

University of Groningen

Titanium dichloro, bis(carbyl), aryne, and alkylidene complexes stabilized by linked cyclopentadienyl-amido auxiliary ligands

Sinnema, PJ; vanderVeen, L; Spek, AL; Veldman, N; Teuben, JH; Veen, Loes van der; Spek, Anthony L.

Published in:
 Organometallics

DOI:
[10.1021/om970472v](https://doi.org/10.1021/om970472v)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
 Publisher's PDF, also known as Version of record

Publication date:
 1997

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Sinnema, P. J., vanderVeen, L., Spek, A. L., Veldman, N., Teuben, J. H., Veen, L. V. D., & Spek, A. L. (1997). Titanium dichloro, bis(carbyl), aryne, and alkylidene complexes stabilized by linked cyclopentadienyl-amido auxiliary ligands. *Organometallics*, 16(20), 4245-4247. DOI: 10.1021/om970472v

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

General Considerations. All compounds are extremely air and moisture sensitive and manipulations were performed under nitrogen atmosphere using Schlenk glassware, glovebox (braun MB-200) or vacuum line techniques. $C_5H_5(CH_2)_3N(H)Me$ was synthesized as reported by Hughes *et al.*¹ Solvents (ether, pentane, cyclohexane, toluene) were purified by distillation from potassium or sodium/potassium alloy. d_5 -bromobenzene was stored at molsieves (4Å). 1H and ^{13}C NMR spectra were recorded in sealed tubes using a Varian Gemini-200 or Varian VXR-300 spectrometer. The chemical shifts are reported in ppm relative to TMS and the resonances of residual protons and ^{13}C carbons in C_6D_6 , C_6D_{12} or C_6D_5Br were used as references (1H NMR: $\delta = 7.16, 1.38, 7.30$ ppm respectively; ^{13}C NMR: $\delta = 128.00, 26.40$ ppm, 122.16 (*ipso-C*) respectively). IR spectra were recorded as Nujol mulls between KBr discs (unless mentioned otherwise) on a Mattson Galaxy 4020 spectrophotometer. GC analyses were performed on a Hewlett Packard 5890A gas chromatograph using a Porasil B packed column. Elemental analyses were performed at the Microanalytical Department of this laboratory. Each value given is the average of at least two independent determinations.

Synthesis of $Br(CH_2)_nN(H)R.HBr$. Preparation of the hydrobromic salts of the secondary aminobromide derivatives was performed by addition of $Cl(CH_2)_nOH$ to a mixture of 8-10 fold excess of the primary amine RNH_2 and 3 eq. of H_2O and stirring overnight. The excess amine and water were removed with the rota-vapor (100 °C) and the remaining viscous oils were treated with 2.2 eq. of hydrobromic acid (aq, 47%) and refluxed for several hours. Afterwards liquid was removed by slowly distillation using a 30 cm Vigreux until 90% of the volume of the added hydrobromic acid was collected leaving cream colored oils which solidified on cooling to room

¹ Hughes, A.K.; Meetsma, A.; Teuben, J.H. *Organometallics* 1993, 12, 1936.

temperature. The remaining hydrobromic acid was removed in vacuum and the $\text{Br}(\text{CH}_2)_n\text{N}(\text{H})\text{R}.\text{HBr}$ compounds except from $\text{Br}(\text{CH}_2)_2\text{N}(\text{H})\text{Me}.\text{HBr}$ were purified by washing with cold ($-20\text{ }^\circ\text{C}$) acetone. $\text{Br}(\text{CH}_2)_2\text{N}(\text{H})\text{Me}.\text{HBr}$ was purified by recrystallisation from acetone.

Br(CH₂)₂N(H)Me.HBr. (70%), ^1H NMR (200 MHz, D_2O): δ 3.65 (t, $^3J_{\text{HH}} = 5.86$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}.\text{HBr}$); 3.46 (t, $^3J_{\text{HH}} = 5.86$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}.\text{HBr}$); 2.70 (s, 3H, NMe).

Br(CH₂)₂N(H)-i-Pr.HBr. (74 %), ^1H NMR (200 MHz, D_2O): δ 3.77 (t, $^3J_{\text{HH}} = 5.77$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$); 3.58 (t, $^3J_{\text{HH}} = 5.77$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$); 3.56 (hept, $^3J_{\text{HH}} = 6.59$ Hz, 1H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$); 1.41 (d, $^3J_{\text{HH}} = 6.59$ Hz, 6H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$).

Br(CH₂)₃N(H)-i-Pr.HBr. (75%), ^1H NMR (200 MHz, D_2O): δ 3.60 (t, $^3J_{\text{HH}} = 6.41$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$); 3.49 (hept, $^3J_{\text{HH}} = 6.41$ Hz, 1H, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$); 3.25 (t, $^3J_{\text{HH}} = 7.69$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$); 2.28 (qint, $^3J_{\text{HH}} = 7.05$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$); 1.37 (d, $^3J_{\text{HH}} = 6.41$ Hz, 6H, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CHMe}_2.\text{HBr}$).

Br(CH₂)₂N(H)-t-Bu.HBr. (70%), ^1H NMR (200 MHz, D_2O): δ 3.73 (t, $^3J_{\text{HH}} = 5.70$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})-t\text{-Bu}.\text{HBr}$); 3.58 (t, $^3J_{\text{HH}} = 5.70$ Hz, 2H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})-t\text{-Bu}.\text{HBr}$); 1.43 (s, 9H, $\text{BrCH}_2\text{CH}_2\text{N}(\text{H})-t\text{-Bu}.\text{HBr}$).

Synthesis of C₅H₅(CH₂)₂N(H)-t-Bu. To a cooled ($0\text{ }^\circ\text{C}$) suspension of 20.7 g (79.3 mmol) of $\text{Br}(\text{CH}_2)_2\text{N}(\text{H})-t\text{-Bu}$ in 100 mL of THF, 230 mL (294 mmol) of a 1.28 M solution of CpNa in THF was added. The mixture became turbid. After stirring for three hours at room temperature the mixture was quenched with 100 mL of water

and the organic layer was separated. The aqueous layer was extracted twice with 70 mL of ether, the combined organic layers were washed with 100 mL of brine, dried over anhydrous Na_2SO_4 and filtered. The solvents were removed in vacuum and the brown residue was distilled at 45-50 °C and 0.005 mm Hg. 9.5 g (57.5 mmol 73%) of colorless $\text{C}_5\text{H}_5(\text{CH}_2)_2\text{N}(\text{H})\text{-}t\text{-Bu}$ was obtained as an approximately 0.4 : 1 : 1 mixture of 1,1, 1,2 and 1,3 isomers. ^1H NMR (200 MHz, CDCl_3): δ 6.38 (overlapped m, 5H, 2 x CH of C_5H_5 ring isomer 1, 2 x CH of C_5H_5 ring isomer 2, 1 CH of C_5H_5 ring isomer 3); 6.22 (m, 1H, CH of C_5H_5 ring isomer 3); 6.19 (m, 1H, CH of C_5H_5 ring isomer 3); 6.04 (overlapped m, 3H, 2 x CH of C_5H_5 ring isomer 1, 1 x CH of C_5H_5 ring isomer 2); 3.57 (t, 1H, $^3J_{\text{HH}} = 6.1$ Hz, CH of C_5H_5 ring isomer 1); 2.91 (m, 2H, CH_2 of C_5H_5 isomer 2); 2.84 (m, 2H, CH_2 of C_5H_5 ring isomer 3); 2.70 (overlapping t, 6H, 3 x $\text{C}_5\text{H}_5\text{CH}_2$); 2.54 (t, 6H, $^3J_{\text{HH}} = 6.8$ Hz, 3 x NCH_2); 1.04 (s, 30H, 3 x $t\text{-Bu}$ + 3 x NH)

Synthesis of $\text{C}_5\text{H}_5(\text{CH}_2)_2\text{N}(\text{H})\text{Me}$. 44 g (0.20 mol) of $\text{Br}(\text{CH}_2)_2\text{N}(\text{H})\text{Me}\cdot\text{HBr}$ was added to a cooled solution (0 °C) of 53 g (0.60 mol) of CpNa in 300 mL of THF. After addition the temperature was raised to 50 °C, the solution became cloudy and a white salt precipitated. The mixture was stirred for two hours and then quenched with 100 mL of water. The clear solution was diluted with 250 mL of light petroleum and the organic layer was separated. The aqueous layer was extracted with 100 mL of light petroleum and the combined organic layers were washed with 100 mL of brine, dried on Na_2SO_4 and filtered. The solvents were removed in vacuum, the crude product (28.7 g) was vacuum transferred at 1 mm Hg and 25-30 °C. 15.7 g (0.13 mol, 64%) of $\text{C}_5\text{H}_5(\text{CH}_2)_2\text{N}(\text{H})\text{Me}$ was obtained as a colorless oil (a \pm 1 : 1 mixture of the 1,2 and 1,3 isomers). ^1H NMR (200 MHz, CDCl_3): δ 6.32 (overlapping m, 3H, 2 x CH of C_5H_5 ring 1,2 isomer, 1 x CH 1,3 isomer); 6.15 (m, 1H, CH of C_5H_5 ring 1,3 isomer); 6.10 (m, 1H, CH of CH ring 1,3 isomer); 5.96 (m, 1H, CH of C_5H_5

ring 1,2 isomer); 2.85 (m, 2H, CH₂ of C₅H₅ ring isomer 1); 2.78 (m, 2H, CH₂ of C₅H₅ ring isomer 2); 2.67 (t, 2H, ³J_{HH} = 6.8 Hz, NCH₂); 2.65 (t, 2H, ³J_{HH} = 6.8 Hz, NCH₂); 2.48 (m, 4H, 2 x C₅H₅CH₂); 2.33 (s, 6H, 2 x NMe); 0.93 (s, 2H, 2 x NH).

Synthesis of C₅H₅(CH₂)₂N(H)-i-Pr. A 200 mL 1.75 M (0.35 mol) CpNa solution in THF was treated with 28.7 g (0.116 mol) of Br(CH₂)₂N(H)-i-Pr.HBr and the mixture was stirred for 4 hours at 45-50 °C. After quenching with 50 mL of water and separation of the organic layer, the water layer was extracted twice with 100 mL of light petroleum. The combined organic layers were washed with 100 mL of brine and dried over Na₂SO₄. Evaporation of the solvents under reduced pressure left a light coloured residue which was vacuum transferred at 65-70 °C and 0.01 torr. Yield: 12.1 g (80 mmol, 69%) of a nearly colorless oil. An NMR sample revealed it to be a 1 : 1 mixture of 1,2 and 1,3 isomers. ¹H NMR (200 MHz, CDCl₃): δ 6.40 (overlapping m, 3H, 2x CH of C₅H₅ ring 1,2 isomer, 1x CH of C₅H₅ ring 1,3 isomer). 6.23 (m, 1H, CH of C₅H₅ ring 1,3 isomer); 6.18 (m, 1H, CH of C₅H₅ ring 1,3 isomer); 2.93 (m, 2H, CH₂ of C₅H₅ ring 1,2 isomer); 2.85 (m, 2H, CH₂ of C₅H₅ ring 1,3 isomer); 2.82-2.70 (overlapping resonances, 2H, NCH₂, 1H, CHMe₂); 2.56 (t, ³J_{HH} = 6.83 Hz, 2H, C₅H₅CH₂ of 1.2 isomer); 2.53 (t, ³J_{HH} = 7.69 Hz, 2H, C₅H₅CH₂ of 1,3 isomer); 1.01 (overlapping resonances, d, ³J_{HH} = 5.99 Hz, 6H, CHMe₂; s, 1H, N(H)).

Synthesis of C₅H₅(CH₂)₃N(H)-i-Pr. To 200 mL of 1.75 M (0.35 mol) of CpNa in THF, 30.5 g (0.117 mol) of Br(CH₂)₃N(H)-i-Pr was added. The mixture became turbid and was stirred at 45-50 °C for 3.5 hours resulting in a pale red solution and a white precipitate. After quenching with 50 mL of water and separation of the organic layer, the water layer was extracted twice with 100 mL of light petroleum. The combined organic layers were washed with brine (100 mL) and dried over Na₂SO₄. Removal of the solvents at reduced pressure left a light colored oil which was vacuum

transferred at 65-70 °C and 0.01 torr yielding 15.4 g (93 mmol, 79%) of $C_5H_5(CH_2)_3N(H)-i\text{-Pr}$. An NMR sample showed to be a 1 : 1 mixture of 1,2 and 1,3 isomers. 1H NMR (200 MHz, $CDCl_3$): δ 6.36 (overlapping m, 3H, 2 x CH of C_5H_5 ring 1,2 isomer, 1x CH of C_5H_5 ring 1,3 isomer); 6.18 (m, 1H, 1x CH of C_5H_5 ring 1,3 isomer); 6.10 (m, 1H, 1x CH of C_5H_5 ring 1,3 isomer); 5.94 (m, 1H, 1x CH of C_5H_5 ring 1,2 isomer); 2.88 (m, 2H, CH_2 of C_5H_5 ring 1,2 isomer); 2.82 (m, 2H, CH_2 of C_5H_5 ring 1,3 isomer); 2.72 (hept, $^3J_{CH} = 6.20$ Hz, 1H, $CHMe_3$); 2.56 (t, $^3J_{HH} = 7.27$ Hz, 2H, NCH_2); 2.39 (t, $^3J_{HH} = 7.69$ Hz, 2H, $C_5H_5CH_2$ of 1,3 isomer); 2.35 (t, $^3J_{HH} = 7.70$ Hz, 2H, $C_5H_5CH_2$ of 1,2 isomer); 1.68 (m, 2H, NCH_2CH_2); 0.99 (d, $^3J_{HH} = 6.20$ Hz, 6H, $CHMe_2$); 0.81 (s, 1H, N(H)).

Synthesis of $[C_5H_4(CH_2)_2NMe]TiCl_2$ (1). To a solution of 1.78 g (9.38 mmol) of $TiCl_4$ in 40 mL of toluene, 1.4 g (11.4 mmol) of $C_5H_5(CH_2)_2N(H)Me$ and 2.6 mL (18.8 mmol) of Et_3N were added in rapid succession giving a dark mixture. Subsequently the mixture was refluxed for 1 hour which gave an orange solution with a tarry brown residue. The orange solution was filtered and the solvent was removed in vacuum yielding a orange solid. Sublimation of the solid at 160-180 °C and 10^{-2} torr gave 1.38 g (5.8 mmol, 62%) of $[C_5H_4(CH_2)_2NMe]TiCl_2$. 1H NMR (200 MHz, C_6D_6): δ 6.01 (t, $^3J_{HH} = 2.57$ Hz, 2H, C_5H_4); 5.84 (t, $^3J_{HH} = 2.57$ Hz, 2H, C_5H_4); 3.53 (t, $^3J_{HH} = 6.41$ Hz, 2H, NCH_2); 3.49 (s, 3H, NMe); 2.42 (t, $^3J_{HH} = 6.41$ Hz, 2H, $C_5H_4CH_2$). ^{13}C NMR (50 MHz, C_6D_6): δ 145.61 (s, C_5H_4 -*ipso*); 118.00 (d, $^1J_{CH} = 175.8$ Hz, C_5H_4); 115.26 (d, $^1J_{CH} = 177.8$ Hz, C_5H_4); 80.08 (t, $^1J_{CH} = 140.6$ Hz, NCH_2); 47.54 (q, $^1J_{CH} = 137.4$ Hz, NMe); 28.09 (t, $^1J_{CH} = 129.9$ Hz, $C_5H_4CH_2$). IR (cm^{-1}): 3109 (w), 3101 (m), 2787 (m), 1836 (w), 1801 (w), 1749 (w), 1713 (m), 1664 (w), 1491 (s), 1429 (m), 1408 (s), 1384 (m), 1342 (m), 1312 (m), 1285 (vw), 1234 (s), 1196 (w), 1170 (m), 1085 (s), 1066 (m), 1051 (m), 1036 (m), 1007 (s), 966 (s), 922 (m), 881 (s), 831 (vs), 719 (m), 642 (s), 569 (s), 524 (m). Anal. Calcd. for $C_8H_{11}Cl_2NTi$: C, 40.04; H, 4.62;

Ti, 19.96. Found: C, 40.18; H, 4.58; Ti, 19.86. Mass spec.: 239 [P, 70.5%, correct isotope pattern for Ti and Cl], 161 [P-C₅H₄CH₂, 78.3%] (100% = [P-CH₂NMe]).

*Synthesis of [C₅H₄(CH₂)₂N-*i*-Pr]TiCl₂ (2).* To a heated (70 °C) solution of 11.3 g (74.7 mmol) of C₅H₅(CH₂)₂N(H)-*i*-Pr and 21 mL (152 mmol) Et₃N in 250 mL of toluene, a solution of 8.5 mL (77 mmol) of TiCl₄ in 100 mL toluene was added in 10 min. The mixture became dark and after the addition was complete, the mixture was heated at 120-125 °C. After 2 hours a red-orange solution and a tarry black residue was obtained. The hot solution was filtered and concentrated to ± 50 mL. Slowly cooling to room temperature gave orange crystals, yielding 11.10 g of product. Concentration of the mother liquor gave a second crop (1.11 g), yielding in total 12.21 g (45.6 mmol, 61%) of product. ¹H NMR (200 MHz, C₆D₆): δ 6.05 (t, ³J_{HH} = 2.57 Hz, 2H, C₅H₄); 5.92 (hept, ³J_{HH} = 6.41 Hz, 1H, CHMe₂); 5.78 (t, ³J_{HH} = 2.57 Hz, 2H, C₅H₄); 3.57 (t, ³J_{HH} = 7.05 Hz, 2H, NCH₂); 2.42 (t, ³J_{HH} = 7.05 Hz, 2H, C₅H₄CH₂); 0.86 (d, ³J_{HH} = 6.41 Hz, 6H, CHMe₂). ¹³C NMR (75.4 MHz, C₆D₆): δ 144.92 (s, C₅H₄-*ipso*); 117.67 (d, ¹J_{CH} = 175.2 Hz, C₅H₄); 115.58 (d, ¹J_{CH} = 177.6 Hz, C₅H₄); 68.15 (t, ¹J_{CH} = 137.6 Hz, NCH₂); 54.59 (d, ¹J_{CH} = 133.7 Hz, CHMe₂); 28.67 (t, ¹J_{CH} = 130.6 Hz, C₅H₄CH₂); 17.78 (q, ¹J_{CH} = 127.0 Hz, CHMe₂). IR (cm⁻¹): 3097 (m), 3084 (m), 1836 (w), 1801 (w), 1757 (w), 1739 (w), 1722(w), 1707 (w), 1680 (w), 1667 (w), 1645 (w), 1493 (m), 1425 (sh, Nujol), 1385 (m), 1362 (m), 1340 (s), 1315 (w), 1292 (w), 1256 (w), 1230 (m), 1170 (s), 1155 (s), 1113 (m), 1070 (m), 1060 (m), 1041 (s), 1020 (m), 985 (s), 966 (m), 927 (w), 918 (w), 881 (s), 856 (vw), 839 (s), 821 (vs), 723 (w), 698 (m), 642 (s), 621 (w), 528 (m). Anal. Calcd for C₁₀H₁₅Cl₂NTi: C, 44.81; H, 5.64; Ti, 17.87. Found: C, 44.80; H, 5.48; Ti, 17.75. Mass spec.: 267 [P, 8.2%, correct isotope pattern for Ti and Cl₂], 252 [P-Me, 100%].

*Synthesis of [C₅H₄(CH₂)₂N-*t*-Bu]TiCl₂ (3).* To a heated (75-80 °C) solution of 32.3 g (0.195 mol) of C₅H₅(CH₂)₂N(H)-*t*-Bu and 55 mL (0.40 mol) of Et₃N in 450 mL of toluene, a solution of 22 mL (0.20 mol) of TiCl₄ in 250 mL of toluene was added under vigorous stirring in 20 min. The solution became dark and a tarry black residue was formed. After addition the mixture was refluxed for 3 hours resulting in a deep red solution and a dark residue. The solution was filtered and the solvent was removed in vacuum giving a dark red crystalline residue. A continuous extraction with 200 mL of ether was performed yielding a red solution with precipitated product. Removal of the solvent in vacuum gave a red micro-crystalline residue which was washed two times with 100 mL of pentane. Drying in vacuum gave 33.65 g (119 mmol, 60%, based on C₅H₅(CH₂)₂N(H)-*t*-Bu). An analytical pure sample was obtained by recrystallization from ether. ¹H NMR (200 MHz, C₆D₆): δ 6.19 (t, ³J_{HH} = 2.56 Hz, 2H, C₅H₄); 5.90 (t, ³J_{HH} = 2.56 Hz, 2H, C₅H₄); 3.66 (t, ³J_{HH} = 6.87 Hz, 2H, CH₂N); 2.37 (t, ³J_{HH} = 6.87 Hz, 2H, C₅H₄CH₂); 1.42 (s, 9H, *t*-Bu). ¹³C NMR (50 MHz, C₆D₆): δ 144.10 (s, C₅H₄-*ipso*); 118.12 (d, ¹J_{CH} = 171.9 Hz, C₅H₄); 118.04 (d, ¹J_{CH} = 178.7 Hz, C₅H₄); 69.96 (t, ¹J_{CH} = 137.4 Hz, CH₂N); 64.59 (s, CMe₃); 29.72 (t, ¹J_{CH} = 130.2 Hz, C₅H₄CH₂); 28.82 (q, ¹J_{CH} = 126.2 Hz, CMe₃). IR (cm⁻¹): 3102 (m), 1756 (w), 1709 (w), 1664 (w), 1656 (w), 1562 (w), 1498 (w), 1469 (sh, Nujol), 1447 (sh, Nujol), 1425 (w), 1392 (w), 1360 (m), 1344 (w), 1319 (m), 1246 (m), 1238 (m), 1224 (m), 1205 (w), 1176 (s), 1159 (sh), 1082 (sh), 1070 (s), 1043 (m), 1024 (sh), 1014 (w), 981 (s), 918 (s), 873 (m), 841 (sh), 829 (vs), 763 (m), 721 (w), 694 (m), 640 (m), 567 (m), 535 (s), 482 (s), 426 (s), 416 (sh). Anal. Calcd. for C₁₁H₁₇Cl₂N₁Ti: C, 46.84; H, 6.08; Ti, 16.98. Found: C, 46.88; H, 6.09; Ti, 16.90. Mass spec.: 281 [P, 4.4%, correct isotope pattern for Ti and Cl₂] (100% = [P-Me]).

Synthesis of [C₅H₄(CH₂)₃NMe]TiCl₂ (4). 7.5 g (54.7 mmol) of C₅H₅(CH₂)₃N(H)Me and 15.3 mL (110 mmol) of Et₃N were quickly added to a solution (room temperature) of

10.47 g (55.2 mmol) of TiCl_4 in 250 mL of toluene. The solution became black immediately. Refluxing for 3 hours gave a orange-red solution with a tarry black residue. The solution was filtered and the solvent was removed in vacuum to give a orange-red solid. Sublimation at 200 °C and 10^{-2} torr gave an orange-red crystalline solid. Yield: 7.88 g (31.0 mmol, 56%) of $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{TiCl}_2$. ^1H NMR (200 MHz, C_6D_6): δ 6.31 (t, $^3J_{\text{HH}} = 2.56$ Hz, 2H, C_5H_4); 5.53 (t, $^3J_{\text{HH}} = 2.56$ Hz, 2H, C_5H_4); 3.82 (s, 3H, NMe); 2.29 (m, 2H, CH_2N); 2.12 (m, 2H, $\text{C}_5\text{H}_4\text{CH}_2$); 1.48 (m, 2H, $\text{CH}_2\text{CH}_2\text{N}$). ^{13}C NMR (50 MHz, C_6D_6): δ 129.68 (s, C_5H_4 -*ipso*); 119.23 (d, $^1J_{\text{CH}} = 177.3$ Hz, C_5H_4); 114.58 (d, $^1J_{\text{CH}} = 181.2$ Hz, C_5H_4); 62.22 (t, $^1J_{\text{CH}} = 135.5$ Hz, CH_2N); 45.62 (q, $^1J_{\text{CH}} = 137.4$ Hz, NMe); 29.6 (t, $^1J_{\text{CH}} = 128.2$ Hz, $\text{C}_5\text{H}_4\text{CH}_2$); 25.69 (t, $^1J_{\text{CH}} = 129.3$ Hz, $\text{CH}_2\text{CH}_2\text{N}$). IR (cm^{-1}): 3103(m), 2704(vw), 1419(m), 1406(m), 1336(m), 1267((m), 1248(m), 1184(m), 1097(m), 1070(m), 1053(w), 1033(m), 981(m), 935(m), 902(s), 875(m), 837(s). Anal. Calcd. for $\text{C}_9\text{H}_{13}\text{Cl}_2\text{NTi}$: C, 42.55; H, 5.16; Ti, 18.86. Found: C, 42.42; H, 5.16; Ti, 18.76. Mass spec.: 253 [P, correct isotope pattern for Ti and Cl_2], 217 [P-HCl, 59%] (100% = [P- $\text{CH}_3\text{NCH}_2\cdot\text{HCl}$]).

Synthesis of $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{N-}i\text{-Pr}]\text{TiCl}_2$ (5). To a hot (70-75 °C) solution of 12.0 g (72.6 mmol) of $\text{C}_5\text{H}_5(\text{CH}_2)_3\text{N(H)-}i\text{-Pr}$ and 21 mL (151 mmol) of Et_3N in 250 mL of toluene, a solution of 8 mL (73 mmol) of TiCl_4 in 100 mL of toluene was added within 10 min. After the addition was complete the temperature was raised to 120-125 °C and the dark mixture was stirred for 2 hours resulting in a red solution with a tarry black residue. The red solution was filtered and concentrated to \pm 50 mL at 100-110 °C. Slowly cooling to room temperature yielded 9.63 g red crystalline product. A second crop (1.99 g) was obtained by concentrating the mother liquor, giving a total yield of 11.62 g (41.2 mmol, 57 %). ^1H NMR (200 MHz, C_6D_6): 6.57 (hept, $^3J_{\text{HH}} = 5.98$ Hz, 1H, CHMe_2); 6.36 (t, $^3J_{\text{HH}} = 2.56$ Hz, 2H, C_5H_4); 5.47 (t, $^3J_{\text{HH}} = 2.56$ Hz, 2H, C_5H_4); 2.43 (m, 2H, NCH_2); 2.16 (m, 2H, $\text{C}_5\text{H}_4\text{CH}_2$); 1.46 (m, 2H, NCH_2CH_2); 1.02 (d, $^3J_{\text{HH}} =$

5.98 Hz, 6H, CHMe_2). ^{13}C NMR (75.4 MHz, C_6D_6): δ 130.36 (s, C_5H_4 -*ipso*); 119.35 (d, $^1J_{\text{CH}} = 177.3$ Hz, C_5H_4); 114.91 (d, $^1J_{\text{CH}} = 173.8$ Hz, C_5H_4); 50.64 (d, $^1J_{\text{CH}} = 128.9$ Hz, CHCMe_2); 50.36 (t, $^1J_{\text{CH}} = 135.5$ Hz, NCH_2); 32.24 (t, $^1J_{\text{CH}} = 128.7$ Hz, $\text{C}_5\text{H}_4\text{CH}_2$); 26.23 (t, $^1J_{\text{CH}} = 128.7$ Hz, NCH_2CH_2); 17.93 (q, $^1J_{\text{CH}} = 127.1$ Hz, CHCMe_2). IR (cm^{-1}): 3111 (w), 3097 (w), 3084 (w), 1844 (w), 1795 (w), 1755 (w), 1697 (w), 1662 (w), 1498 (s), 1417 (s), 1398 (m), 1361 (s), 1330 (m), 1278 (m), 1244 (m), 1226 (m), 1174 (m), 1153 (s), 1116 (m), 1085 (w), 1074 (m), 1057 (m), 1039 (m), 1012 (m), 966 (m), 939 (s), 895 (m), 875 (m), 827 (vs), 800 (s), 661 (m), 609 (m), 536 (s), 447 (vs). Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{Cl}_2\text{NTi}$: C, 46.84; H, 6.08; Ti, 16.98. Found: C, 46.94; H, 6.09; Ti, 16.88. Mass spec.: 281 [P, 13%, correct isotope pattern for Ti and Cl_2], 266 [P-Me, 100%].

Synthesis of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiMe}_2$ (6). To a cooled (-80 °C) solution of 0.85 g (3.0 mmol) of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiCl}_2$ in 30 mL of ether, 4.3 mL of 1.4 M (6.0 mmol) MeLi in ether was added. The mixture was allowed to warm to 0 °C in 1 hour and a yellow solution with a white precipitate was obtained. The ether was removed in vacuum and the yellow residue was stripped with 5 mL of pentane. The solids were extracted with 30 mL of pentane and the yellow solution was concentrated to ± 2 mL. Cooling to -50 °C gave yellow crystals and the remaining mother liquor was removed. The crystals were dried in vacuum, however upon warming up to room temperature the crystals began to melt to a yellow-brown oil. 0.55 g (2.3 mmol, 76%) of product was isolated. ^1H NMR (200 MHz, C_6D_6): δ 6.30 (t, $^3J_{\text{HH}} = 2.56$ Hz, 2H, C_5H_4); 5.64 (t, $^3J_{\text{HH}} = 2.56$ Hz, 2H, C_5H_4); 3.41 (t, $^3J_{\text{HH}} = 6.41$ Hz, 2H, NCH_2); 2.27 (t, $^3J_{\text{HH}} = 6.41$ Hz, 2H, $\text{C}_5\text{H}_4\text{CH}_2$); 1.54 (s, 9H, *t*-Bu); 0.47 (s, 6H, 2 Me). ^{13}C NMR (50 MHz, C_6D_6): δ 133.24 (s, C_5H_4 -*ipso*); 114.60 (d, $^1J_{\text{CH}} = 171.6$ Hz, C_5H_4); 113.62 (d, $^1J_{\text{CH}} = 178.7$ Hz, C_5H_4); 62.34 (t, $^1J_{\text{CH}} = 134.9$ Hz, NCH_2); 59.50 (s, CMe_3); 47.14 (q, $^1J_{\text{CH}} = 118.9$ Hz, Me); 29.88 (q, $^1J_{\text{CH}} = 125.3$ Hz, CMe_3); 29.46 (t, $^1J_{\text{CH}} =$

128.5 Hz, $C_5H_4CH_2$). IR (cm^{-1} , neat): 3088 (w), 2968 (vs), 2933 (vs), 2864 (s), 2835 (s), 2789 (w), 2764 (w), 2673 (w), 1811 (w), 1774 (w), 1720 (w), 1678 (w), 1628 (w), 1494 (w), 1471 (m), 1442 (m), 1388 (m), 1357 (s), 1342 (m), 1321 (w), 1244 (s), 1224 (m), 1194 (vs), 1105 (w), 1074 (s), 1043 (m), 1026 (w), 983 (s), 947 (s), 904 (vw), 868 (s), 844 (m), 815 (vs), 769 (m), 680 (m), 646 (m), 567 (s), 534 (w), 497 (s).

Synthesis of $[C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2Ph)_2$ (7). 10.2 mL of 0.84 M (8.6 mmol) $PhCH_2MgCl$ in ether was added to a cooled ($-80\text{ }^\circ C$) solution of 1.21 g (4.3 mmol) of $[C_5H_4(CH_2)_2N-t-Bu]TiCl_2$ in 30 mL of ether. The mixture was warmed to room temperature in 2 hour resulting in a deep red solution with a white precipitate. The ether was removed in vacuum and the oily red residue was stripped with 15 mL of pentane and subsequently extracted with 50 mL of pentane. On concentrating the solution the compound appeared to be an oil which did not solidify on cooling to $-80\text{ }^\circ C$. The pentane was pumped off to 10^{-2} torr and the compound was isolated as a dark red oil. Yield: 1.15 g (3.0 mmol, 69%). 1H NMR (200 MHz, C_6D_6): δ 7.22 (m, 4H, 2 x *m*-Ph); 6.90 (m, 2H, 2 x *p*-Ph); 6.82 (m, 4H, 2 x *o*-Ph); 5.92 (t, $^3J_{HH} = 2.56$ Hz, 2H, C_5H_4); 5.27 (t, $^3J_{HH} = 2.56$ Hz, 2H, C_5H_4); 3.29 (t, $^3J_{HH} = 6.63$ Hz, 2H, NCH_2); 2.73 (d, $^2J_{HH} = 9.40$ Hz, 2H, $PhCH_2$); 2.27 (d, $^2J_{HH} = 9.40$ Hz, 2H, $PhCH_2$); 2.10 (t, $^3J_{HH} = 6.63$ Hz, 2H, $C_5H_4CH_2$); 1.50 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 150.70 (s, *Ph-ipso*); 135.67 (s, C_5H_4-ipso); 128.45 (d, $^1J_{CH} = 154.0$ Hz, *o*-Ph); 125.73 (d, $^1J_{CH} = 153.1$ Hz, *m*-Ph); 121.59 (d, $^1J_{CH} = 156.3$ Hz, *p*-Ph); 118.04 (d, $^1J_{CH} = 173.7$ Hz, C_5H_4); 117.42 (d, $^1J_{CH} = 171.4$ Hz, C_5H_4); 78.04 (t, $^1J_{CH} = 120.5$ Hz, CH_2Ph); 62.61 (d, $^1J_{CH} = 135.4$ Hz, CH_2N); 60.96 (s, CMe_3); 30.16 (t, $^1J_{CH} = 129.0$ Hz, $C_5H_4CH_2$); 30.11 (d, $^1J_{CH} = 125.3$ Hz, CMe_3). IR (cm^{-1} , neat): 3084 (m), 3061 (m), 3026 (m), 2966 (s), 2916 (m), 2837 (s), 2702 (w), 1946 (w), 1863 (w), 1805 (w), 1805 (w), 1662 (w), 1595 (s), 1493 (s), 1450 (s), 1388 (m), 1359 (s), 1302 (w), 1240

(m), 1203 (vs), 1097 (vs), 1072 (vs), 1026 (m), 983 (m), 945 (m), 908 (w), 868 (m), 842 (sh), 815 (vs), 746 (vs), 698 (vs), 682 (sh), 656 (m), 605 (w), 561 (m), 459 (m).

*Synthesis of [C₅H₄(CH₂)₂N-*t*-Bu]TiPh₂ (8).* To a cooled (-80 °C) solution of 1.13 g (4.0 mmol) of [C₅H₄(CH₂)₂N-*t*-Bu]TiCl₂ in 30 mL of ether, 5.6 mL of 1.44 M (8.1 mmol) PhMgBr in ether was added. The mixture was warmed up to -20 °C and stirred for one more hour. The ether was pumped off and the yellow-brown residue was stripped with 20 mL of pentane. The dark yellow residue was extracted with 50 mL of pentane which gave a dark yellow solution. Concentration at -10 °C to 10 mL and cooling overnight to -50 °C gave 0.64 g (1.75 mmol, 44%) product as a orange-yellow crystals. ¹H NMR (300 MHz, C₆D₁₂): δ 7.31 (m, 4H, 2 x *m*-Ph); 6.99 (m, 6H, 2 x *p*-Ph + 2 x *o*-Ph); 6.21 (t, ³J_{HH} = 2.56 Hz, 2H, C₅H₄); 6.04 (t, ³J_{HH} = 2.56 Hz, 2H, C₅H₄); 4.01 (t, ³J_{HH} = 6.47 Hz, 2H, NCH₂); 2.83 (t, ¹J_{HH} = 6.47 Hz, 2H, C₅H₄CH₂); 1.41 (s, 9H, *t*-Bu). ¹³C NMR (75.4 MHz, C₆D₁₂): δ 192.50 (s, Ph-*ipso*); 136.49 (s, C₅H₄-*ipso*); 134.25 (d, ¹J_{CH} = 154.1 Hz, *m*-Ph); 127.19 (d, ¹J_{CH} = 155.1 Hz, *o*-Ph); 126.93 (d, ¹J_{CH} = 157.6 Hz, *p*-Ph); 117.84 (d, ¹J_{CH} = 175.3 Hz, C₅H₄); 115.18 (d, ¹J_{CH} = 174.8 Hz, C₅H₄); 64.07 (t, ¹J_{CH} = 134.5 Hz, NCH₂); 61.87 (s, CMe₃); 30.89 (t, ¹J_{CH} = 128.4 Hz, C₅H₄CH₂); 28.96 (q, ¹J_{CH} = 125.4 Hz, CMe₃). IR (cm⁻¹): 3113 (w), 3090 (w), 3043 (m), 1952 (w), 1874 (w), 1726 (w), 1631 (w), 1562 (w), 1552 (w), 1493 (m), 1460 (sh, Nujol), 1411 (m), 1357 (m), 1344 (w), 1325 (w), 1298 (w), 1240 (m), 1207 (sh), 1190 (s), 1074 (s), 1055 (s), 1016 (w), 985 (s), 941 (m), 906 (w), 869 (m), 844 (m), 820 (vs), 773 (m), 727 (vs), 702 (vs), 565 (m), 526 (m), 480 (w), 453 (m). Anal. Calcd. for C₂₃H₂₇NTi: C, 75.61; H, 7.45; Ti, 13.11 Found: 75.17; H, 7.35; Ti, 12.97.

*Synthesis of [C₅H₄(CH₂)₂N-*t*-Bu]Ti(CH₂CMe₃)₂ (9).* A solution of 1.65 g (21.1 mmol) of LiCH₂CMe₃ in 30 mL of ether was added to a cooled (-80 °C) solution of 2.97 g (10.54 mmol) of [C₅H₄(CH₂)₂N-*t*-Bu]TiCl₂ in 90 mL of ether. The mixture was warmed

up to 0 °C in 2.5 hours resulting in a dark yellow solution with a pale precipitate. The solvent was removed in vacuum and the residue was stripped with 20 mL of pentane. Extraction with 50 mL pentane gave a dark yellow solution from which a yellow compound crystallized upon concentration and cooling to -30 °C. In two crops 2.54 g (7.2 mmol, 68%) of $[C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2CMe_3)_2$ was isolated. 1H NMR (200 MHz, C_6D_6): δ 6.60 (t, $^3J_{HH} = 2.56$ Hz, C_5H_4); 5.90 (t, $^3J_{HH} = 2.56$ Hz, 2H, C_5H_4); 3.41 (t, $^3J_{HH} = 6.63$ Hz, 2H, NCH_2); 2.25 (t, $^3J_{HH} = 6.63$ Hz, 2H, $C_5H_4CH_2$); 2.05 (d, $^2J_{HH} = 11.11$ Hz, 2H, CH_2CMe_3); 1.58 (s, 9H, $N-t-Bu$); 1.00 (s, 18H, 2 x CH_2CMe_3); 0.97 (d, $^2J_{HH} = 11.11$ Hz, 2H, CH_2CMe_3). ^{13}C NMR (50 MHz, C_6D_6): δ 131.73 (s, C_5H_4 -*ipso*); 115.41 (d, $^1J_{CH} = 170.2$ Hz, C_5H_4); 110.67 (d, $^1J_{CH} = 173.2$ Hz, C_5H_4); 93.94 (t, $^1J_{CH} = 109.0$ Hz, CH_2CMe_3); 63.04 (t, $^1J_{CH} = 134.5$ Hz, NCH_2); 60.77 (s, $NCMe_3$); 38.31 (s, CH_2CMe_3); 34.64 (q, $^1J_{CH} = 123.9$ Hz, CH_2CMe_3); 30.61 (t, $^1J_{CH} = 128.4$ Hz, $C_5H_4CH_2$); 30.56 (q, $^1J_{CH} = 125.4$ Hz, $NCMe_3$). IR (cm^{-1}): 2805 (sh, *nujol*); 2724 (w); 1796 (w); 1755 (w); 1738 (w); 1699 (w); 1659 (w); 1640 (w); 1499 (m); 1356 (vs); 1323 (sh, 1356 cm^{-1}); 1263 (m); 1229 (vs); 1190 (vs); 1098 (w); 1082 (m); 1063 (s); 1042 (m); 1017 (vw); 982 (s); 945 (s); 930 (m); 905 (w); (856 (m); 839 (m); 810 (vs); 766 (m); 748 (s); 723 (vw); 679 (m); 644 (m); 579 (w); 554 (w); 532 (m); 511 (m); 478 (s). Anal. Calcd. for $C_{21}H_{29}NTi$: C, 71.36; H, 11.12; Ti, 13.55. Found: C, 71.31; H, 11.11; Ti, 13.43.

Synthesis of $[C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2CMe_2Ph)_2$ (10). A solution of 1.32 g (9.42 mmol) of $LiCH_2CMe_2Ph$ in 25 mL of ether was added to a cooled (-70 °C) suspension of 1.37 g (4.85 mmol) of $[C_5H_4(CH_2)_2N-t-Bu]TiCl_2$ in 25 mL of ether. The reaction mixture was stirred for 1.5 hour while reaching room temperature. The ether was removed in vacuum and the sticky orange-yellow residue was stripped with 10 mL of pentane. Extraction with 40 mL of pentane and concentration to 10 mL gave after overnight cooling to -30 °C an orange-yellow crystalline material. A

second crop was obtained by concentrating and cooling of the mother liquor. Total yield: 1.56 g (3.27 mmol, 67%). ^1H NMR (200 MHz, C_6D_6): δ 7.41-7.15 (m, 10H, 2 x $\text{CH}_2\text{CMe}_2\text{Ph}$); 5.71 (t, $^3J_{\text{HH}} = 2.35$ Hz, 2H, C_5H_4); 5.49 (t, $^3J_{\text{HH}} = 2.35$ Hz, 2H, C_5H_4); 3.48 (t, $^3J_{\text{HH}} = 6.41$ Hz, 2H, NCH_2); 2.28 (d, $^2J_{\text{HH}} = 10.69$ Hz, 2H, 2 x $\text{CH}_2\text{CMe}_2\text{Ph}$); 2.23 (t, $^3J_{\text{HH}} = 6.41$ Hz, 2H, $\text{C}_5\text{H}_4\text{CH}_2$); 1.65 (s, 9H, *t*-Bu); 1.45 (d, $^2J_{\text{HH}} = 10.69$ Hz, 2H, 2 x $\text{CH}_2\text{CMe}_2\text{Ph}$); 1.37 (s, 6H, 2 x $\text{CH}_2\text{CMe}_2\text{Ph}$); 1.32 (s, 6H, 2 x $\text{CH}_2\text{CMe}_2\text{Ph}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 152.82 (s, $\text{CH}_2\text{CMe}_2\text{Ph-}ipso$); 131.80 (s, $\text{C}_5\text{H}_4-ipso$); 128.18 (d, $^1J_{\text{CH}} = 158.6$ Hz, $\text{CH}_2\text{CMe}_2-*o*-\text{Ph}$); 125.81 (d, $^1J_{\text{CH}} = 155.1$ Hz, $\text{CH}_2\text{CMe}_2-*m*-\text{Ph}$); 125.49 (d, $^1J_{\text{CH}} = 160.1$ Hz, $\text{CH}_2\text{CMe}_2-*p*-\text{Ph}$); 116.43 (d, $^1J_{\text{CH}} = 171.2$ Hz, C_5H_4); 111.02 (d, $^1J_{\text{CH}} = 174.25$ Hz, C_5H_4); 92.59 (t, $^1J_{\text{CH}} = 109.8$ Hz, $\text{CH}_2\text{CMe}_2\text{Ph}$); 92.53 (t, $^1J_{\text{CH}} = 109.8$ Hz, $\text{CH}_2\text{CMe}_2\text{Ph}$); 62.88 (t, $^1J_{\text{CH}} = 134.7$ Hz, NCH_2); 60.65 (s, NCMe_3); 44.26 (s, $\text{CH}_2\text{CMe}_2\text{Ph}$); 35.68 (q, $^1J_{\text{CH}} = 125.4$ Hz, $\text{CH}_2\text{CMe}_2\text{Ph}$); 35.64 (q, $^1J_{\text{CH}} = 125.4$ Hz, $\text{CH}_2\text{CMe}_2\text{Ph}$); 33.37 (q, $^1J_{\text{CH}} = 125.4$ Hz, $\text{CH}_2\text{CMe}_2\text{Ph}$); 30.56 (q, $^1J_{\text{CH}} = 124.9$ Hz, NCMe_3); 30.44 (t, $^1J_{\text{CH}} = 128.4$ Hz, $\text{C}_5\text{H}_4\text{CH}_2$). IR (cm^{-1}): 3105 (w), 3082 (m), 3053 (m), 3028 (m), 3016 (w), 1946 (w), 1597 (s), 1493 (s), 1442 (m), 1358 (s), 1344 (sh), 1325 (w), 1276 (m), 1244 (m), 1228 (w), 1184 (vs), 1155 (w), 1116 (m), 1078 (w), 1064 (s), 1040 (s), 1028 (s), 981 (s), 941 (m), 927 (m), 908 (w), 869 (m), 842 (m), 827 (vs), 765 (vs), 702 (vs); 684 (w), 646 (m), 588 (m), 569 (m), 561 (m), 530 (m), 488 (w), 474 (m). Anal. Calcd. for $\text{C}_{31}\text{H}_{43}\text{NTi}$: C, 77.96; H, 9.08; Ti, 10.03. Found: C, 77.94; H, 9.04; Ti, 10.12

*Thermolysis of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiPh}_2$ (**8**) in the presence of 2 eq PMe_3 in C_6D_{12} .* In an NMR tube 121.0 mg (0.331 mmol) of **8** was dissolved in 0.6 mL of C_6D_{12} and 72 mL (0.66 mmol) of PMe_3 was added. The tube was sealed under N_2 and heated to 75 °C. After 30 min a ^1H NMR spectrum was recorded, **8** appeared to be completely converted into $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti}(\text{C}_6\text{H}_4)\cdot\text{PMe}_3$ (**11**) and benzene was liberated. ^1H NMR (200 MHz, C_6D_{12}): δ 7.65 (br, 2H, C_6H_4); 7.20 (s, 6H, benzene); 7.10 (m, 2H,

C₆H₄); 6.45 (m, 1H, C₅H₄); 6.06 (m, 1H, C₅H₄); 5.13 (m, 1H, C₅H₄); 4.38 (m, 1H, C₅H₄); 3.83 (m, 1H, NCH₂); 3.69 (m, 1H, NCH₂); 2.71 (m, 2H, C₅H₄CH₂); 1.44 (d, ²J_{HP} = 5.98 Hz, 9H, PMe₃); 0.64 (s, 9H, *t*-Bu). The remaining uncoordinated PMe₃ was found as a broad resonance at 0.92 ppm

*Synthesis of [C₅H₄(CH₂)₂N-*t*-Bu]Ti(C₆H₄).PMe₃ (11).* To a solution of 1.13 g (3.10 mmol) of [C₅H₄(CH₂)₂N-*t*-Bu]TiPh₂ in 50 mL of hexane 0.70 mL (6.4 mmol) of PMe₃ was added. The vessel was closed and the brown solution was heated at 70 °C for 1.5 hours while the solution became yellow. Subsequently the mixture was cooled to room temperature and about 25 mL of solvent was removed in vacuum. On cooling overnight to -30 °C dark yellow crystals were obtained, yield: 0.59 g (1.63 mmol, 53%). ¹H NMR (200 MHz, C₇D₁₄, -60 °C): δ 7.82 (m, 1H, C₆H₄); 7.64 (m, 1H, C₆H₄); 7.16 (m, 2H, C₆H₄); 6.45, 6.00, 5.26, 4.26 (m, 4H, C₅H₄); 3.75 (m, 2H, NCH₂); 2.71 (m, 2H, C₅H₄CH₂); 1.40 (d, ²J_{HP} = 5.86 Hz, 9H, PMe₃); 0.63 (s, 9H, N-*t*-Bu). ¹³C NMR (75.4 MHz, C₇D₁₄, -60 °C): δ 190.73 (d, ²J_{CP} = 8.06 Hz, C_q-C₆H₄); 184.53 (d, ²J_{CP} = 35.25 Hz, C_q-C₆H₄); 131.54, 130.34, 130.12, 129.35 (d, ¹J_{CH} = 148.6, 154.1, 155.6, 138.0 Hz, C₆H₄); 129.56 (s, C₅H₄-*ipso*); 111.13, 109.49, 107.75, 100.27 (d, ¹J_{CH} = 178.3, 183.3, 175.4, 172.2 Hz, C₅H₄); 62.85 (t, ¹J_{CH} = 133.0 Hz, NCH₂); 59.25 (s, N-CMe₃); 32.44 (s, N-CMe₃); 32.24 (t, ¹J_{CH} = 126.7 Hz, C₅H₄CH₂); 19.15 (dq, ¹J_{CH} = 126.4 Hz, ²J_{CP} = 15.6 Hz, PMe₃). ³¹P NMR (80.96 MHz, C₆D₆): δ -3.73 (PMe₃). IR (cm⁻¹): 2726 (w), 2627 (w), 1545 (w), 1420 (w), 1400 (w), 1323 (m), 1300 (m), 1281 (m), 1244 (w), 1192 (m), 1150 (w), 1069 (w), 1053 (w), 986 (w), 978 (m), 951 (s), 936 (m), 849 (w), 835 (w), 799 (m), 793 (m), 735 (s), 681 (w), 556 (w), 436 (w), 411 (w). Anal. Calcd for C₂₀H₃₀NPTi: C, 66.11; H, 8.32; Ti, 13.18. Found: C, 66.40; H, 8.38; Ti, 13.12.

*Thermolysis of [C₅H₄(CH₂)₂N-*t*-Bu]Ti(CH₂CMe₃)₂ (9) in C₆D₁₂ in the presence of 2 eq. PMe₃.* In an NMR tube a solution of 42.7 mg (0.120 mmol) of **9** and 25 μ L (0.242 mmol) of PMe₃ in 0.4 mL of C₆D₁₂ was prepared and the tube was sealed. The tube was heated at 75 °C and a ¹H NMR spectrum was recorded every 30 min. After 90 min. **9** appeared to be completely converted. ¹H NMR (200 MHz, C₆D₁₂): δ 6.73 (m, 1H, C₅H₄); 6.28 (d, ¹J_{PH} = 1.47 Hz, 1H, =CHCMe₃); 5.80 (m, 1H, C₅H₄); 5.41 (m, 1H, C₅H₄); 4.88 (m, 1H, C₅H₄); 3.57 (m, 1H, NCH₂); 3.14 (m, 1H, NCH₂); 2.40 (m, 1H, C₅H₄CH₂); 1.99 (m, 1H, C₅H₄CH₂); 1.31 (d, ²J_{PH} = 6.10 Hz, 9H, PMe₃); 1.28 (s, 9H, N-*t*-Bu); 0.94 (s, 9H, =CHCMe₃, this singlet coincides with those of the liberated neopentane and the remaining uncoordinated PMe₃).

*Thermolysis of [C₅H₄(CH₂)₂N-*t*-Bu]Ti(CH₂CMe₂Ph)₂ (10) in C₆D₆ in the presence of excess PMe₃.* A solution of 70.2 mg (0.147 mmol) of **10** and 20 mL of PMe₃ in 0.4 mL of C₆D₆ was sealed in a NMR tube and heated at 75 °C. A ¹H NMR spectrum was recorded after resp. 50, 140, 210, 360, 510 min. After 8.5 hours the starting material was completely converted into [C₅H₄(CH₂)₂N-*t*-Bu]Ti=C(H)CMe₂Ph).PMe₃ and *t*-butylbenzene. ¹H NMR (200 MHz, C₆D₆): δ 7.52 (m, 2H, =C(H)CMe₂-*o*-Ph); 7.30-7.16 (m, 6H, =C(H)CMe₂-*m*-Ph + *t*-Bu-*m,o*-Ph); 7.08 (m, 2H, =C(H)CMe₂-*p*-Ph + *t*-Bu-*p*-Ph); 6.76 (m, 1H, C₅H₄); 6.45 (s, 1H, =C(H)CMe₂Ph); 6.05 (m, 1H, C₅H₄); 4.94 (m, 1H, C₅H₄); 3.45 (m, 1H, NCH₂); 3.06 (m, 1H, NCH₂); 2.41 (m, 1H, C₅H₄CH₂); 2.06 (m, 1H, C₅H₄CH₂); 1.55 (s, 3H, =C(H)CMe₂Ph); 1.49 (s, 3H, =C(H)CMe₂Ph); 1.32 (s, 9H, N-*t*-Bu); 1.22 (s, 9H, *t*-BuPh); 0.81 (s, remaining uncoordinated PMe₃); 0.75 (d, ¹J_{PH} = 6.35 Hz, 9H, coordinated PMe₃).

*Synthesis of [C₅H₄(CH₂)₂N-*t*-Bu]Ti=C(H)CMe₃.PMe₃ (12).* A solution of 2.50 g (7.07 mmol) of [C₅H₄(CH₂)₂N-*t*-Bu]Ti(CH₂CMe₃)₂ and 1.5 mL (14 mmol) of PMe₃ in 35 mL

of cyclohexane was heated at 75-80 °C during 3 hours. The yellow-brown solution became red-brown. After the reaction was completed the solvent was removed in vacuum and the red-brown residue was stripped with 20 mL of pentane. The residue was extracted with 20 mL of pentane and the solution was concentrated while refluxing. When crystallisation started to occur 3 mL of pentane was added and after refluxing the solution it was allowed to attain room temperature in 16 hours. 0.45 g (1.26 mmol) of product was isolated. Concentration of the mother liquor and cooling to -30 °C gave a second crop 1.26 g (3.52 mmol) of product. Yield: 1.71 g (4.78 mmol, 68%) of **12**. ^1H NMR (300 MHz, C_6D_6): δ 7.01 (m, 1H, C_5H_4); 6.39 (d, $^3J_{\text{PH}} = 1.70$ Hz, 1H, $=\text{C}(\text{H})\text{CMe}_3$); 6.10 (m, 1H, C_5H_4); 5.39 (m, 1H, C_5H_4); 4.98 (m, 1H, C_5H_4); 3.46 (m, 1H, NCH_2); 3.07 (m, 1H, NCH_2); 2.44 (m, 1H, $\text{C}_5\text{H}_4\text{CH}_2$); 2.07 (m, 1H, C_5H_4); 1.37 (s, 9H, *N-t*-Bu); 1.16 (s, 9H, $=\text{C}(\text{H})\text{CMe}_3$); 0.91 (d, $^2J_{\text{PH}} = 6.1$ Hz, 9H, PMe_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ 251.39 (dd, $^1J_{\text{CH}} = 83.1$ Hz, $^2J_{\text{PC}} = 13.1$ Hz, $=\text{C}(\text{H})\text{CMe}_3$); 127.79 (s, C_5H_4 -*ipso*); 105.97 (d, $^1J_{\text{CH}} = 169.2$ Hz, C_5H_4); 103.24 (d, $^1J_{\text{CH}} = 172.2$ Hz, C_5H_4); 101.39 (d, $^1J_{\text{CH}} = 167.19$ Hz, C_5H_4); 100.79 (d, $^1J_{\text{CH}} = 166.2$ Hz, C_5H_4); 57.94 (t, $^1J_{\text{CH}} = 132.5$ Hz, NCH_2); 56.70 (s, NCMe_3); 45.48 (s, $=\text{C}(\text{H})\text{CMe}_3$); 33.63 (dq, $^1J_{\text{CH}} = 124.6$ Hz, $^4J_{\text{CP}} = 3.0$ Hz, $=\text{C}(\text{H})\text{CMe}_3$); 32.79 (q, $^1J_{\text{CH}} = 124.6$ Hz, NCMe_3); 31.87 (t, $^1J_{\text{CH}} = 126.9$ Hz, $\text{C}_5\text{H}_4\text{CH}_2$); 17.70 (dq, $^1J_{\text{CH}} = 128.9$ Hz, $^1J_{\text{CP}} = 17.1$ Hz, PMe_3). ^{31}P NMR (80.96 MHz, C_6D_6): δ -6.01 (PMe_3). IR (cm^{-1}): 3117 (vw), 3094 (w), 2814 (w), 2714 (vw), 2675 (m), 1572 (w), 1458 (sh, Nujol), 1420 (m), 1350 (s), 1302 (m), 1279 (s), 1244 (s), 1227 (m), 1190 (s), 1146 (m), 1059 (m), 1045 (m), 1030 (s), 984 (w), 972 (w), 951 (vs), 856 (m), 839 (m), 828 (w), 787 (vs), 762 (m), 729 (m), 687 (m), 673 (m), 554 (m), 542 (m). Anal. Calcd. for $\text{C}_{19}\text{H}_{36}\text{NPTi}$: C, 63.86; H, 10.15; Ti, 13.40. Found: C, 64.13; H, 9.89; Ti, 13.55.

*Synthesis of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{Ti}=\text{C}(\text{H})\text{CMe}_2\text{Ph.PMe}_3$ (**13**).* A solution of 3.07 g (6.46 mmol) of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{Ti}(\text{CH}_2\text{CMe}_2\text{Ph})_2$ and 1.6 mL (15 mmol) of PMe_3 in

40 mL of cyclohexane was heated at 80 °C for 8 hours. During that time the dark yellow solution became red-brown. The solvent was removed in vacuum and the red-brown residue was stripped three times with 30 mL of pentane and dried in vacuum (10^{-1} torr) for 1 hour. The residue was extracted with 50 mL of pentane and the solution was concentrated while refluxing until the complex started to crystallize. 3 mL of pentane was added, on refluxing all crystals dissolved and the solution was cooled overnight to -30 °C. In a first crop 1.36 g (3.24 mmol) of dark red crystals were obtained. Concentration and slow cooling of the mother liquor gave a second crop 0.43 g (1.03 mmol) of product. Yield: 1.79 g (4.27 mmol, 66%) of 13. ^1H NMR (300 MHz, C_6D_6): δ 7.51 (m, 2H, =C(H)CMe₂-*o*-Ph); 7.23 (m, 2H, =C(H)CMe₂-*m*-Ph); 7.07 (m, 2H, =C(H)CMe₂-*p*-Ph); 6.74 (m, 1H, C₅H₄); 6.44 (s, 1H, =C(H)CMe₂Ph); 6.03 (m, 1H, C₅H₄); 5.38 (s, 1H, C₅H₄); 4.94 (m, 1H, C₅H₄); 3.46 (m, 1H, NCH₂); 3.06 (m, 1H, NCH₂); 2.43 (m, 1H, C₅H₄CH₂); 2.05 (m, 1H, C₅H₄CH₂); 1.55 (s, 3H, =C(H)CMe₂Ph); 1.48 (s, 3H, =C(H)CMe₂Ph); 1.33 (s, 9H, N-*t*-Bu); 0.77 (d, $^2\text{J}_{\text{PH}} = 6.35$ Hz, 9H, PMe₃). ^{13}C NMR (75.4 MHz, C_6D_6): δ 245.96 (dd, $^1\text{J}_{\text{CH}} = 88.0$ Hz, $^2\text{J}_{\text{CP}} = 12.8$ Hz, =C(H)CMe₂Ph); 152.61 (d, $^4\text{J}_{\text{CP}} = 3.2$ Hz, =C(H)CMe₂Ph-*ipso*); 127.85 (d, $^1\text{J}_{\text{CH}} = 155.8$ Hz, 127.78 (s, C₅H₄-*ipso*); 126.06 (d, $^1\text{J}_{\text{CH}} = 153.96$ Hz, =C(H)CMe₂-*m*-Ph); 124.77 (d, $^1\text{J}_{\text{CH}} = 159.0$ Hz, =C(H)CMe₂-*p*-Ph); 106.20 (d, $^1\text{J}_{\text{CH}} = 168.2$ Hz, C₅H₄); 103.96 (d, $^1\text{J}_{\text{CH}} = 172.8$ Hz, C₅H₄); 101.94 (d, $^1\text{J}_{\text{CH}} = 168.2$ Hz, C₅H₄); 101.19 (dd, $^1\text{J}_{\text{CH}} = 165.9$ Hz, $^2\text{J}_{\text{CP}} = 0.9$ Hz, C₅H₄); 58.05 (t, $^1\text{J}_{\text{CH}} = 132.7$ Hz, NCH₂); 57.03 (s, NMe₃); 52.02 (s, =C(H)CMe₂Ph); 33.35 (dq, $^1\text{J}_{\text{CH}} = 125.9$ Hz, $^4\text{J}_{\text{CP}} = 3.2$ Hz, =C(H)CMe₂Ph); 32.78 (q, $^1\text{J}_{\text{CH}} = 124.6$ Hz, NMe₃); 32.26 (dq, $^1\text{J}_{\text{CH}} = 125.7$ Hz, $^4\text{J}_{\text{CP}} = 2.3$ Hz, =C(H)CMe₂Ph); 31.85 (t, $^1\text{J}_{\text{CH}} = 126.9$ Hz, C₅H₄); 17.09 (dq, $^1\text{J}_{\text{CH}} = 128.9$ Hz, $^1\text{J}_{\text{CP}} = 17.0$ Hz, PMe₃). ^{31}P NMR (80.96 MHz, C_6D_6): δ -7.26 (PMe₃). IR (cm⁻¹): 3151 (vw), 3128 (vw), 3082 (w), 3057 (m), 3020 (w), 2729 (w), 2674 (m), 19469 (w), 1874 (w), 1805 (w), 1753 (vw), 1658 (w), 1593 (s), 1493 (m), 1467 (m), 1421 (w),

1354 (s), 1336 (w), 1309 (w), 1302 (w), 1280 (s), 1246 (m), 1224 (m), 1190 (vs), 1157 (w), 1120 (w), 1091 (m), 1068 (m), 1043 (s), 1028 (s), 1006 (w), 970 (w), 954 (vs), 910 (m), 873 (m), 839 (s), 823 (s), 787 (vs), 765 (s), 727 (m), 700 (s), 682 (m), 578 (s), 559 (w), 540 (m), 489 (w), 468 (m), 445 (vw). Anal. Calcd. for $C_{24}H_{38}NPTi$: C, 68.72; H, 9.13; Ti, 11.42. Found: C, 68.40; H, 9.13; Ti, 11.58.

Synthesis of $[C_5H_4(CH_2)_2N-t-Bu]Ti(C_2H_4).PMe_3$ (14). To a cooled ($-60\text{ }^\circ\text{C}$) solution of 1.82 g (6.45 mmol) of $[C_5H_4(CH_2)_2N-t-Bu]TiCl_2$ and 1.5 mL (14 mmol) of PMe_3 in 40 mL of ether, 7.8 mL of 1.65 M (13 mmol) of $EtMgBr$ in ether was added quickly. On warming up the reaction mixture to $-40\text{ }^\circ\text{C}$, the solution became yellow. Further warming to room temperature resulted in darkening of the solution and after 16 hours stirring a deep purple solution and a light coloured precipitate was obtained. The solvent was removed in vacuum resulting in a dark tarry residue. The residue was stripped with 20 mL of pentane and extracted with 40 mL of pentane. The solution was concentrated to 5 mL and cooled to $-50\text{ }^\circ\text{C}$. Crystallisation of a dark purple compound was observed but on warming to room temperature the crystals began to melt and for isolation the pentane was removed in vacuum. Yield: 1.73 g (5.49 mmol, 85%) of **14**. 1H NMR (300 MHz, C_6D_6): δ 6.59 (m, 1H, C_5H_4); 5.78 (m, 1H, C_5H_4); 4.97 (m, 1H, C_5H_4); 4.27 (m, 1H, C_5H_4); 3.54 (m, 1H, NCH_2); 3.09 (m, 1H, NCH_2); 2.57 (m, 1H, $C_5H_4CH_2$); 2.47 (m, 1H, $C_5H_4CH_2$); 2.18 (m, 1H, C_2H_4); 1.64 (m, 1H, C_2H_4); 1.39 (m, 1H, C_2H_4); 0.90 (d, $^2J_{PH} = 5.38$ Hz, 9H, PM_3); 0.87 (s, 9H, $N-t-Bu$); 0.35 (m, 1H, C_2H_4). ^{13}C NMR (50 MHz, C_6D_6): δ 130.38 (C_5H_4 -*ipso*); 110.58 (d, $^1J_{CH} = 170.6$ Hz, C_5H_4); 105.43 (d, $^1J_{CH} = 172.0$ Hz, C_5H_4); 102.80 (d, $^1J_{CH} = 167.8$ Hz, C_5H_4); 100.21 ($^1J_{CH} = 167.6$ Hz, C_5H_4); 57.62 (t, $^1J_{CH} = 132.9$ Hz, NCH_2); 56.51 (s, $NCMe_3$); 49.14 (dt, $^1J_{CH} = 145.8$ Hz, $^2J_{CP} = 10.0$ Hz, C_2H_4); 44.45 (t, $^1J_{CH} = 147.5$ Hz, C_2H_4); 31.21 (t, $^1J_{CH} = 127.2$ Hz, $C_5H_4CH_2$); 29.54 (q, $^1J_{CH} = 124.5$ Hz, $NCMe_3$); 16.74 (dq, $^1J_{CH} = 128.1$ Hz, $^1J_{CP} = 13.6$ Hz, PMe_3). IR (cm^{-1} , neat):

Reaction of $[C_5H_4(CH_2)_2N-t-Bu]Ti=C(H)CMe_3.PMe_3$ with 2 eq of ethylene. To an NMR tube containing a solution of 26.3 mg (0.0737 mmol) of $[C_5H_4(CH_2)_2N-t-Bu]Ti=C(H)CMe_3.PMe_3$ in 0.4 mL of C_6D_6 , 0.148 mmol of ethylene was added using vacuum-line techniques. The tube was sealed and kept at 50 °C. The reaction was monitored with 1H NMR spectroscopy. The reaction was complete within 30 hours. Apart from the resonances of $[C_5H_4(CH_2)_2N-t-Bu]Ti(C_2H_4).PMe_3$ (**14**), additional resonances in the region of 6-4.7 ppm and 2-0.8 ppm were observed. All volatiles of the NMR tube reaction were collected and examined by GC-MS. Three isomers of C_7H_{14} were present and identified as 4,4-dimethylpentene, *cis*-4,4-dimethylpent-2-ene and *trans*-4,4-dimethylpent-2-ene. Traces of neopentane and higher olefins ($C_{11}H_{22}$, $C_{12}H_{24}$) were found.

Polymerisation of propene with $\{[C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$. 55.6 mg (108.6 μ mol) of $B(C_6F_5)_3$ was reacted with 29.5 mg (75.0 μ mol) of $[C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2Ph)_2$ in 20 mL of benzene yielding a dark red solution. The solution was transferred in to a 50 mL autoclave which was pressurized with 3.5-4 bar propene. The solution was stirred at room temperature. After 17 min. no further uptake of propene was observed. The dark red color had almost disappeared. The mixture was poured in 100 mL of methanol and a sticky white solid precipitated. The solvents were decanted and the residue was subsequently washed with methanol and light petroleum. The residue was dissolved in chloroform and filtrated giving a clear solution. The solvent was removed in vacuum and a very viscous oil was obtained. Yield: 1.93 g of polymer. From 1H NMR spectroscopy a molecular weight of 1600 was estimated. An activity of 90 Kg mol $^{-1}$ h $^{-1}$ was found.

Table S1 - Crystal Data and Details of the Structure Determination for: s1400a C11 H17 Cl2 N Ti

Crystal Data

Empirical Formula	C11 H17 Cl2 N Ti		
Formula Weight	282.04		
Crystal System	Monoclinic		
Space group	P21/c	(No. 14)	
a, b, c [Angstrom]	8.5385(5)	12.9690(7)	11.9157(6)
alpha, beta, gamma [deg]	90	108.722(4)	90
V [Ang**3]	1249.68(12)		
Z	4		
D(calc) [g/cm**3]	1.499		
F(000) [Electrons]	584		
Mu(MoKa) [/cm]	10.8		
Crystal Size [mm]	0.25 x	0.50 x	0.50

Data Collection

Temperature (K), Exposure Time (H)	150, 9.0		
Radiation [Angstrom]	MoKa (with monochromator)	0.71073	
Theta Min-Max [Deg]	2.4, 27.5		
Scan, (Type & Range) [Deg]	omega,	0.66 + 0.35 Tan(Theta)	
Hor. and vert. aperture [mm]	1.82	4.00	
Reference Reflection(s)	1 2 4, 2 1 1, -2 2 2		
Dataset	-11: 11 ; 0: 16 ; -15: 15		
Tot., Uniq. Data, R(int)	5981,	2857,	0.0337
Observed data [I > 2.0 sigma(I)]	2552		

Refinement

Nref, Npar	2857, 187		
R, wR, S	0.0314, 0.0817, 1.08		
w = 1/[s^2^(Fo^2^)+(0.0480P)^2^+0.2037P] where P=(Fo^2^+2Fc^2^)/3			
Max. and Av. Shift/Error	0.000, 0.000		
Min. and Max. resd. dens. [e/Ang^3]	-0.34, 0.68		

Table S2 - Final Coordinates and Equivalent Isotropic Thermal Parameters of the non-Hydrogen atoms for: s1400a C11 H17 Cl2 N Ti

Atom ----	x ---	y ---	z ---	U(eq) [Ang ²] -----
Ti(1)	0.21899(3)	0.14723(2)	0.16565(2)	0.0160(1)
Cl(1)	0.35892(5)	0.05596(3)	0.06410(3)	0.0248(1)
Cl(2)	0.16869(6)	0.02654(4)	0.29162(4)	0.0294(1)
N(1)	0.3733(2)	0.23814(11)	0.26268(12)	0.0185(4)
C(1)	0.0918(2)	0.24105(14)	-0.00895(14)	0.0222(5)
C(2)	-0.0023(2)	0.15102(14)	-0.0118(2)	0.0236(5)
C(3)	-0.0696(2)	0.15707(15)	0.0812(2)	0.0257(5)
C(4)	-0.0159(2)	0.25013(14)	0.1425(2)	0.0235(5)
C(5)	0.0818(2)	0.30386(13)	0.08524(14)	0.0207(4)
C(6)	0.1573(2)	0.40809(13)	0.11838(15)	0.0236(5)
C(7)	0.2559(2)	0.41536(13)	0.2501(2)	0.0234(5)
C(8)	0.4083(2)	0.34791(13)	0.2844(2)	0.0242(5)
C(9)	0.5145(2)	0.17082(13)	0.32973(14)	0.0215(4)
C(10)	0.5395(3)	0.1714(2)	0.4626(2)	0.0322(6)
C(11)	0.6712(2)	0.1973(2)	0.3011(2)	0.0295(5)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S3 - Hydrogen Atom Positions and Isotropic Thermal Parameters

for: s1400a C11 H17 Cl2 N Ti

Atom	x	y	z	U(iso) [Ang^2]
H(1)	0.159(3)	0.2538(16)	-0.0579(18)	0.0270
H(2)	-0.014(3)	0.0991(17)	-0.0651(19)	0.0280
H(3)	-0.134(3)	0.1119(18)	0.0999(19)	0.0310
H(4)	-0.043(3)	0.2730(17)	0.2099(19)	0.0280
H(6A)	0.068(3)	0.4582(17)	0.1008(19)	0.0280
H(6B)	0.230(3)	0.4243(16)	0.0746(19)	0.0280
H(7A)	0.293(3)	0.4883(18)	0.2725(19)	0.0280
H(7B)	0.184(3)	0.3995(17)	0.2975(19)	0.0280
H(8A)	0.480(3)	0.3674(16)	0.244(2)	0.0290
H(8B)	0.463(3)	0.3551(16)	0.367(2)	0.0290
H(9)	0.483(3)	0.1037(16)	0.3001(18)	0.0260
H(10A)	0.627(4)	0.123(2)	0.500(2)	0.0480
H(10B)	0.434(4)	0.153(2)	0.474(2)	0.0480
H(10C)	0.572(3)	0.236(2)	0.496(2)	0.0480
H(11A)	0.759(3)	0.149(2)	0.339(2)	0.0440
H(11B)	0.712(3)	0.262(2)	0.329(2)	0.0440
H(11C)	0.654(3)	0.196(2)	0.217(2)	0.0440

=====

The Temperature Factor has the Form of $\text{Exp}(-T)$ Where
 $T = 8 * (\text{Pi} ** 2) * U * (\text{Sin}(\text{Theta}) / \text{Lambda}) ** 2$ for Isotropic Atoms

Table S4 - (An)isotropic Thermal Parameters
for: s1400a C11 H17 Cl2 N Ti

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
----	-----	-----	-----	-----	-----	-----
Ti(1)	0.0155(2)	0.0175(2)	0.0136(2)	-0.0003(1)	0.0029(1)	-0.0003(1)
Cl(1)	0.0261(2)	0.0277(2)	0.0197(2)	-0.0029(2)	0.0063(2)	0.0071(2)
Cl(2)	0.0305(2)	0.0332(2)	0.0230(2)	0.0071(2)	0.0063(2)	-0.0086(2)
N(1)	0.0163(6)	0.0198(7)	0.0173(6)	-0.0010(5)	0.0025(5)	0.0005(5)
C(1)	0.0221(8)	0.0264(9)	0.0151(7)	0.0014(6)	0.0018(6)	0.0043(6)
C(2)	0.0203(8)	0.0257(9)	0.0185(8)	-0.0030(6)	-0.0026(6)	0.0017(6)
C(3)	0.0161(8)	0.0292(9)	0.0283(9)	0.0015(7)	0.0022(7)	-0.0010(7)
C(4)	0.0172(7)	0.0299(9)	0.0231(8)	0.0003(7)	0.0059(6)	0.0041(7)
C(5)	0.0198(8)	0.0230(8)	0.0173(7)	0.0026(6)	0.0030(6)	0.0046(6)
C(6)	0.0303(9)	0.0204(8)	0.0205(8)	0.0021(6)	0.0088(7)	0.0048(7)
C(7)	0.0289(9)	0.0181(8)	0.0228(8)	-0.0025(6)	0.0077(7)	0.0002(7)
C(8)	0.0237(8)	0.0209(8)	0.0250(9)	-0.0021(6)	0.0035(7)	-0.0030(6)
C(9)	0.0189(7)	0.0221(8)	0.0196(8)	-0.0017(6)	0.0006(6)	0.0008(6)
C(10)	0.0317(10)	0.0392(11)	0.0194(8)	0.0001(8)	-0.0004(7)	0.0031(9)
C(11)	0.0182(8)	0.0319(10)	0.0348(10)	-0.0058(8)	0.0036(7)	-0.0004(7)

=====

The Temperature Factor has the Form of $\text{Exp}(-T)$ Where
 $T = 8 * (\text{Pi}^{**2}) * U * (\text{Sin}(\text{Theta}) / \text{Lambda})^{**2}$ for Isotropic Atoms
 $T = 2 * (\text{Pi}^{**2}) * \text{Sum}_{ij} (h(i) * h(j) * U(i,j) * \text{Astar}(i) * \text{Astar}(j))$, for
 Anisotropic Atoms. $\text{Astar}(i)$ are Reciprocal Axial Lengths and
 $h(i)$ are the Reflection Indices.

Table S5 - Bond Distances (Angstrom)
 for: s1400a C11 H17 Cl2 N Ti

Ti(1)	-Cl(1)	2.2849(5)	C(9)	-C(11)	1.522(3)
Ti(1)	-Cl(2)	2.3025(6)	C(1)	-H(1)	0.95(2)
Ti(1)	-N(1)	1.8668(15)	C(2)	-H(2)	0.91(2)
Ti(1)	-C(1)	2.3533(17)	C(3)	-H(3)	0.88(3)
Ti(1)	-C(2)	2.341(2)	C(4)	-H(4)	0.95(2)
Ti(1)	-C(3)	2.347(2)	C(6)	-H(6A)	0.97(2)
Ti(1)	-C(4)	2.3504(19)	C(6)	-H(6B)	0.95(3)
Ti(1)	-C(5)	2.3866(17)	C(7)	-H(7A)	1.01(2)
N(1)	-C(8)	1.461(2)	C(7)	-H(7B)	0.98(3)
N(1)	-C(9)	1.495(2)	C(8)	-H(8A)	0.93(3)
C(1)	-C(2)	1.412(3)	C(8)	-H(8B)	0.95(2)
C(1)	-C(5)	1.411(2)	C(9)	-H(9)	0.95(2)
C(2)	-C(3)	1.405(3)	C(10)	-H(10A)	0.97(3)
C(3)	-C(4)	1.409(3)	C(10)	-H(10B)	0.98(3)
C(4)	-C(5)	1.419(3)	C(10)	-H(10C)	0.93(3)
C(5)	-C(6)	1.495(2)	C(11)	-H(11A)	0.97(3)
C(6)	-C(7)	1.527(3)	C(11)	-H(11B)	0.93(3)
C(7)	-C(8)	1.511(3)	C(11)	-H(11C)	0.97(2)
C(9)	-C(10)	1.528(3)			

Table S6 - Bond Angles
for: s1400a(Degrees)
C11 H17 Cl2 N Ti

Cl(1)	-Ti(1)	-Cl(2)	103.40(2)	Ti(1)	-N(1)	-C(8)	142.08(13)
Cl(1)	-Ti(1)	-N(1)	105.67(5)	Ti(1)	-N(1)	-C(9)	104.47(10)
Cl(1)	-Ti(1)	-C(1)	88.34(4)	C(8)	-N(1)	-C(9)	112.98(14)
Cl(1)	-Ti(1)	-C(2)	86.57(5)	Ti(1)	-C(1)	-C(2)	72.01(11)
Cl(1)	-Ti(1)	-C(3)	117.17(5)	Ti(1)	-C(1)	-C(5)	73.97(9)
Cl(1)	-Ti(1)	-C(4)	143.47(6)	C(2)	-C(1)	-C(5)	108.50(16)
Cl(1)	-Ti(1)	-C(5)	120.07(4)	Ti(1)	-C(2)	-C(1)	72.99(11)
Cl(2)	-Ti(1)	-N(1)	105.54(5)	Ti(1)	-C(2)	-C(3)	72.82(12)
Cl(2)	-Ti(1)	-C(1)	142.95(5)	C(1)	-C(2)	-C(3)	107.98(17)
Cl(2)	-Ti(1)	-C(2)	109.74(5)	Ti(1)	-C(3)	-C(2)	72.31(11)
Cl(2)	-Ti(1)	-C(3)	85.79(5)	Ti(1)	-C(3)	-C(4)	72.67(11)
Cl(2)	-Ti(1)	-C(4)	97.57(5)	C(2)	-C(3)	-C(4)	108.02(17)
Cl(2)	-Ti(1)	-C(5)	132.08(5)	Ti(1)	-C(4)	-C(3)	72.42(11)
N(1)	-Ti(1)	-C(1)	104.76(6)	Ti(1)	-C(4)	-C(5)	73.98(10)
N(1)	-Ti(1)	-C(2)	138.66(6)	C(3)	-C(4)	-C(5)	108.37(18)
N(1)	-Ti(1)	-C(3)	131.79(7)	Ti(1)	-C(5)	-C(1)	71.39(10)
N(1)	-Ti(1)	-C(4)	96.90(7)	Ti(1)	-C(5)	-C(4)	71.18(10)
N(1)	-Ti(1)	-C(5)	82.47(6)	Ti(1)	-C(5)	-C(6)	123.30(12)
C(1)	-Ti(1)	-C(2)	35.00(6)	C(1)	-C(5)	-C(4)	107.10(16)
C(1)	-Ti(1)	-C(3)	57.98(7)	C(1)	-C(5)	-C(6)	126.93(16)
C(1)	-Ti(1)	-C(4)	57.89(7)	C(4)	-C(5)	-C(6)	125.97(16)
C(1)	-Ti(1)	-C(5)	34.64(6)	C(5)	-C(6)	-C(7)	112.08(14)
C(2)	-Ti(1)	-C(3)	34.87(7)	C(6)	-C(7)	-C(8)	112.64(16)
C(2)	-Ti(1)	-C(4)	58.07(7)	N(1)	-C(8)	-C(7)	114.00(16)
C(2)	-Ti(1)	-C(5)	57.97(6)	N(1)	-C(9)	-C(10)	111.79(16)
C(3)	-Ti(1)	-C(4)	34.91(7)	N(1)	-C(9)	-C(11)	111.37(15)
C(3)	-Ti(1)	-C(5)	57.94(6)	C(10)	-C(9)	-C(11)	112.99(17)
C(4)	-Ti(1)	-C(5)	34.84(6)	Ti(1)	-C(1)	-H(1)	115.6(14)

Table S6 - Bond Angles (Degrees) (continued)
 for: s1400a C11 H17 Cl2 N Ti

C(2)	-C(1)	-H(1)	125.3 (13)	N(1)	-C(8)	-H(8A)	107.8 (13)
C(5)	-C(1)	-H(1)	126.0 (13)	N(1)	-C(8)	-H(8B)	106.5 (13)
Ti(1)	-C(2)	-H(2)	119.4 (15)	C(7)	-C(8)	-H(8A)	110.9 (14)
C(1)	-C(2)	-H(2)	124.3 (16)	C(7)	-C(8)	-H(8B)	108.5 (15)
C(3)	-C(2)	-H(2)	127.7 (16)	H(8A)	-C(8)	-H(8B)	109 (2)
Ti(1)	-C(3)	-H(3)	120.7 (16)	N(1)	-C(9)	-H(9)	104.7 (14)
C(2)	-C(3)	-H(3)	127.6 (15)	C(10)	-C(9)	-H(9)	108.7 (13)
C(4)	-C(3)	-H(3)	124.4 (15)	C(11)	-C(9)	-H(9)	106.8 (16)
Ti(1)	-C(4)	-H(4)	120.5 (14)	C(9)	-C(10)	-H(10A)	107.7 (15)
C(3)	-C(4)	-H(4)	125.3 (14)	C(9)	-C(10)	-H(10B)	108.2 (13)
C(5)	-C(4)	-H(4)	126.3 (14)	C(9)	-C(10)	-H(10C)	111.8 (15)
C(5)	-C(6)	-H(6A)	107.8 (14)	H(10A)	-C(10)	-H(10B)	113 (2)
C(5)	-C(6)	-H(6B)	110.9 (13)	H(10A)	-C(10)	-H(10C)	108 (2)
C(7)	-C(6)	-H(6A)	108.4 (13)	H(10B)	-C(10)	-H(10C)	109 (2)
C(7)	-C(6)	-H(6B)	107.9 (14)	C(9)	-C(11)	-H(11A)	110.7 (15)
H(6A)	-C(6)	-H(6B)	109.8 (19)	C(9)	-C(11)	-H(11B)	112.3 (16)
C(6)	-C(7)	-H(7A)	110.7 (12)	C(9)	-C(11)	-H(11C)	112.1 (16)
C(6)	-C(7)	-H(7B)	109.8 (14)	H(11A)	-C(11)	-H(11B)	106 (2)
C(8)	-C(7)	-H(7A)	107.6 (15)	H(11A)	-C(11)	-H(11C)	108 (2)
C(8)	-C(7)	-H(7B)	111.5 (14)	H(11B)	-C(11)	-H(11C)	108 (2)
H(7A)	-C(7)	-H(7B)	104.3 (19)				

Table S7 - Torsion Angles (Degrees)
for: s1400a C11 H17 Cl2 N Ti

Cl(1)	-Ti(1)	-N(1)	-C(8)	117.6(2)
Cl(1)	-Ti(1)	-N(1)	-C(9)	-53.39(11)
Cl(2)	-Ti(1)	-N(1)	-C(8)	-133.3(2)
Cl(2)	-Ti(1)	-N(1)	-C(9)	55.75(11)
C(1)	-Ti(1)	-N(1)	-C(8)	25.1(2)
C(1)	-Ti(1)	-N(1)	-C(9)	-145.84(10)
C(2)	-Ti(1)	-N(1)	-C(8)	14.6(3)
C(2)	-Ti(1)	-N(1)	-C(9)	-156.38(10)
C(3)	-Ti(1)	-N(1)	-C(8)	-34.9(2)
C(3)	-Ti(1)	-N(1)	-C(9)	154.16(11)
C(4)	-Ti(1)	-N(1)	-C(8)	-33.4(2)
C(4)	-Ti(1)	-N(1)	-C(9)	155.62(11)
C(5)	-Ti(1)	-N(1)	-C(8)	-1.6(2)
C(5)	-Ti(1)	-N(1)	-C(9)	-172.58(11)
Cl(1)	-Ti(1)	-C(1)	-C(2)	86.39(10)
Cl(1)	-Ti(1)	-C(1)	-C(5)	-157.48(10)
Cl(2)	-Ti(1)	-C(1)	-C(2)	-23.88(14)
Cl(2)	-Ti(1)	-C(1)	-C(5)	92.25(12)
N(1)	-Ti(1)	-C(1)	-C(2)	-167.84(11)
N(1)	-Ti(1)	-C(1)	-C(5)	-51.71(12)
C(2)	-Ti(1)	-C(1)	-C(5)	116.13(15)
C(3)	-Ti(1)	-C(1)	-C(2)	-37.45(11)
C(3)	-Ti(1)	-C(1)	-C(5)	78.68(11)
C(4)	-Ti(1)	-C(1)	-C(2)	-78.91(12)
C(4)	-Ti(1)	-C(1)	-C(5)	37.22(10)
C(5)	-Ti(1)	-C(1)	-C(2)	-116.13(15)
Cl(1)	-Ti(1)	-C(2)	-C(1)	-92.00(10)
Cl(1)	-Ti(1)	-C(2)	-C(3)	152.37(11)

Table S7 - Torsion Angles (Degrees) (continued)
 for: s1400a C11 H17 Cl2 N Ti

Cl(2)	-Ti(1)	-C(2)	-C(1)	164.98(9)
Cl(2)	-Ti(1)	-C(2)	-C(3)	49.36(11)
N(1)	-Ti(1)	-C(2)	-C(1)	17.97(16)
N(1)	-Ti(1)	-C(2)	-C(3)	-97.66(14)
C(1)	-Ti(1)	-C(2)	-C(3)	-115.62(16)
C(3)	-Ti(1)	-C(2)	-C(1)	115.62(16)
C(4)	-Ti(1)	-C(2)	-C(1)	78.35(11)
C(4)	-Ti(1)	-C(2)	-C(3)	-37.28(11)
C(5)	-Ti(1)	-C(2)	-C(1)	37.01(10)
C(5)	-Ti(1)	-C(2)	-C(3)	-78.61(12)
Cl(1)	-Ti(1)	-C(3)	-C(2)	-31.35(12)
Cl(1)	-Ti(1)	-C(3)	-C(4)	-147.43(11)
Cl(2)	-Ti(1)	-C(3)	-C(2)	-134.26(11)
Cl(2)	-Ti(1)	-C(3)	-C(4)	109.66(12)
N(1)	-Ti(1)	-C(3)	-C(2)	118.61(12)
N(1)	-Ti(1)	-C(3)	-C(4)	2.53(16)
C(1)	-Ti(1)	-C(3)	-C(2)	37.59(10)
C(1)	-Ti(1)	-C(3)	-C(4)	-78.49(13)
C(2)	-Ti(1)	-C(3)	-C(4)	-116.08(17)
C(4)	-Ti(1)	-C(3)	-C(2)	116.08(17)
C(5)	-Ti(1)	-C(3)	-C(2)	78.71(11)
C(5)	-Ti(1)	-C(3)	-C(4)	-37.37(11)
Cl(1)	-Ti(1)	-C(4)	-C(3)	53.56(15)
Cl(1)	-Ti(1)	-C(4)	-C(5)	-62.22(13)
Cl(2)	-Ti(1)	-C(4)	-C(3)	-71.34(12)
Cl(2)	-Ti(1)	-C(4)	-C(5)	172.87(10)
N(1)	-Ti(1)	-C(4)	-C(3)	-178.10(12)
N(1)	-Ti(1)	-C(4)	-C(5)	66.12(11)

Table S7 - Torsion Angles (Degrees) (continued)
 for: s1400a C11 H17 Cl2 N Ti

C(1)	-Ti(1)	-C(4)	-C(3)	78.78(13)
C(1)	-Ti(1)	-C(4)	-C(5)	-37.00(10)
C(2)	-Ti(1)	-C(4)	-C(3)	37.24(12)
C(2)	-Ti(1)	-C(4)	-C(5)	-78.55(12)
C(3)	-Ti(1)	-C(4)	-C(5)	-115.78(18)
C(5)	-Ti(1)	-C(4)	-C(3)	115.78(18)
Cl(1)	-Ti(1)	-C(5)	-C(1)	26.25(11)
Cl(1)	-Ti(1)	-C(5)	-C(4)	142.51(10)
Cl(1)	-Ti(1)	-C(5)	-C(6)	-96.25(13)
Cl(2)	-Ti(1)	-C(5)	-C(1)	-125.80(9)
Cl(2)	-Ti(1)	-C(5)	-C(4)	-9.54(13)
Cl(2)	-Ti(1)	-C(5)	-C(6)	111.70(13)
N(1)	-Ti(1)	-C(5)	-C(1)	130.04(11)
N(1)	-Ti(1)	-C(5)	-C(4)	-113.70(12)
N(1)	-Ti(1)	-C(5)	-C(6)	7.54(14)
C(1)	-Ti(1)	-C(5)	-C(4)	116.26(16)
C(1)	-Ti(1)	-C(5)	-C(6)	-122.50(19)
C(2)	-Ti(1)	-C(5)	-C(1)	-37.41(10)
C(2)	-Ti(1)	-C(5)	-C(4)	78.86(12)
C(2)	-Ti(1)	-C(5)	-C(6)	-159.91(16)
C(3)	-Ti(1)	-C(5)	-C(1)	-78.81(12)
C(3)	-Ti(1)	-C(5)	-C(4)	37.45(12)
C(3)	-Ti(1)	-C(5)	-C(6)	158.69(16)
C(4)	-Ti(1)	-C(5)	-C(1)	-116.26(16)
C(4)	-Ti(1)	-C(5)	-C(6)	121.24(18)
Ti(1)	-N(1)	-C(8)	-C(7)	27.5(3)
C(9)	-N(1)	-C(8)	-C(7)	-162.08(16)
Ti(1)	-N(1)	-C(9)	-C(10)	-115.57(15)

Table S7 - Torsion Angles (Degrees) (continued)
 for: s1400a C11 H17 Cl2 N Ti

Ti(1)	-N(1)	-C(9)	-C(11)	116.97(14)
C(8)	-N(1)	-C(9)	-C(10)	70.5(2)
C(8)	-N(1)	-C(9)	-C(11)	-57.0(2)
Ti(1)	-C(1)	-C(2)	-C(3)	64.91(15)
C(5)	-C(1)	-C(2)	-Ti(1)	-65.50(12)
C(5)	-C(1)	-C(2)	-C(3)	-0.6(2)
Ti(1)	-C(1)	-C(5)	-C(4)	-62.63(13)
Ti(1)	-C(1)	-C(5)	-C(6)	118.14(17)
C(2)	-C(1)	-C(5)	-Ti(1)	64.22(13)
C(2)	-C(1)	-C(5)	-C(4)	1.6(2)
C(2)	-C(1)	-C(5)	-C(6)	-177.64(17)
Ti(1)	-C(2)	-C(3)	-C(4)	64.37(14)
C(1)	-C(2)	-C(3)	-Ti(1)	-65.02(14)
C(1)	-C(2)	-C(3)	-C(4)	-0.6(2)
Ti(1)	-C(3)	-C(4)	-C(5)	65.77(13)
C(2)	-C(3)	-C(4)	-Ti(1)	-64.14(14)
C(2)	-C(3)	-C(4)	-C(5)	1.6(2)
Ti(1)	-C(4)	-C(5)	-C(1)	62.77(12)
Ti(1)	-C(4)	-C(5)	-C(6)	-117.99(17)
C(3)	-C(4)	-C(5)	-Ti(1)	-64.75(14)
C(3)	-C(4)	-C(5)	-C(1)	-2.0(2)
C(3)	-C(4)	-C(5)	-C(6)	177.25(17)
Ti(1)	-C(5)	-C(6)	-C(7)	-38.75(19)
C(1)	-C(5)	-C(6)	-C(7)	-129.67(18)
C(4)	-C(5)	-C(6)	-C(7)	51.2(2)
C(5)	-C(6)	-C(7)	-C(8)	66.88(19)
C(6)	-C(7)	-C(8)	-N(1)	-60.7(2)

Table S1 - Crystal Data and Details of the Structure Determination for: shelxl

Crystal Data

Empirical Formula	C10 H15 Cl2 N Ti		
Formula Weight	268.01		
Crystal System	Triclinic		
Space group	P-1	(No. 2)	
a, b, c [Angstrom]	7.6327(11)	7.810(2)	10.716(2)
alpha, beta, gamma [deg]	102.821(10)	102.618(10)	101.211(10)
V [Ang**3]	587.7(2)		
Z	2		
D(calc) [g/cm**3]	1.515		
F(000) [Electrons]	276		
Mu(MoKa) [/cm]	11.4		
Crystal Size [mm]	0.25 x	0.25 x	0.40

Data Collection

Temperature (K)	150		
Radiation [Angstrom]	MoKa	0.71073	
Theta Min-Max [Deg]	2.0, 27.5		
Scan, (Type & Range) [Deg]	0.80 + 0.35 Tan(Theta)		
Hor. and vert. aperture [mm]	3.00	4.00	
Reference Reflection(s)	2 2 -1 ; 0 2 -6		
Dataset	0: 9 ; -10: 9 ; -13: 13		
Tot., Uniq. Data, R(int)	2848,	2646,	0.047
Observed data [I > 2.0 sigma(I)]	2016		

Refinement

Nref, Npar	2646, 187		
R, wR, S	0.0441, 0.1024, 1.06		
w = 1/[s^2^(Fo^2^)+(0.0457P)^2^]	where P=(Fo^2^+2Fc^2^)/3		
Max. and Av. Shift/Error	0.00, 0.00		
Min. and Max. resd. dens. [e/Ang^3]	-0.31, 0.51		

Table S2 - Final Coordinates and Equivalent Isotropic Thermal Parameters of the non-Hydrogen atoms for: shelxl

Atom ----	x ---	y ---	z ---	U(eq) [Ang ²] -----
Ti1	1.10687(7)	0.29236(7)	0.26608(5)	0.0184(2)
Cl1	1.19831(11)	0.21389(11)	0.07756(8)	0.0289(2)
Cl2	1.25412(11)	0.59635(11)	0.35220(8)	0.0271(2)
N1	0.8553(3)	0.2835(3)	0.2116(2)	0.0184(7)
C1	1.0748(5)	0.0006(5)	0.2956(3)	0.0254(12)
C2	1.2580(5)	0.1014(5)	0.3643(4)	0.0313(12)
C3	1.2524(5)	0.2438(5)	0.4668(3)	0.0310(12)
C4	1.0641(5)	0.2324(5)	0.4612(3)	0.0259(12)
C5	0.9544(4)	0.0810(4)	0.3555(3)	0.0236(12)
C6	0.7487(5)	0.0384(5)	0.3021(4)	0.0292(12)
C7	0.7014(5)	0.1996(5)	0.2582(4)	0.0259(12)
C8	0.8094(4)	0.3870(4)	0.1147(3)	0.0214(11)
C9	0.7144(5)	0.5315(5)	0.1656(3)	0.0277(12)
C10	0.6953(5)	0.2607(5)	-0.0210(3)	0.0255(12)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S3 - Hydrogen Atom Positions and Isotropic Thermal Parameters
for: shelxl

Atom	x	y	z	U(iso) [Ang ²]
H501	0.915 (4)	0.446 (4)	0.103 (3)	0.007 (7)
H502	0.597 (5)	0.164 (5)	0.186 (3)	0.024 (9)
H503	0.685 (5)	0.012 (5)	0.366 (4)	0.039 (11)
H504	1.024 (5)	0.310 (4)	0.509 (3)	0.017 (8)
H505	0.694 (5)	0.603 (5)	0.108 (4)	0.031 (10)
H506	0.784 (5)	0.616 (5)	0.248 (4)	0.031 (10)
H507	1.037 (5)	-0.102 (5)	0.221 (4)	0.038 (11)
H508	0.685 (5)	0.325 (5)	-0.088 (4)	0.033 (10)
H509	0.598 (5)	0.480 (5)	0.180 (3)	0.027 (9)
H510	1.356 (5)	0.334 (5)	0.529 (4)	0.035 (10)
H511	0.681 (5)	0.294 (5)	0.333 (4)	0.031 (10)
H512	0.754 (5)	0.168 (5)	-0.046 (4)	0.037 (11)
H513	1.361 (6)	0.074 (5)	0.337 (4)	0.041 (11)
H514	0.572 (6)	0.202 (6)	-0.019 (4)	0.044 (11)
H515	0.707 (5)	-0.065 (6)	0.228 (4)	0.040 (11)

=====

The Temperature Factor has the Form of $\text{Exp}(-T)$ Where
 $T = 8 * (\text{Pi} ** 2) * U * (\text{Sin}(\text{Theta}) / \text{Lambda}) ** 2$ for Isotropic Atoms

Table S4 - (An)isotropic Thermal Parameters
for: shelxl

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
----	-----	-----	-----	-----	-----	-----
Ti1	0.0148(3)	0.0224(3)	0.0203(3)	0.0097(2)	0.0053(2)	0.0051(2)
Cl1	0.0247(4)	0.0255(4)	0.0320(4)	0.0063(3)	0.0043(3)	0.0020(3)
Cl2	0.0272(4)	0.0339(4)	0.0256(4)	0.0111(3)	0.0128(3)	0.0102(3)
N1	0.0167(13)	0.0232(13)	0.0192(12)	0.0108(10)	0.0059(10)	0.0069(10)
C1	0.030(2)	0.025(2)	0.030(2)	0.0155(14)	0.0117(14)	0.0142(14)
C2	0.025(2)	0.047(2)	0.038(2)	0.029(2)	0.014(2)	0.020(2)
C3	0.022(2)	0.044(2)	0.028(2)	0.021(2)	-0.0004(14)	0.006(2)
C4	0.028(2)	0.031(2)	0.024(2)	0.0126(14)	0.0091(14)	0.0115(15)
C5	0.023(2)	0.029(2)	0.027(2)	0.0197(14)	0.0102(13)	0.0081(13)
C6	0.021(2)	0.034(2)	0.038(2)	0.022(2)	0.0070(15)	0.0068(14)
C7	0.020(2)	0.030(2)	0.033(2)	0.0179(15)	0.0080(14)	0.0073(14)
C8	0.019(2)	0.024(2)	0.0210(15)	0.0102(12)	0.0036(12)	0.0027(13)
C9	0.029(2)	0.029(2)	0.024(2)	0.0065(14)	0.0024(14)	0.011(2)
C10	0.028(2)	0.022(2)	0.026(2)	0.0099(14)	0.0032(14)	0.0064(14)

=====

The Temperature Factor has the Form of $\text{Exp}(-T)$ Where
 $T = 8 * (\text{Pi} ** 2) * U * (\text{Sin}(\text{Theta}) / \text{Lambda}) ** 2$ for Isotropic Atoms
 $T = 2 * (\text{Pi} ** 2) * \text{Sum}_{ij} (h(i) * h(j) * U(i, j) * \text{Astar}(i) * \text{Astar}(j))$, for
Anisotropic Atoms. $\text{Astar}(i)$ are Reciprocal Axial Lengths and
 $h(i)$ are the Reflection Indices.

Table S5 - Bond Distances (Angstrom)
for: shelxl

Ti1	-Cl1	2.2752(11)	C8	-C9	1.521(5)
Ti1	-Cl2	2.2996(12)	C8	-C10	1.524(4)
Ti1	-N1	1.864(2)	C1	-H507	0.94(4)
Ti1	-C1	2.343(4)	C2	-H513	0.94(5)
Ti1	-C2	2.345(4)	C3	-H510	0.95(4)
Ti1	-C3	2.342(3)	C4	-H504	0.85(3)
Ti1	-C4	2.318(3)	C6	-H503	0.96(4)
Ti1	-C5	2.332(3)	C6	-H515	0.94(4)
N1	-C7	1.470(5)	C7	-H502	0.93(3)
N1	-C8	1.476(4)	C7	-H511	1.02(4)
C1	-C2	1.408(6)	C8	-H501	0.90(3)
C1	-C5	1.398(5)	C9	-H505	0.93(4)
C2	-C3	1.394(5)	C9	-H506	0.95(4)
C3	-C4	1.410(6)	C9	-H509	0.96(4)
C4	-C5	1.410(5)	C10	-H508	0.96(4)
C5	-C6	1.491(5)	C10	-H512	0.94(4)
C6	-C7	1.517(6)	C10	-H514	0.97(5)

Table S6 - Bond Angles (Degrees)
for: shelxl

Cl1	-Ti1	-Cl2	103.01(4)	Ti1	-N1	-C7	129.2(2)
Cl1	-Ti1	-N1	106.53(7)	Ti1	-N1	-C8	114.23(19)
Cl1	-Ti1	-C1	92.88(9)	C7	-N1	-C8	116.4(3)
Cl1	-Ti1	-C2	92.62(10)	Ti1	-C1	-C2	72.6(2)
Cl1	-Ti1	-C3	122.57(10)	Ti1	-C1	-C5	72.2(2)
Cl1	-Ti1	-C4	149.19(10)	C2	-C1	-C5	108.1(3)
Cl1	-Ti1	-C5	123.39(8)	Ti1	-C2	-C1	72.4(2)
Cl2	-Ti1	-N1	104.98(8)	Ti1	-C2	-C3	72.6(2)
Cl2	-Ti1	-C1	146.84(9)	C1	-C2	-C3	108.6(3)
Cl2	-Ti1	-C2	114.31(10)	Ti1	-C3	-C2	72.8(2)
Cl2	-Ti1	-C3	88.98(10)	Ti1	-C3	-C4	71.44(19)
Cl2	-Ti1	-C4	98.08(10)	C2	-C3	-C4	107.4(3)
Cl2	-Ti1	-C5	132.34(8)	Ti1	-C4	-C3	73.3(2)
N1	-Ti1	-C1	97.90(12)	Ti1	-C4	-C5	72.92(18)
N1	-Ti1	-C2	130.81(13)	C3	-C4	-C5	108.4(3)
N1	-Ti1	-C3	124.32(12)	Ti1	-C5	-C1	73.0(2)
N1	-Ti1	-C4	89.12(12)	Ti1	-C5	-C4	71.78(19)
N1	-Ti1	-C5	73.81(11)	Ti1	-C5	-C6	111.8(2)
C1	-Ti1	-C2	34.95(13)	C1	-C5	-C4	107.5(3)
C1	-Ti1	-C3	58.11(12)	C1	-C5	-C6	126.2(3)
C1	-Ti1	-C4	58.14(12)	C4	-C5	-C6	125.3(3)
C1	-Ti1	-C5	34.79(12)	C5	-C6	-C7	107.9(3)
C2	-Ti1	-C3	34.59(13)	N1	-C7	-C6	107.8(3)
C2	-Ti1	-C4	57.96(14)	N1	-C8	-C9	111.7(2)
C2	-Ti1	-C5	58.10(13)	N1	-C8	-C10	111.2(3)
C3	-Ti1	-C4	35.21(14)	C9	-C8	-C10	111.9(3)
C3	-Ti1	-C5	58.58(12)	Ti1	-C1	-H507	120(2)
C4	-Ti1	-C5	35.31(12)	C2	-C1	-H507	127(2)

Table S6 - Bond Angles
for: shelxl (Degrees) (continued)

C5	-C1	-H507	125 (2)	C6	-C7	-H511	113 (2)
Ti1	-C2	-H513	118 (2)	H502	-C7	-H511	109 (3)
C1	-C2	-H513	122 (3)	N1	-C8	-H501	109 (2)
C3	-C2	-H513	129 (3)	C9	-C8	-H501	106 (2)
Ti1	-C3	-H510	121 (2)	C10	-C8	-H501	107 (2)
C2	-C3	-H510	127 (2)	C8	-C9	-H505	112 (2)
C4	-C3	-H510	126 (2)	C8	-C9	-H506	114 (2)
Ti1	-C4	-H504	115 (2)	C8	-C9	-H509	112 (2)
C3	-C4	-H504	125 (2)	H505	-C9	-H506	104 (3)
C5	-C4	-H504	126 (2)	H505	-C9	-H509	109 (3)
C5	-C6	-H503	112 (2)	H506	-C9	-H509	105 (3)
C5	-C6	-H515	110 (2)	C8	-C10	-H508	111 (2)
C7	-C6	-H503	111 (2)	C8	-C10	-H512	109 (2)
C7	-C6	-H515	109 (3)	C8	-C10	-H514	112 (2)
H503	-C6	-H515	107 (4)	H508	-C10	-H512	108 (3)
N1	-C7	-H502	106 (2)	H508	-C10	-H514	109 (4)
N1	-C7	-H511	110 (2)	H512	-C10	-H514	107 (4)
C6	-C7	-H502	112 (2)				

Table S7 - Torsion Angles (Degrees)
for: shelxl

C11	-Ti1	-N1	-C7	133.1(3)
C11	-Ti1	-N1	-C8	-51.60(19)
C12	-Ti1	-N1	-C7	-118.1(3)
C12	-Ti1	-N1	-C8	57.21(19)
C1	-Ti1	-N1	-C7	37.7(3)
C1	-Ti1	-N1	-C8	-147.01(19)
C2	-Ti1	-N1	-C7	24.5(3)
C2	-Ti1	-N1	-C8	-160.2(2)
C3	-Ti1	-N1	-C7	-18.9(3)
C3	-Ti1	-N1	-C8	156.44(19)
C4	-Ti1	-N1	-C7	-20.0(3)
C4	-Ti1	-N1	-C8	155.3(2)
C5	-Ti1	-N1	-C7	12.3(3)
C5	-Ti1	-N1	-C8	-172.4(2)
C11	-Ti1	-C1	-C2	90.5(2)
C11	-Ti1	-C1	-C5	-153.28(18)
C12	-Ti1	-C1	-C2	-28.8(3)
C12	-Ti1	-C1	-C5	87.4(3)
N1	-Ti1	-C1	-C2	-162.4(2)
N1	-Ti1	-C1	-C5	-46.14(19)
C2	-Ti1	-C1	-C5	116.3(3)
C3	-Ti1	-C1	-C2	-36.7(2)
C3	-Ti1	-C1	-C5	79.6(2)
C4	-Ti1	-C1	-C2	-78.4(2)
C4	-Ti1	-C1	-C5	37.86(19)
C5	-Ti1	-C1	-C2	-116.3(3)
C11	-Ti1	-C2	-C1	-91.3(2)
C11	-Ti1	-C2	-C3	152.0(2)

Table S7 - Torsion Angles (Degrees) (continued)
for: shelxl

C12	-Ti1	-C2	-C1	163.17(18)
C12	-Ti1	-C2	-C3	46.4(2)
N1	-Ti1	-C2	-C1	23.3(3)
N1	-Ti1	-C2	-C3	-93.4(3)
C1	-Ti1	-C2	-C3	-116.7(3)
C3	-Ti1	-C2	-C1	116.7(3)
C4	-Ti1	-C2	-C1	79.0(2)
C4	-Ti1	-C2	-C3	-37.8(2)
C5	-Ti1	-C2	-C1	37.1(2)
C5	-Ti1	-C2	-C3	-79.7(2)
C11	-Ti1	-C3	-C2	-33.8(3)
C11	-Ti1	-C3	-C4	-149.57(19)
C12	-Ti1	-C3	-C2	-138.7(2)
C12	-Ti1	-C3	-C4	105.6(2)
N1	-Ti1	-C3	-C2	113.8(2)
N1	-Ti1	-C3	-C4	-1.9(3)
C1	-Ti1	-C3	-C2	37.1(2)
C1	-Ti1	-C3	-C4	-78.7(2)
C2	-Ti1	-C3	-C4	-115.7(3)
C4	-Ti1	-C3	-C2	115.7(3)
C5	-Ti1	-C3	-C2	78.2(2)
C5	-Ti1	-C3	-C4	-37.5(2)
C11	-Ti1	-C4	-C3	56.4(3)
C11	-Ti1	-C4	-C5	-59.4(3)
C12	-Ti1	-C4	-C3	-76.6(2)
C12	-Ti1	-C4	-C5	167.56(19)
N1	-Ti1	-C4	-C3	178.4(2)
N1	-Ti1	-C4	-C5	62.6(2)

Table S7 - Torsion Angles (Degrees) (continued)
for: shelxl

C1	-Ti1	-C4	-C3	78.6 (2)
C1	-Ti1	-C4	-C5	-37.3 (2)
C2	-Ti1	-C4	-C3	37.1 (2)
C2	-Ti1	-C4	-C5	-78.8 (2)
C3	-Ti1	-C4	-C5	-115.9 (3)
C5	-Ti1	-C4	-C3	115.9 (3)
C11	-Ti1	-C5	-C1	32.5 (2)
C11	-Ti1	-C5	-C4	148.11 (19)
C11	-Ti1	-C5	-C6	-90.4 (2)
C12	-Ti1	-C5	-C1	-132.34 (17)
C12	-Ti1	-C5	-C4	-16.8 (3)
C12	-Ti1	-C5	-C6	104.8 (2)
N1	-Ti1	-C5	-C1	132.0 (2)
N1	-Ti1	-C5	-C4	-112.5 (2)
N1	-Ti1	-C5	-C6	9.1 (2)
C1	-Ti1	-C5	-C4	115.6 (3)
C1	-Ti1	-C5	-C6	-122.9 (3)
C2	-Ti1	-C5	-C1	-37.2 (2)
C2	-Ti1	-C5	-C4	78.3 (2)
C2	-Ti1	-C5	-C6	-160.1 (3)
C3	-Ti1	-C5	-C1	-78.1 (2)
C3	-Ti1	-C5	-C4	37.4 (2)
C3	-Ti1	-C5	-C6	159.0 (3)
C4	-Ti1	-C5	-C1	-115.6 (3)
C4	-Ti1	-C5	-C6	121.5 (3)
Ti1	-N1	-C7	-C6	-30.0 (4)
C8	-N1	-C7	-C6	154.7 (3)
Ti1	-N1	-C8	-C9	-121.9 (2)