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Novel aspects of the transamination reaction between $Ti(NMe_2)_4$ and primary amines.

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Electronic Supplementary Information 1

Full experimental details for the preparation/characterization of all compounds.

General Methods and Instrumentation

All manipulations were carried out using standard Schlenk line or dry box techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon and collected by distillation. NMR spectra were recorded on Bruker DPX300 and Avance500 spectrometers (equipped with a 5 mm triple resonance inverse Z-gradient probe (TBI ^{1}H, ^{31}P, BB)), and referenced internally to residual protio-solvent (^{1}H) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). The spectral parameters for recording of ^{1}H–^{15}N HMQC spectra were: π/2 pulse lengths 6.9 (^{1}H) and 14 (^{15}N) μs; acquisition time 0.2 s; spectral windows 5000 (*F*2) and 25000 (*F*1) Hz; 2048 data points in the ^{1}H dimension and 192 increments in that of ^{15}N; ^{n}J(N,H) = 6 Hz and ^{1}J(N,H) = 70 Hz; relaxation delay 1 s; 8–208 transients per increment. Chemical shifts are quoted in δ (ppm). Infrared spectra were prepared as KBr pellets under argon in a glove box and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France) (C,H,N) or by the Service Central de Microanalyses du CNRS at Vernaison (France) (C,H,N,Cl).

The $Ti(NMe_2)_4$ used in this study was prepared by a literature procedure,[45] or purchased from commercial sources (Aldrich). $V(NMe_2)_4$ was prepared by a modification of a literature procedure.[14] Trimethylchlorosilane was distilled and stored over 4 Å molecular sieves under argon before use. Ar*NH_2 was stirred over KOH, distilled, dried over CaH_2, redistilled, and stored over 4 Å molecular sieves under argon before use in the glove box. $[Ti(=NAr^{*})Cl_2(NHMe_2)_2]$ was prepared according to our published procedure.[9]

[Ti(μ-N-1-Adamantyl)$(NMe_2)_2$]$_2$ (1).

To a toluene solution (3 mL) of 500 mg of $Ti(NMe_2)_4$ (2.230 mmol) was added 1-adamantyl amine (337 mg, 2.230 mmol) at room temperature. The resulting red solution was left without stirring and red crystals started to form after 1-2 hours at RT. Pentane (2 mL) was slowly added to complete crystallization overnight. The crystals were separated by decantation, washed with pentane (3 x 3 mL), and dried under vacuum. Yield 420 mg (66 %). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.33 (s, 24H, N*Me*$_2$), 1.88 (s, 6H, C*H*), 1.54 (s, 12H, C*H*$_2$), 1.53 (s, 12H, C*H*$_2$). ^{13}C{^{1}H} NMR (125.81 MHz, CD_2Cl_2): δ 47.7 (*C*H$_2$), 45.6 (N*Me*$_2$), 36.3 (*C*H$_2$), 30.6 (*C*H) (C_Q not observed due to very poor solubility). IR: 2907s, 2848s, 2763s, 1447m, 1418w, 1345w, 1297w, 1149m, 1117m, 1091m, 947vs, 813w, 655s, 631s, 595m,

541w. Anal. Calcd for $C_{28}H_{54}N_6Ti_2$ (570.50): C, 58.95; H, 9.54; N, 14.73. Found: C, 58.83; H, 9.66; N, 14.61.

[V(μ-N-1-Adamantyl)(NMe$_2$)$_2$]$_2$.

This compound was prepared by a procedure similar to that of titanium analogue **1** by reacting 250 mg of V(NMe$_2$)$_4$ (1.100 mmol) with 161 mg 1-adamantyl amine (161 mg, 1.065 mmol) in 2 mL of toluene. The reaction was heated at 100°C overnight. Large crystals were formed upon slow cooling. Pentane (2 mL) was slowly added to complete crystallization overnight. The crystals were separated by decantation, washed with pentane (3 x 3 mL), and dried under vacuum. Yield 180 mg (57 %). ^{1}H NMR (300 MHz, C_6D_6): δ 3.08 (s, 24H, N*Me$_2$*), 2.27 (br s, 6H, C*H*), 2.19 (s, 12H, C*H$_2$*), 1.88 (app q, 12H, C*H$_2$*). ^{13}C{^{1}H} NMR (125.81 MHz, C_6D_6): δ 47.8 (*C*H$_2$), 47.5 (N*Me$_2$*), 37.1 (*C*H$_2$), 30.9 (*C*H) (*C$_Q$* not observed due to very poor solubility). IR: 2901s, 2842s, 2759s, 1448m, 1413m, 1297m, 1246s, 1150s, 940vs, 813m, 799m, 669s, 601m, 546m. Anal. Calcd for $C_{28}H_{54}N_6V_2$ (576.66): C, 58.32; H, 9.44; N, 14.57. Found: C, 58.18; H, 9.38; N, 14.47.

[Ti(μ-N^{t}Bu)(NMe$_2$)$_2$]$_2$ (2).

In a closed vial, a toluene solution (2 mL) of 400 mg of Ti(NMe$_2$)$_4$ (1.784 mmol) and 142 mg of ^{t}BuNH$_2$ (1.941 mmol) was heated at 100°C for 1.5 hours. The resulting red solution crystallized on cooling to room temperature, and was dried under vacuum. The sticky residue was washed with cold pentane (3 x 2 mL) to afford 330 mg of red solid. Yield: 89%. ^{1}H NMR (300 MHz, C_6D_6): δ 3.40 (s, 24H, N*Me$_2$*), 1.20 (s, 18H, *Me$_{tBu}$*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 69.2 (*C*Me$_3$), 45.5 (N*Me$_2$*), 34.2 (C*Me$_3$*). IR: 2957s, 2838s, 2765s, 1452m, 1441m, 1352m, 1247s, 1181s, 1146s, 1054m, 963m, 946vs, 785w, 645vs, 597s, 547m, 409w. Anal. Calcd for $C_{16}H_{42}N_6Ti_2$ (414.28): C, 46.39; H, 10.22; N, 20.29. Found: C, 46.34; H, 10.20; N, 20.21.

[Ti(μ-NSiPh$_3$)(NMe$_2$)$_2$]$_2$ (3) and [(Me$_2$N)$_2$Ti(μ-NSiPh$_3$)$_2$Ti(NMe$_2$)(NHSiPh$_3$)] (4)

Pentane (2 mL) was slowly added to complete crystallization overnight. The crystals were separated by decantation, washed with pentane (3 x 3 mL), and dried under vacuum.

Complex **3** was prepared at RT by a procedure similar to that of **1**; which is very similar to that reported during the course of our studies[5f] (reaction at 70°C). To a toluene solution (1 mL) of 125 mg of Ti(NMe$_2$)$_4$ (0.558 mmol) was added Ph$_3$SiNH$_2$ (154 mg, 0.559 mmol) at room temperature. The

resulting orange solution was left without stirring for 3 hours. Crystallization occurred during the reaction, affording a first crop of orange crystals of **3** that were separated by filtration and washed with pentane (135 mg, 60%). Addition of 1 mL of pentane to the filtrate solution afforded at -20°C a second crop (90 mg) of crystals of **3** but contaminated with small amounts (<5% by ^{1}H NMR) of red crystals of **4**. Compound **4** was later more selectively prepared by the procedure described below for **8,** but at 100°C for 24 hours and in moderate yield (20% after two necessary recrystallizations from toluene-pentane solutions to separate from **3**). For **3**: ^{1}H NMR (300 MHz, C_6D_6): δ 7.74-7.62 (br m, 12H, *o*-C_6H_5), 7.19-7.02 (br m, 18H, *m*- and *p*-C_6H_5), 2.92 (s, 24H, NMe_2). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 139.1 (C_{ipso}), 136.0 (C_{ortho}), 129.2 (C_{para}), C_{meta} obscured by C_6D_6, 44.1 (NMe_2). ^{29}Si NMR (59.6 MHz, C_6D_6): δ -28.7 (Ph_3SiN). Anal. Calcd for $C_{44}H_{54}N_6Si_2Ti_2$ (818.84): C, 64.54; H, 6.65; N, 10.26. Found: C, 64.58; H, 6.60; N, 10.19. For **4**: ^{1}H NMR (300 MHz, C_6D_6): δ 7.81-7.50 (br m, 18H, *o*-C_6H_5), 7.21-7.00 (br m, 27H, *m*- and *p*-C_6H_5), 3.00 (s, 6H, NMe_2), 2.81 (s, 6H, NMe_2), 2.62 (s, 6H, NMe_2) (N*H* not observed). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 139.0, 138.1 (C_{ipso}); 135.7, 135.9 (C_{ortho}); 129.5, 129.2 (C_{para}); C_{meta} obscured by C_6D_6; 45.6, 44.8, 44.3 (NMe_2). ^{29}Si NMR (59.6 MHz, C_6D_6): δ -16.0 (Ph_3SiNH), -28.7 (Ph_3SiN). Anal. Calcd for $C_{60}H_{64}N_6Si_3Ti_2$ (1049.18): C, 68.69; H, 6.15; N, 8.01. Found: C, 68.60; H, 6.09; N, 8.11.

[Ti(μ-NPh)$_3$(μ^3-NPh)(NMe$_2$)$_4$(NHMe$_2$)] (5)

To a toluene solution (4 mL) of 500 mg of $Ti(NMe_2)_4$ (2.230 mmol) was added $PhNH_2$ (207 mg, 2.223 mmol) at room temperature. The resulting dark solution was heated at 100°C under stirring for 6 hours. The solution was filtered through celite, and the volatiles were removed under vacuum. At this point the crude mixture was shown by ^{1}H NMR to contain **5** and **6** in ratio of ca. 3:1. Washing with cold pentane (3 x 5 mL) and recrystallization in pentane at -20°C afforded pure **5** (195 mg, 36% based on Ti). ^{1}H NMR (300 MHz, C_6D_6): δ 7.22 (br, 8H, Ph, partially obscured by benzene-d_6), 6.96 (br d, 4H, Ph), 6.83 (br m, 8H, Ph), 3.14 (s, 12H, NMe_2), 2.95 (s, 12H, NMe_2), 1.55 (s, 6H, NHMe_2) (N*H* not observed). Anal. Calcd for $C_{34}H_{51}N_9Ti_3$ (729.43): C, 55.98; H, 7.05; N, 17.28. Found: C, 55.75; H, 7.12; N, 17.42.

Reaction of Ti(NMe$_2$)$_4$ and Ar*NH$_2$ (1:2). Preparation of [Ti(μ-NAr*)(NMe$_2$)$_2$]$_2$ (7).

Method A (from toluene solution). To a toluene solution (3 mL) of 250 mg of $Ti(NMe_2)_4$ (1.115 mmol) was added Ar^*NH_2 (197 mg, 1.111 mmol) at room temperature. The resulting dark solution was

left under stirring overnight at RT. The solution was filtered through celite, and the volatiles were removed under vacuum. Pentane (3 mL) was added to the oily residue, triturated, and the volatiles were removed under vacuum. This cycle of pentane addition/vacuum drying was repeated 3-5 times, to afford a red-purple solid containing **7** (80-90%) contaminated with **8** (20-10%) (Note: under reflux conditions, we noticed a ratio **7:8** of *ca.* 40:60). Pure **7** can be obtained by washing the crude product with cold pentane or by recrystallization from pentane or toluene-pentane solution.

Method B (solventless reaction). A schlenk tube with 500 mg of $Ti(NMe_2)_4$ (2.230 mmol) and 395 mg Ar^*NH_2 (2.228 mmol) was heated at 100°C under a very slow stream of argon for 1 hour (via a needle connected to a bubbler). The neat liquid solidifies within about 20-30 minutes. The solid was vacuum dried at 100°C for 30 minutes, and extracted with toluene (3 x 1 mL). The toluene solution was filtered through celite, and the solvent was removed under vacuum, to afford 565 mg of **7** (yield 81 %). The solid generally contained less than 1-2 % **8** (that can be removed by recrystallization in pentane or toluene-pentane solutions at -20°C).

Method C (from $Ti(=NAr^*)Cl_2(NHMe_2)_2$). To a toluene solution (2 mL) of 100 mg of $Ti(=NAr^*)Cl_2(NHMe_2)_2$ (0.2603 mmol) were added by portions 2 equiv. of $KN(SiMe_3)_2$ (103.8 mg, 0.5204 mmol) at room temperature. The resulting red solution was stirred for 2 hours at RT. The volatiles were pumped off, and the dark red-purple residue was extracted with pentane (3 x 2 mL). The pentane solution was dried under vacuum to give 70 mg of crystals of **7** (86 %). ^{1}H NMR (300 MHz, C_6D_6): δ 7.21 (d, ^3J = 7.8 Hz, 4H, $C_6H_3Pr^i_2$), 7.07 (t, ^3J = 7.6 Hz, 2H, $C_6H_3Pr^i_2$), 4.05 (sept, ^3J = 6.8 Hz, 4H, C*H*Me$_2$), 2.99 (s, 24H, N*Me*$_2$), 1.32 (d, ^3J = 6.7 Hz, 24H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 152.3 (*ipso*-C_6H_3), 140.1 (*o*-C_6H_3), 123.7 (*p*-C_6H_3), 123.4 (*m*-C_6H_3), 45.1 (N*Me*$_2$), 28.1 (*C*HMe$_2$), 24.8 (CH*Me*$_2$). IR: 2959s, 2853s, 2765s, 1651m, 1459m, 1417s, 1316w, 1237vs, 1201m, 1149m, 1110m, 950m, 938s, 907m, 751vs, 589m, 570m, 498m. Anal. Calcd for $C_{32}H_{58}N_6Ti_2$ (622.58): C, 61.73; H, 9.39; N, 13.50. Found: C, 61.67; H, 9.30; N, 13.40.

Reaction of $Ti(NMe_2)_4$ and Ar^*NH_2 (2:3). Preparation of $[(Me_2N)_2Ti(\mu\text{-}NAr^*)_2Ti(NMe_2)(NHAr^*)]$ (8).

A schlenk tube with 200 mg of $Ti(NMe_2)_4$ (0.892 mmol), 237 mg Ar^*NH_2 (1.337 mmol), and 4 mL of toluene was heated for 1 hour at 100°C under argon. The volatiles were removed under vacuum, first at RT until dry and then 5 minutes at 100°C. Extraction of the residue with toluene (6 x 1 mL), filtration of the resulting solution to remove small amount of pale purple insoluble materials, afforded a

red-purple solution. The solvent was removed under vacuum to give 306 mg of dark red crystals of **8** (yield 91 %). The product can further be recrystallized from cold pentane solutions. ^{1}H NMR (300 MHz, C_6D_6): δ 7.41 (s, 1H, N*H*), 7.28 (d, ^{3}J = 7.8 Hz, 4H, m-$C_6H_3Pr^i_2$ μ-NAr*), 7.08-6.94 (5H, $C_6H_3Pr^i_2$ μ-NAr* + NHAr*), 4.14 (sept, ^{3}J = 6.6 Hz, 4H, C*H*Me$_2$ μ-NAr*), 3.30 (s, 6H, N*Me*$_2$), 3.05 (s, 6H, N*Me*$_2$), 2.91 (sept, ^{3}J = 6.6 Hz, 2H, C*H*Me$_2$ NHAr*), 2.43 (s, 6H, N*Me*$_2$), 1.46 (d, ^{3}J = 6.7 Hz, 24H, CH*Me*$_2$ μ-NAr*), 1.04 (d, ^{3}J = 6.7 Hz, 12H, CH*Me*$_2$ NHAr*). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ 152.1 (*ipso*-C_6H_3 μ-NAr*), 147.9 (*ipso*-C_6H_3 NHAr*), 140.4 (*o*-C_6H_3 NHAr*), 139.1 (*o*-C_6H_3 μ-NAr*), 124.2 (*p*-C_6H_3 μ-NAr*), 123.3 (*p*-C_6H_3 NHAr*), 122.5 (*m*-C_6H_3 μ-NAr*), 121.8 (*m*-C_6H_3 NHAr*), 47.5 (N*Me*$_2$), 45.4 (N*Me*$_2$), 42.0 (N*Me*$_2$), 28.9 (*C*HMe$_2$ μ-NAr* + NHAr*), 24.7 (CH*Me*$_2$ NHAr*), 24.3 (CH*Me*$_2$ μ-NAr*). IR: 3305w, 3051w, 2960s, 2864s, 2772m, 1619w, 1586w, 1462m, 1420m, 1311m, 1238vs, 1197m, 1107m, 1055m, 959m, 796m, 752s, 573s, 504m. Anal. Calcd for $C_{42}H_{70}N_6Ti_2$ (754.78): C, 66.83; H, 9.35; N, 11.13. Found: C, 66.82; H, 9.42; N, 11.16.

Reaction of Ti(NMe$_2$)$_4$ and Ar*NH$_2$ (1:2). Preparation of [Ti(NMe$_2$)$_3$]$_2$(μ-NAr*) (9).

Method A (from Ti(NMe$_2$)$_4$ and Ar*NH$_2$). A toluene solution (2 mL) of Ti(NMe$_2$)$_4$ (200 mg, 0.892 mmol) and 79 mg Ar*NH$_2$ (0.446 mmol) was stirred at RT for 4 hours. The yellow solution turned orange-red. The volatiles were removed under vacuum to afford a red oil. This oil was treated with 2 mL of pentane, and evaporated to dryness (3 times). The red sticky solid was solubilized in the minimum of pentane (ca. 1 mL), filtered through celite, and left overnight in the glove box with an opened cap for slow evaporation that lead to complete crystallization. The solid was further dried under vacuum. Yield 190 mg (80 %) (alternatively, 160 mg of crystals were also obtained by placing the pentane solution at -20°C). ^{1}H NMR (300 MHz, C_6D_6): δ7.20 (d, ^{3}J = 7.7 Hz, 2H, $C_6H_3Pr^i_2$), 7.00 (t, ^{3}J = 7.6 Hz, 2H, $C_6H_3Pr^i_2$), 3.76 (sept, ^{3}J = 6.7 Hz, 2H, C*H*Me$_2$), 3.01 (s, 36H, N*Me*$_2$), 1.27 (d, ^{3}J = 6.7 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ150.0 (*ipso*-C_6H_3), 140.8 (*o*-C_6H_3), 123.7 (*p*-C_6H_3), 122.7 (*m*-C_6H_3), 44.8 (N*Me*$_2$), 27.7 (*C*HMe$_2$), 24.4 (CH*Me*$_2$). IR: 2959m, 2856s, 2767s, 1463s, 1417s, 1246s, 1170m, 1145m, 1053m, 945vs, 832m, 761s, 661vs, 594s, 548w, 524w. Anal. Calcd for $C_{24}H_{53}N_7Ti_2$ (535.46): C, 53.83; H, 9.98; N, 18.31. Found: C, 53.66; H, 9.82; N, 17.85.

Method B (from Ti(NMe$_2$)$_4$ and **7***).* A toluene solution (1 mL) of Ti(NMe$_2$)$_4$ (36 mg, 0.1606 mmol) and 50 mg **7** (0.0803 mmol) was stirred at RT 14 hours. The volatiles were removed under vacuum to afford a red oil. This oil was solubilized in the minimum of pentane (ca. 1 mL), filtered through celite, and left overnight in the glove box with an opened cap for slow evaporation that lead to complete

crystallization. The sticky solid was further dried under vacuum and was shown by ^{1}H NMR to have the composition Ti(NMe$_2$)$_4$/**9**/**7** = 2:1:1.

Reaction of Ti(NMe$_2$)$_4$ and Ar*NH$_2$ (1:2) (attempted synthesis of C). Preparation of [(Me$_2$N)(Me$_2$NH)Ti(μ-NAr*)$_2$Ti(NMe$_2$)(=NAr*)] (11).

Complex **11** was observed or isolated in many reactions involving Ti(NMe$_2$)$_4$ and Ar*NH$_2$ (various ratios, various experimental conditions, see text). We describe here one synthesis that gave good yields of **11**. In a closed vial, a toluene solution (2 mL) of Ti(NMe$_2$)$_4$ (100 mg, 0.4460 mmol) and Ar*NH$_2$ (158 mg, 0.8912 mmol) was stirred at 100°C for 2 hours. Red crystals of **11** separated on cooling to RT. The crystals were collected, washed with portions of pentane (2 x 3 mL) and dried under vacuum (Yield: 100 mg, 59%). In some experiments (or if one does not want to wait for crystallization), the reaction mixture was dried under vacuum, and the dark brown solid residue was washed with pentane (4 x 3 mL) and dried under vacuum (the pentane washings contained unreacted Ar*NH$_2$, **8**, **13**, …). Crystals of **11** were obtained from toluene (see above) or from C$_6$D$_6$ solutions, and were shown to contain solvent molecules in the cell. Once isolated, the solubility of **11** in C$_6$D$_6$ is very poor and a clean spectrum could not be obtained, therefore the spectra were recorded in CD$_2$Cl$_2$. The NMR is given at 193K to avoid the reverse reaction giving back **8**. At that temperature, rotation around the μ-NAr* is blocked as well as around one -NMe$_2$ (the one linked to the Ti center having a terminal imido). For immediate characterization a ^{1}H NMR spectrum of **11** at 300K is also given. Note: When conducted under solventless conditions, the same reaction afforded 38% of isolated **11**, whereas the same reaction conducted in toluene with two cycles of heating at 120°C/vacuum drying afforded 5% **11**, 25% **8** and 9% **10**.

For **11**: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 193K): δ 7.08 (d, ^3J = 7.8 Hz, 2H, m^a-C$_6$H$_3$Pr$^i_2$ μ-NAr*), 6.99 (d, ^3J = 7.8 Hz, 2H, m^b-C$_6$H$_3$Pr$^i_2$ μ-NAr*), 6.85 (t, ^3J = 7.6 Hz, 2H, p-C$_6$H$_3$Pr$^i_2$ μ-NAr*), 6.56 (d, ^3J = 7.6 Hz, 2H, m-C$_6$H$_3$Pr$^i_2$ Ti=NAr*), 6.37 (d, ^3J = 7.7 Hz, 1H, p-C$_6$H$_3$Pr$^i_2$ Ti=NAr*), 3.87 (m, 2H, CH^aMe$_2$ μ-NAr*), 3.52 (s, 3H, NMe^aMe^b), 3.39 (s, 3H, NMe^aMe^b), 3.29 (br m, 1H, NHMe$_2$), 3.19 (m, 2H, CH^bMe$_2$ μ-NAr*), 3.06 (s, 6H, NMe_2), 2.58 (d, ^3J = 6.5 Hz, 6H, NHMe_2), 2.08 (sept, ^3J = 6.6 Hz, 2H, CHMe$_2$ Ti=NAr*), 1.33 (d, ^3J = 6.6 Hz, 6H, CHMe^aMe^b μ-NAr*), 1.19 (d, ^3J = 6.6 Hz, 6H, CHMe^aMe^b μ-NAr*), 1.14 (d, ^3J = 6.6 Hz, 6H, CHMe^cMe^d μ-NAr*), 1.07 (d, ^3J = 6.6 Hz, 6H, CHMe^cMe^d μ-NAr*), 0.54 (br d, 12H, CHMe_2 Ti=NAr*). ^{13}C{^{1}H} NMR (125.8 MHz, CD$_2$Cl$_2$, 193K): δ 152.1 (*ipso*-C_6H$_3$ Ti=NAr*), 154.8 (*ipso*-C_6H$_3$ μ-NAr*), 141.4 (*o*-C_6H$_3$ Ti=NAr*), 138.1 and 134.1 (*o*-

C_6H_3 μ-NAr^*), 128.4 and 124.0 (*m*-C_6H_3 μ-NAr^*), 121.6 (*p*-C_6H_3 μ-NAr^*), 121.5 (*m*-C_6H_3 Ti=NAr^*), 117.7 (*p*-C_6H_3 Ti=NAr^*), 53.3 and 46.3 (NMe^aMe^b), 43.0 (NMe_2), 39.6 (N*H*Me_2), 30.0 (CH^aMe_2 μ-NAr^*), 27.45 (CH^bMe_2 μ-NAr^*), 27.38 (*C*HMe_2 Ti=NAr^*), 25.7 (CHMe^aMe^b μ-NAr^*), 25.3 (CHMe$^aMe^b$ μ-NAr^*), 25.0 (CHMe_2 Ti=NAr^*), 24.6 (CHMe^cMe^d μ-NAr^*), 24.1 (CHMe$^cMe^d$ μ-NAr^*). ^{1}H NMR (300 MHz, CD_2Cl_2, 300K): δ 7.15 (br d, 2H, m^a-$C_6H_3Pr^i_2$ μ-NAr^*), 7.05 (br m, 2H, m^b-$C_6H_3Pr^i_2$ μ-NAr^*), 6.91 (t, ^3J = 7.6 Hz, 2H, *p*-$C_6H_3Pr^i_2$ μ-NAr^*), 6.62 (d, ^3J = 7.6 Hz, 2H, *m*-$C_6H_3Pr^i_2$ Ti=NAr^*), 6.43 (d, ^3J = 7.7 Hz, 1H, *p*-$C_6H_3Pr^i_2$ Ti=NAr^*), 3.97 (m, 2H, CH^aMe$_2$ μ-NAr^*), 3.55 (s, 3H, NMe_2), 3.30 (br m, 3H, N*H*Me_2 + CH^bMe$_2$ μ-NAr^*), 3.08 (s, 6H, NMe_2), 2.65 (d, ^3J = 6.5 Hz, 6H, NHMe_2), 2.37 (sept, ^3J = 6.5 Hz, 2H, C*H*Me_2 Ti=NAr^*), 1.39 (d, ^3J = 6.6 Hz, 6H, CHMe^aMe^b μ-NAr^*), 1.30 (br, 12H, CHMe$^aMe^b$ + CHMe^cMe^d μ-NAr^*), 1.17 (d, ^3J = 6.6 Hz, 6H, CHMe$^cMe^d$ μ-NAr^*), 0.70 (d, ^3J = 6.6 Hz, 6H, CHMe_2 Ti=NAr^*), 0.64 (d, ^3J = 6.6 Hz, 6H, CHMe_2 Ti=NAr^*). IR: 3402w, 3259w, 2960s, 2866s, 1617m, 1458m, 1412m, 1339m, 1288w, 1237m, 1200w, 1102w, 986w, 941m, 912w, 749vs, 620w, 573m, 499w. Anal. Calcd for $C_{42}H_{70}N_6Ti_2$ (754.78): C, 66.83; H, 9.35; N, 11.13. Found: C, 67.25; H, 9.44; N, 10.42. (A perfect analysis could not be obtained, probably due to the presence of residual toluene molecule even after extensive drying (half a molecule), as seen by NMR spectroscopy and X-ray study).

Reaction of $Ti(NMe_2)_4$ and Ar^*NH_2 (1:3). Preparation of $Ti(NHAr^*)_4$ (12), and $[(Me_2N)(Me_2NH)Ti(\mu\text{-}NAr^*)_2Ti(NMe_2)(=NAr^*)]$ (11).

In a closed vial, a toluene solution (2 mL) of $Ti(NMe_2)_4$ (100 mg, 0.4460 mmol) and Ar^*NH_2 (237.2 mg, 1.338 mmol) was stirred at room temperature for 3 days. The volatiles were removed under vacuum, and the residue was washed with pentane (2 x 2 mL). The dark solid, **11**, (insoluble in pentane) was dried under vacuum (yield 70 mg). From the pentane washing, placed at -20°C, was obtained 20 mg of crystals of **12**. Note: the same reaction conducted at 110°C afforded after selective crystallization **11** (40 mg), **12** (20 mg), and **13** (10 mg).

Reaction of $Ti(NMe_2)_4$ and Ar^*NH_2 (1:4) in toluene. Selective preparation of $[(Ar^*NH)_2Ti(\mu\text{-}NAr^*)_2Ti(NMe_2)(NHAr^*)]$ (10), or $[(Me_2N)(Me_2NH)Ti(\mu\text{-}NAr^*)_2Ti(NMe_2)(=NAr^*)]$ (11), and $[(Ar^*NH)_2Ti(\mu\text{-}NAr^*)_2Ti(NMe_2)(NHAr^*)]$ (13).

Method A (1 cycle of heating): In a closed vial, a toluene solution (2 mL) of $Ti(NMe_2)_4$ (500 mg, 2.230 mmol) and Ar^*NH_2 (1.581 g, 8.918 mmol) was stirred at 120°C for 2 hours. The volatiles were removed under vacuum, and the oily residue was extracted with pentane (4 x 3 mL). The dark solid, **11**, (insoluble in pentane) was dried under vacuum (yield in **11** 480 mg, 57%). The pentane solution was dried under vacuum, and extracted again with pentane (3 x 2 mL). This left a red insoluble solid (120 mg) composed of **13** and **10** (in a ratio *ca*. 2:1, and from which 40 mg of pure **13** could be separated by washing the solid with 5 x 2 mL of pentane, yield in isolated **13**: 4%), and the solution was concentrated (about half volume) and placed at -20°C to afford another crop containing crystals 25 mg of **10** (yield in isolated **10**: 3 %).

Method B (2 cycles of heating): In a closed vial, a toluene solution (2 mL) of $Ti(NMe_2)_4$ (500 mg, 2.230 mmol) and Ar^*NH_2 (1.581 g, 8.918 mmol) was stirred at 120°C for 2 hours. The volatiles were removed under vacuum, and toluene (2 mL) was added and the solution was again heated at 120°C for 2 hours. The volatiles were removed under vacuum, and the oily residue was extracted with pentane (5-10 mL). Selective recrystallization at -20°C afforded 386 mg of **10** as a red solid (yield in **10**: 39%) and 650 mg of **13** (yield in **13**: 57%).

For **10**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.97 (s, 2H, N*H*), 7.15-6.90 (12H, $C_6H_3Pr^i_2$ μ-NAr^* + $NHAr^*$), 4.55 (sept, ^3J = 6.6 Hz, 2H, C*H*Me_2 μ-NAr^*), 3.95 (sept, ^3J = 6.6 Hz, 2H, C*H*Me_2 μ-NAr^*), 3.24 (s, 12H, N*Me*$_2$), 2.54 (sept, ^3J = 6.5 Hz, 4H, C*H*Me_2 $NHAr^*$), 1.46 (d, ^3J = 6.6 Hz, 12H, CH*Me*$_2$ μ-NAr^*), 1.29 (d, ^3J = 6.7 Hz, 12H, CH*Me*$_2$ μ-NAr^*), 0.97 (d, ^3J = 6.7 Hz, 24H, CH*Me*$_2$ $NHAr^*$). ^{1}H NMR (300 MHz, C_6D_6): δ8.24 (s, 2H, N*H*), 7.13 (4H, *m*-$C_6H_3Pr^i_2$ μ-NAr^* or $NHAr^*$), 7.08-6.95 (d + t, 6H, $C_6H_3Pr^i_2$ μ-NAr^* + $NHAr^*$), 6.86 (t, 2H, *p*-$C_6H_3Pr^i_2$ μ-NAr^* + $NHAr^*$), 3.93 (br, 4H, C*H*Me_2 μ-NAr^* or $NHAr^*$), 3.35 (sept, ^3J = 6.6 Hz, 4H, C*H*Me_2 μ-NAr^* or $NHAr^*$), 2.75 (s, 12H, N*Me*$_2$), 1.28-1.07 (br, 48H, CH*Me*$_2$ μ-NAr^* + $NHAr^*$). ^{13}C{^{1}H} NMR (75.47 MHz, $C_6D_5CD_3$): δ 150.90 (*ipso*-$C_6H_3Pr^i_2$ μ-NAr^{*1}), 149.49 (*ipso*-$C_6H_3Pr^i_2$ $NHAr^{*2}$), 142.60 (*o*-$C_6H_3Pr^i_2$ μ-NAr^{*1}), 137.10 (*o*-$C_6H_3Pr^i_2$ $NHAr^{*2}$), 125.15 (*p*-$C_6H_3Pr^i_2$ μ-NAr^{*1}), 123.59 (*m*-$C_6H_3Pr^i_2$ μ-NAr^{*1}), 123.03 (*m*-$C_6H_3Pr^i_2$ $NHAr^{*2}$), 120.31 (*p*-$C_6H_3Pr^i_2$ $NHAr^{*2}$), 45.00 (N*Me*$_2$), 29.91 (*C*HMe_2 $NHAr^{*2}$), 28.57 (*C*HMe_2 μ-NAr^{*1}), 24.35 (CH*Me*$_2$ $NHAr^{*2}$), 23.97 (CH*Me*$_2$ μ-NAr^{*1}). ^{15}N ($C_6D_5CD_3$, HMQC ^{1}H-^{15}N): δ -448.0 (μ-*N*Ar^{*1}), -179.5 (*N*HAr^{*2}), -143 (*N*Me_2). IR: 3224w, 3051w, 2958s, 2866m, 1619w, 1589w, 1459m, 1429m, 1316s, 1239s, 1193m, 1107s, 1053m, 958m, 917m, 849m, 793w, 755m, 744s, 698w, 603s, 577s, 505m,

477m, 415w. Anal. Calcd for $C_{52}H_{82}N_6Ti_2$ (886.98): C, 70.41; H, 9.32; N, 9.47. Found: C, 70.55; H, 9.38; N, 9.37.

For **13**: ^{1}H NMR (300 MHz, C_6D_6): δ 8.63 (s, 1H, N*H*Ar^{*1}), δ 8.43 (s, 1H, N*H*Ar^{*3}), δ 8.32 (s, 1H, N*H*Ar^{*2}), 7.07-6.81 (m, 15H, $C_6H_3Pr^i_2$ μ-NAr* + NHAr*), 4.38 (sept, ^3J = 6.6 Hz, 2H, C*H*Me$_2$ μ-NAr^{*4}), 3.86 (sept, ^3J = 6.6 Hz, 2H, C*H*Me$_2$ μ-NAr^{*5}), 3.56 (sept, ^3J = 6.5 Hz, 2H, C*H*Me$_2$ NHAr^{*3}), 3.21 (s, 6H, N*Me*$_2$), 3.20 (sept, ^3J = 6.5 Hz, 2H, C*H*Me$_2$ NHAr^{*1}), 2.20 (sept, ^3J = 6.5 Hz, 2H, C*H*Me$_2$ NHAr^{*2}), 1.47 (d, ^3J = 6.5 Hz, 6H, CH*Me*$_2$ μ-NAr^{*4a}), 1.37 (d, ^3J = 6.5 Hz, 6H, CH*Me*$_2$ μ-NAr^{*4b}), 1.17 (d, ^3J = 6.5 Hz, 6H, CH*Me*$_2$ μ-NAr^{*5a}), 1.12 (d, ^3J = 6.5 Hz, 12H, CH*Me*$_2$ NHAr^{*3}), 1.07 (d, ^3J = 6.5 Hz, 6H, CH*Me*$_2$ μ-NAr^{*5b}), 0.84 (d, ^3J = 6.5 Hz, 12H, CH*Me*$_2$ NHAr^{*2}). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ 153.48 (*ipso*-$C_6H_3Pr^i_2$ NAr^{*5}), 149.75 (*ipso*-$C_6H_3Pr^i_2$ NHAr^{*1}), 149.29 (*ipso*-$C_6H_3Pr^i_2$ NHAr^{*3}), 148.16 (*ipso*-$C_6H_3Pr^i_2$ NHAr^{*2}), 143.48 (*ipso*-$C_6H_3Pr^i_2$ NAr^{*4}), 141.06 (*o*-$C_6H_3Pr^i_2$ NAr^{*4}), 140.44 (*o*-$C_6H_3Pr^i_2$ NAr^{*5}), 138.23 (*o*-$C_6H_3Pr^i_2$ NHAr^{*2}), 136.26 (*o*-$C_6H_3Pr^i_2$ NHAr^{*1}), 136.24 (*o*-$C_6H_3Pr^i_2$ NHAr^{*3}), 125.27 (*p*-$C_6H_3Pr^i_2$ NHAr^{*2}), 124.56 (*m*-$C_6H_3Pr^i_2$ NAr^{*4} + NAr^{*5}), 123.73 (*m*-$C_6H_3Pr^i_2$ NHAr^{*1}), 123.57 (*m*-$C_6H_3Pr^i_2$ NHAr^{*2}), 123.40 (*m*-$C_6H_3Pr^i_2$ NHAr^{*3}), 123.30 (*p*-$C_6H_3Pr^i_2$ NAr^{*4} + NAr^{*5}), 121.06 (*p*-$C_6H_3Pr^i_2$ NHAr^{*3}), 121.03 (*p*-$C_6H_3Pr^i_2$ NHAr^{*1}), 47.68 (N*Me*$_2$), 30.17 (*C*HMe$_2$ NHAr^{*1}), 29.51 (*C*HMe$_2$ NHAr^{*3}), 29.11 (*C*HMe$_2$ NHAr^{*2}), 28.05 (*C*HMe$_2$ NAr^{*5}), 26.81 (*C*HMe$_2$ NAr^{*4}), 25.25 (CH*Me*$_2$ NAr^{*5}), 24.60 (CH*Me*$_2$ NHAr^{*2}), 23.54 (CH*Me*$_2$ NHAr^{*3}), 24.50 (CH*Me*$_2$ NHAr^{*1}), 24.07 (CH*Me*$_2$ NAr^{*4}). ^{15}N ($C_6D_5CD_3$, HMQC ^{1}H-^{15}N): δ -178.5 (*N*HAr^{*3}), -172.3 (*N*HAr^{*1}), -152.0 (*N*HAr^{*2}). IR: 3408w, 3292w, 2962s, 2866s, 1617w, 1590w, 1458s, 1430s, 1382w, 1361w, 1240s, 1190m, 1104s, 947w, 885w, 850m, 747vs, 701m, 581s, 508m, 418w. Anal. Calcd for $C_{62}H_{94}N_6Ti_2$ (1019.18): C, 73.06; H, 9.30; N, 8.25. Found: C, 73.15; H, 9.34; N, 8.14.

Solventless reaction of Ti(NMe$_2$)$_4$ and Ar*NH$_2$ (1:4 or 1:5). Selective preparation of Ti(NHAr*)$_4$ (12), and [(Ar*NH)$_2$Ti(μ-NAr*)$_2$Ti(NMe$_2$)(NHAr*)] (13)

In a schlenk flask, and under solventless conditions, Ti(NMe$_2$)$_4$ (500 mg, 2.230 mmol) and Ar*NH$_2$ (1.581 g, 8.918 mmol) was stirred at 120°C for 2 hours with brief vacuum cycle (a few seconds every 20 minutes to remove liberated NHMe$_2$). The volatiles were removed under vacuum at 100°C for 30 minutes. The solid residue was extracted with pentane (3 x 2 mL). The light-orange solid, **12**, (insoluble in pentane) was dried under vacuum (yield 90 mg, 5%). The pentane solution was dried under vacuum, and the residue was washed with pentane (3 x 2 mL) to afford a purple solid (**13**, 450 mg, 40%) (the washings still contains **12** and **13**). Note: **12** and **13** were obtained in variable ratio

depending on the Ar*NH_2/Ti(NMe_2)$_4$ ratio used (4 or 5) (increasing further the ratio of Ar*NH_2:Ti(NMe_2)$_4$ to 8 lead only to slightly higher yields in **12** (120 mg)). We also noticed that their solubility is very close and therefore the first product to be separated by washing with pentane can vary.

For **12**: ^{1}H NMR (300 MHz, C_6D_6): δ 9.05 (s, 4H, N*H*), 7.06 (d, ^3J = 7.6 Hz, 8H, *m*-$C_6H_3Pr^i_2$), 6.91 (t, ^3J = 7.6 Hz, 4H, *p*-$C_6H_3Pr^i_2$), 3.55 (sept, ^3J = 6.6 Hz, 8H, C*H*Me$_2$), 1.20 (d, ^3J = 6.6 Hz, 48H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 149.2 (*ipso*-C_6H_3), 137.3 (*o*-C_6H_3 NHAr*), 139.1 (*o*-C_6H_3), 123.9 (*p*-C_6H_3), 122.9 (*m*-C_6H_3), 28.7 (*C*HMe$_2$), 23.5 (CH*Me*$_2$). ^{15}N ($C_6D_5CD_3$, HMQC ^{1}H-^{15}N): δ -154.0 (*N*H). IR: 3293m, 3051w, 2961s, 2867s, 1619w, 1859w, 1459s, 1431s, 1315s, 1242vs, 1220sh, 1191s, 1106s, 885m, 748s, 701m, 582s, 508m, 415w. Anal. Calcd for $C_{48}H_{72}N_4Ti$ (752.98): C, 76.56; H, 9.64; N, 7.44. Found: C, 76.44; H, 9.68; N, 7.43.

NMR tube reaction of 7 with pyridine. Characterization of the pyridine-adduct [(Me_2N)$_2$Ti(μ-NAr*)$_2$Ti(NMe_2)$_2$(Py)] (14).

In a Young-type NMR tube was placed 20 mg of **7** (1 equiv) and 10 mg of pyridine (4 equiv) in toluene-d_8, and the reaction was monitored by VT NMR spectroscopy after standing 1 hour at 25°C. The studies demonstrated a dynamic equilibrium in solution between **7**, **14**, and free pyridine, and permitted to fully characterized **14**.

For **14**: ^{1}H NMR (500 MHz, Toluene-d_8, 193K): δ 8.30 (d, 2H, *o*-Py), 7.35 (d, 1H, *m*-$C_6H_3Pr^i_2$ μ-NAr*^{2}), 7.31 (d, 1H, *m*-$C_6H_3Pr^i_2$ μ-NAr*^{1}), 7.16 (d, 1H, *m'*-$C_6H_3Pr^i_2$ μ-NAr*^{2}), 7.00 (br app. t, 2H, *p*-$C_6H_3Pr^i_2$ μ-NAr*^{1}), 6.97 (br app. t, 2H, *p*-$C_6H_3Pr^i_2$ μ-NAr*^{2}), 6.90 (d, 1H, *m'*-$C_6H_3Pr^i_2$ μ-NAr*^{1}), 6.43 (br t, 1H, *p*-Py), 6.24 (br t, 2H, *m*-Py), 4.16 (br m, 1H, C*H*^{c}Me$_2$ μ-NAr*^{2}), 4.74 (br m, 1H, C*H*^{d}Me$_2$ μ-NAr*^{2}), 4.36 (s, 3H, N*Me*^{g}Me^x),4.15 (br m, 1H, C*H*^{b}Me$_2$ μ-NAr*^{1}), 2.43 (br m, 1H, C*H*^{a}Me$_2$ μ-NAr*^{1}), 3.67 (s, 3H, N*Me*^{f}Me^x), 3.27 (s, 3H, N*Me*^{e}Me^x), 3.07 (s, 3H, N*Me*^{d}Me^x), 2.94 (s, 3H, N*Me*^{c}Me^x), 2.87 (s, 3H, N*Me*^{b}Me^x), 2.50 (s, 6H, N*Me*$_2$), 1.57 (br, 3H, CH^{b}Me^c*Me*^{d} μ-NAr*^{1}), 1.56 (br, 6H, CH^c*Me*$^e_2$ μ-NAr*^{2}), 1.56 (br, 3H, CH^d*Me*^{f}Me^g μ-NAr*^{2}), 1.44 (d, 3H, CH^{d}Me^f*Me*^{g} μ-NAr*^{2}), 1.35 (d, 3H, CH^b*Me*^{c}Me^d μ-NAr*^{1}), 1.19 (d, 3H, CH^{a}Me^a*Me*^{b} μ-NAr*^{1}), 0.41 (d, 3H, CH^a*Me*^{a}Me^b μ-NAr*^{1}). ^{13}C{^{1}H} NMR (125.8 MHz, Toluene-d_8, 193K): δ 151.62 (*o-Py*), 150.20 (*ipso*-C_6H_3 μ-NAr*^{1}), 150.05 (*ipso*-C_6H_3 μ-NAr*^{2}), 142.11 (*o*-C_6H_3 μ-NAr*^{2}), 138.66 (*o'*-C_6H_3 μ-NAr*^{2}), 137.83 (*o'*-C_6H_3 μ-NAr*^{1}), 137.09 (*p-Py*), 135.32 (*o*-C_6H_3 μ-NAr*^{1}), 123.73 (*m*-C_6H_3 μ-NAr*^{1}), 123.41 (*m'*-C_6H_3 μ-NAr*^{2}), 123.40

(*m-Py*), 123.00 (*m*-C_6H_3 μ-NAr^{*2}), 121.83 (*m'*-C_6H_3 μ-NAr^{*1}), 121.46 (*p*-C_6H_3 μ-NAr^{*1}), 119.08 (*p*-C_6H_3 μ-NAr^{*2}), 54.88 (N$Me^g$$Me^x$), 53.88 (N$Me^f$$Me^x$), 46.66 (N$Me^e$$Me^x$), 46.04 (N$Me^b$$Me^x$), 45.87 (N$Me^c$$Me^x$), 44.75 (N$Me^d$$Me^x$), 41.94 (N$Me^a{}_2$), 29.53 ($CH^aMe_2$ μ-NAr^{*1}), 28.02 (CH^aMe_2 μ-NAr^{*2}), 27.58 (CH^bMe_2 μ-NAr^{*1}), 27.19 (CH^cMe_2 μ-NAr^{*2}), 25.94 ($CH^bMe^cMe^d$ μ-NAr^{*1}), 25.79 ($CH^bMe^cMe^d$ μ-NAr^{*1}), 25.25 ($CH^dMe^fMe^g$ μ-NAr^{*2}), 25.02 ($CH^dMe^fMe^g$ μ-NAr^{*2}), 24.02 ($CH^cMe^e{}_2$ μ-NAr^{*2}), 22.82 ($CH^aMe^aMe^b$ μ-NAr^{*1}).

Reaction of 7 with pyridine. Preparation of [$(Me_2N)(Py)_2Ti(\mu\text{-}NAr^*)_2Ti(NMe_2)(=NAr^*)$] (15).

A toluene solution (1 mL) of **7** (100 mg, 0.1606 mmol) and pyridine (101 mg, 1.277 mmol) was stirred for 3 days at room temperature. Pentane (5 was mL) was added to the solution that was left for 5 days at -20°C for crystallization. Red crystals of **15** were separated by decantation, and dried under vacuum (16 mg). A second crop of 5 mg was obtained by addition pentane (5 mL) to the solution (after decantation) and crystallization at -20°C. Overall yield: 21 mg (22%). **15** is poorly soluble in C_6D_6 therefore we report its ^{1}H NMR in CD_2Cl_2, a solvent in which **15** exhibits only broad signals (the reasons are unclear) before decomposition occurs (recording a ^{13}C NMR was not possible). We also noticed a low integration of Py signals in some samples (integrating between 1 and 2 Py), including on crystals used for X-ray studies, which suggests a possible decoordination of one Py ligand (due to vacuum drying) and may explain the lower stability in solution and broad signals in NMR.

For **15**: ^{1}H NMR (500 MHz, CD_2Cl_2, 300K): δ 8.67 (br, 4H, *o*-Py), 7.92 (br, 2H, *p*-Py), 7.50 (br, 4H, *m*-Py), 7.18 (br d, 4H, *m*-$C_6H_3Pr^i{}_2$ μ-NAr^*), 6.95 (br t, 2H, *p*-$C_6H_3Pr^i{}_2$ μ-NAr^*), 6.52 (br d, 2H, *m*-$C_6H_3Pr^i{}_2$ =NAr^*), 6.43 (d, 1H, *p*-$C_6H_3Pr^i{}_2$ =NAr^*), 4.00 (br m, 2H, CH^aMe_2 μ-NAr^*), 3.32 (br s, 6H, NMe_2), 3.22 (br m, 2H, CH^bMe_2 μ-NAr^*), 3.03 (br s, 6H, NMe_2), 2.48 (br m, 2H, $CHMe_2$ Ti=NAr^*), 1.31 (br d, 24H, $CHMe_2$ μ-NAr^*), 0.71 (br d, 12H, $CHMe_2$ Ti=NAr^*). IR: 3293w, 3051w, 2961s, 2867sh, 1619w, 1589w, 1459m, 1431s, 1315s, 1242s, 1191m, 1106m, 885w, 851m, 748s, 401w, 582s, 508m, 415w. Anal. Calcd for $C_{50}H_{73}N_7Ti$. (867.90): C, 69.19; H, 8.48; N, 11.30. Found: C, 69.05; H, 8.35; N, 11.12.

Reaction of 8 with pyridine. Preparation of [$(Me_2N)(Py)_2Ti(\mu\text{-}NAr^*)_2Ti(NMe_2)(=NAr^*)$] (15).

8 (20 mg, 0.0265 mmol) and pyridine (16 mg, 0.202 mmol) were placed in a Young type NMR tube with C_6D_6. The reaction was monitored by ^{1}H NMR spectroscopy. After 1 hour crystals of **15** (12 mg,

75%) were formed (and confirmed to be **15** by X-ray study and by separation and recording ^{1}H NMR in CD_2Cl_2).

Reaction of $Ti(NMe_2)_4$ and Ar^*NH_2 (2:3 or 1:2) in the presence of pyridine. Preparation of $Ti(=NAr^*)(NHAr^*)(NMe_2)(Py)_2$ (16).

Compound **16** was first crystallized from a reaction composed of $Ti(NMe_2)_4$, Ar^*NH_2, and pyridine in a ration 2:3:8 (with likely concomitant formation of **I**). We described below an improved synthesis of **16** using the appropriate stoichiometry of reactants (1:2). A toluene solution (2 mL) of $Ti(NMe_2)_4$ (100 mg, 0.446 mmol), Ar^*NH_2 (118.6 g, 0.669 mmol), and pyridine (282 mg, 2.792 mmol) was stirred at room temperature for 2 days. The volatiles were removed very slowly under vacuum affording red-orange crystals of **16.** The product was further recrystallized from cold pentane solutions. Yield: 240 mg (77%). The compound crystallized with one molecule of toluene, as judged by X-ray and ^{1}H NMR studies. (Note: the same reaction, when conducted at 80°C, afforded complex **17** as major isolated species (see below for the synthesis of **17**)). ^{1}H NMR (300 MHz, C_6D_6): δ 8.74 (br d, 4H, *o*-Py), 8.05 (br s, 1H, N*H*), 7.23 (d, ^3J = 7.2 Hz, 2H, $C_6H_3Pr^i_2$ $NHAr^*$), 7.05-6.99 (m, 4H, $C_6H_3Pr^i_2$ =NAr^* + $NHAr^*$), 6.87 (app t, 2H, *p*-Py), 6.55 (app t, 4H, *m*-Py), 4.02 (sept, ^3J = 6.5 Hz, 2H, C*H*Me_2 =NAr^*), 3.30 (s, 6H, NMe_2), 3.24 (sept, ^3J = 6.6 Hz, 2H, C*H*Me_2 $NHAr^*$), 1.29 (br d, 12H, CH*Me*$_2$ $NHAr^*$), 0.70 (d, ^3J = 6.5 Hz, 12H, CH*Me*$_2$ =NAr^*). **16** was found not to be very stable in C_6D_6 solution, and after a few minutes in solution the ^{1}H NMR spectrum exhibits signals assigned to **7**, **15**, and **17**, in addition to those of **16** (the ^{1}H NMR study was done with the crystals used for the X-ray structure determination of **16**), which also precluded recording a ^{13}C NMR spectrum. Anal. Calcd for $C_{36}H_{51}N_5Ti.(C_6H_5CH_3)$ (693.83): C, 74.44; H, 8.57; N, 10.09. Found: C, 74.44; H, 8.60; N, 9.99.

Reaction of $Ti(NMe_2)_4$ and Ar^*NH_2 (1:2, 1:3 or 1:4) in the presence of pyridine. Preparation of $Ti(=NAr^*)(NHAr^*)_2(Py)_2$ (17).

Complex **17** was obtained using a procedure similar to the one described for **16**, using a ratio $Ti(NMe_2)_4$ / Ar^*NH_2 of either 1:2, 1,3 or 1:4, but working at 80°C. It can be more conveniently prepared by the reaction 1 equiv. of $Ti(NMe_2)_4$, 3 equiv. of Ar^*NH_2 and 5 equiv. of pyridine in toluene at 100°C (yield 76% on a 500 mg $Ti(NMe_2)_4$ scale), or under solventless conditions as recently reported.[43] ^{1}H NMR (300 MHz, C_6D_6): δ 8.93 (br d, 4H, *o*-Py), 8.20 (br s, 2H, N*H*), 7.21 (d, ^3J = 7.2 Hz, 4H, $C_6H_3Pr^i_2$ $NHAr^*$), 6.98 (m, ^3J = 7.2 Hz, 4H, $C_6H_3Pr^i_2$ =NAr^* + $NHAr^*$), 6.86 (t, ^3J = 7.2 Hz,

1H, $C_6H_3Pr^i_2$ =NAr*), 6.78 (app t, 2H, *p*-Py), 6.43 (app t, 4H, *m*-Py), 3.67 (sept, ^3J = 6.6 Hz, 2H, C*H*Me$_2$ =NAr*), 3.45 (sept, ^3J = 6.6 Hz, 4H, C*H*Me$_2$ NHAr*), 1.19 (d, ^3J = 6.6 Hz, 24H, CH*Me*$_2$ NHAr*), 1.05 (d, ^3J = 6.7 Hz, 12H, CH*Me*$_2$ =NAr*). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): δ 158.5 (*ipso*-C_6H_3 =NAr*), 151.3 (*o*-Py), 150.7 (*ipso*-C_6H_3 NHAr*), 141.6 (*o*-C_6H_3 =NAr*), 136.6 (*m*-Py), 134.5 (*o*-C_6H_3 NHAr*), 123.8 (*p*-Py), 123.6 (*m*-C_6H_3 NHAr*), 121.8 (*m*-C_6H_3 =NAr*), 119.7 (*p*-C_6H_3 =NAr*), 117.7 (*p*-C_6H_3 NHAr*), 29.1 (*C*HMe$_2$ NHAr*), 28.1 (*C*HMe$_2$ =NAr*), 24.0(CH*Me*$_2$ NHAr*), 23.7(CH*Me*$_2$ =NAr*). IR: 3394w, 3059w, 2960s, 2867m, 1620m, 1559w, 1587w, 1458s, 1439s, 1423s, 1329m, 1263s, 1209m, 849m, 747vs, 703m, 629m, 567m. Anal. Calcd for $C_{46}H_{63}N_5Ti$ (733.89): C, 75.28; H, 8.65; N, 9.54. Found: C, 75.22; H, 8.59; N, 9.66.