H_5). − EI MS; *m/z* (%): 608 (100) [M^+], 452 (22) [$C_{22}H_{28}N_2FeSiTi^+$], 407 (7) [$C_{20}H_{21}NFeSiTi^+$], 365 (50)

Table 2. Crystallographic data and parameters of the crystal structure determinations

Compound	**8**	**9**	**12**
Chem. formula	$C_{27}H_{37}ClN_2SiTi$	$C_{23}H_{37}ClN_2SiTi$	$C_{31}H_{41}ClFeN_2SiTi$
Form wght	501.03	452.99	608.95
Cryst size [mm]	0.8 × 0.2 × 0.2	0.3 × 0.4 × 0.8	0.40 × 0.45 × 0.7
Cryst system	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$
a [Å]	7.912(2)	8.545(2)	9.955(3)
b [Å]	11.233(1)	11.925(2)	14.297(3)
c [Å]	28.881(4)	12.755(4)	21.438(3)
α [°]		106.70(2)	
β [°]		100.47(2)	92.79(2)
γ [°]		92.51(1)	
V [$Å^3$]	2566.8(8)	1217.8(5)	3047(1)
Z	4	2	4
ρ_{calcd} [g cm^{-3}]	1.297	1.235	1.327
μ[mm^{-1}]	0.502	0.521	0.887
F(000)	1064	484	1280
T [K]	296(2)	296(2)	296(2)
$2\theta_{max}$ [°]	60.0	60.0	56.0
Index ranges	$-7 \leq h \leq 11, -10 \leq k \leq 15,$ $-27 \leq l \leq 40$	$0 \leq h \leq 12, -16 \leq k \leq 16,$ $-17 \leq l \leq 17$	$0 \leq h \leq 13, 0 \leq k \leq 18,$ $-28 \leq l \leq 28$
Absorption correction	empirical (ψ-scans)	none	empirical (ψ-scans)
Transmission (min/max)	95.57/99.97	98.66/99.98	91.91/99.91
Reflections			
Collected/independent	5612/5178 [R_{int} = 0.016]	7493/7054 [R_{int} = 0.008]	7715/7310 [R_{int} = 0.010]
Independent with I>2σ(I)	3916	5960	4950
No. of parameters	437	402	393
$R1/wR2/s$ (all data)	0.0791/0.1222/1.171	0.0436/0.0965/1.127	0.0826/0.1305/1.138
$R1/wR2/s$ [I>2σ(I)]	0.0515/0.1020/1.138	0.0325/0.0857/1.094	0.0435/0.1011/1.083
Resid. electron density [e $Å^{-3}$]	0.474/−0.610	0.390/−0.349	0.489/−0.367

[$C_{18}H_{24}ClNSiTi^+$], 329 (3) [$C_{18}H_{23}NSiTi^+$], 298 (5) [$C_{16}H_{16}NSiTi^+$], 261 (12) [M^+ − FcN, − NCH_2Ph], 243 (29) [$C_{13}H_{17}NFe^+$], 199 (47) [$C_{11}H_{11}Fe^+$], 186 (3) [$C_{11}H_{26}Si^+$], 177 (8) [$C_{11}H_{17}Si^+$], 121 (49) [$C_5H_5Fe^+$], 91 (54) [$PhCH_2^+$], 77 (2) [Ph^+], 58 (10) [$C_2H_6Si^+$]. − $C_{31}H_{41}N_2ClFeSiTi$ (609.0): calcd. C 61.15, H 6.79, N 4.60; found C 60.99, H 6.76, N 4.66.

Crystal Structure Determination of **8**, **9 and 12**: X-ray data were collected with an Enraf-Nonius CAD4 diffractometer at room temperature by using Mo-K_α radiation and ω scans. The structures were solved by direct methods (SHELXS-86) and refined by full-matrix least squares (SHELXL-93) against F^2. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in difference Fourier maps and refined isotropically, except for **12** where the hydrogen atoms of the methyl groups are included in calculated positions. For **8** and **9**, isotropic temperature factors were refined. Crystallographic data are summarized in Table 2[18].

Polymerization: A 0.5 l Büchi reactor was charged with 200 ml of toluene and at constant ethene pressure of 3 bar (c = 0.432 mol/l) a mixture of 1.25 ml of catalyst (c = 4 mmol/l) and 1.5 ml of MAO ($c \approx$ 1.658 mol/l) was added at the pressure of 3.5 bar and stirred for 2 h at 23°C. After the reaction mixture was drained into 0.5 l of methanol acidified with 10 ml of concentrated aqueous HCl, the polymer was collected by filtration, washed with methanol, and dried to constant weight. Melting points were determined by DSC.

☆ Dedicated to Professor *Pascual Royo* on the occasion of his 60th birthday.

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[18] 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 number CSD-407857 for **8**, -407855 for **9**, and -407856 for **12**, the names of the authors and the journal citation.

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