Macrocycle-Supported Titanium Complexes with Chelating Imido Ligands: Analogues of ansa-Metallocenes

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Reactions of 1,4-dimethyl-1,4,7-triazacyclononane (L^{1a}) and 1,4-diisopropyl-1,4,7-triazacyclononane (L^{1b}) to form 1-aminopropyl-4,7-di-R-1,4,7-triazacyclononane [R = Me (H_2L^{3a}) or Pr^i (H_2L^{3b})] and 1-(2-aminobenzyl)-4,7-di-R-1,4,7-triazacyclononane [R = Me (H_2L^{5a}) or Pr^i (H_2L^{5b})] are reported. Reaction of H_2L^{3a} and H_2L^{5a} with [Ti(NMe_2)$_2$$Cl_2$] gives the ansa-linked macrocycle−imido complexes [Ti(κ^4-L^{3a})Cl_2] (**5a**) and [Ti(κ^4-L^{5a})Cl_2] (**6a**), respectively, and $NHMe_2$. Reaction of H_2L^{3a} with [Ti(NBu^t)Cl_2(py)$_3$] gives [Ti(NBu^t)(κ^3-H_2L^{3a})Cl_2] (**7**), which possesses a pendant alkylamine group that does not undergo amine/*tert*-butylimido group exchange to give **5a** and Bu^tNH_2. However, reaction of H_2L^{3b} and H_2L^{5b} with [Ti(NBu^t)Cl_2(py)$_3$] does give amine/*tert*-butylimido group exchange to form [Ti(κ^4-L^{3b})Cl_2] (**5b**), [Ti(κ^4-L^{5b})Cl_2] (**8b**), and Bu^tNH_2. The compounds **5a**,**b** and **6a**,**b** are isolobal analogues of group 4 ansa-metallocene complexes and relatives of titanium cyclopentadienyl−amido constrained geometry olefin polymerization catalysts. Reaction of **5b** with AgOTf affords [Ti(κ^4-L^{3b})(OTf)Cl] (**8**) as the major product, the crystal structure of which has been determined. Alkylation of **6b** by RLi gives the dialkyl derivatives [Ti(κ^4-L^{5b})(R)$_2$] [R = Me (**9**) or CH_2SiMe_3 (**10**)]. The ethylene polymerization capability of the compounds **5a,b**, **6a,b**, and **10** in the presence of methylaluminoxane has been determined and compared to that of [Ti(NBu^t)(κ^3-$L^{1a,b}$)Cl_2] (**11a,b**); in all instances, low yields of high-molecular-weight polymer are obtained.

Introduction

ansa-metallocenes (**I**), their bridged bis(tetrahydroindenyl) analogues, and the constrained geometry cyclopentadienyl−amide systems such as those of type **II** are of immense importance in the development of well-defined homogeneous Ziegler−Natta catalysts.[1−5] More recently, and building upon Brintzinger's original observations,[6] it has been found that the reaction chemistry in general of ansa-metallocenes very often differs substantially from that of their nonbridged analogues.[7−15] This phenomenon has been referred to as the "ansa effect". In all of this chemistry, the key differences between compounds of types **I** and **II** and their nonbridged analogues can be traced to the configurational stability and geometric restrictions imposed by the ansa bridge.

As part of a program in early-transition-metal imido chemistry,[16−22] we recently reported compounds of type **III**[23] and their triazacyclohexane analogues.[24] Because both the *fac*-coordinating triazacyclononane and the dianionic imide ligands are valence isoelectronic and isolobal with the cyclopentadienide anion,[25−27] the compounds of type **III** are novel analogues of group 4 metallocenes, and we were therefore interested in

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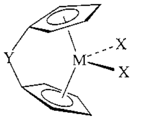
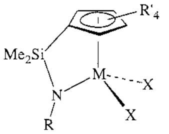
preparing ansa-linked, pendant arm derivatives. Such compounds will allow important comparisons to be made with both the bis(cyclopentadienyl) **I** and cyclopentadienyl−amide **II** systems, and also with the non-ansa-linked homologues **III**, and therefore contribute to the understanding and wider applicability of the ansa effect.[28]



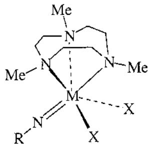
I

M = Group 4 metal;
Y = SiMe$_2$, CR$_2$, C$_2$H$_4$



II

M = Ti, Zr;
X = halide, alkyl



III

M = Ti, Zr;
X = halide, alkyl

Experimental Section

General Methods and Instrumentation. All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or drybox techniques. All protonic solvents and commercially available reagents were predried over activated molecular sieves, refluxed over an appropriate drying agent under an atmosphere of dinitrogen, and collected by distillation. NMR solvents for air- and/or moisture-sensitive compounds were dried over freshly ground calcium hydride at room temperature (CD$_2$Cl$_2$) or molten potassium (C$_6$D$_6$), distilled under reduced pressure, and stored under N$_2$ in J. Young ampules. NMR samples of air- and/or moisture-sensitive compounds were prepared in the drybox in 5 mm Wilmad tubes equipped with a Young Teflon valve.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 500 spectrometer and referenced internally to residual protiosolvent (^{1}H) or solvent (^{13}C) resonances. Chemical shifts are reported relative to tetramethylsilane ($\delta = 0$ ppm) in δ (ppm) and coupling constants in hertz. ^{19}F NMR spectra were recorded on a Varian Mercury Vx300 and referenced to external CF$_3$Cl. ^{1}H and ^{13}C NMR shift assignments were supported by DEPT-135 and DEPT-90, homo- and heteronuclear, one- and two-dimensional experiments as appropriate. Mass spectra were recorded on an AEI MS902 or Micomass Autospec 500 mass spectrometer. Elemental analyses were carried out by the analysis laboratory of this department. Polymer GPC analyses were performed under the supervision of Dr. S. Holding at RAPRA Technology Ltd.

Literature Preparations. 1,4-HR$_2$[9]aneN$_3$ [R = Me (L^{1a}) or Pr^i (L^{1b})],[29,30] [Ti(NBu^t)Cl$_2$(py)$_3$],[31] and [Ti(NMe$_2$)$_2$Cl$_2$][32] were prepared according to literature methods. All other reagents were purchased from Sigma−Aldrich or Strem and used as received.

1-Cyanoethyl-4,7-dimethyl-1,4,7-triazacyclononane (L^{2a}; 1a). 1,4-Dimethyl-1,4,7-triazacyclononane (L^{1a}; 0.60 g, 3.8 mmol) was transferred to a multineck flask equipped with a reflux condenser and dissolved in degassed acrylonitrile (25 cm^3). The mixture was brought to reflux with stirring for 16 h. The volatiles were removed in vacuo, leaving the cyanoethyl compound **1a**. Yield: 0.78 g (97%).

Data for **1a**. ^{1}H NMR (CDCl$_3$, 300.13 MHz, 298 K): δ 2.93 (t, 2H, $J = 7$ Hz, Me$_2$[9]aneN$_3$CH$_2$C*H*$_2$CN), 2.74−2.78 (m, 4H, NC(CH$_2$)$_2$N(C*H*$_2$CH$_2$N(Me)CH$_2$)$_2$), 2.73 (s, 4H, NC(CH$_2$)$_2$N(CH$_2$CH$_2$N(Me)C*H*$_2$)$_2$), 2.68−2.71 (m, 4H, NC(CH$_2$)$_2$N(CH$_2$C*H*$_2$N(Me)CH$_2$)$_2$), 2.47 (t, 2H, $J = 7$ Hz, Me$_2$[9]aneN$_3$C*H*$_2$CH$_2$CN), 2.39 (s, 6H, NC(CH$_2$)$_2$[9]aneN$_3$(*Me*)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.47 MHz, 298 K): δ 119.26 (Me$_2$[9]aneN$_3$(CH$_2$CH$_2$*C*N)), 57.16 (NC(CH$_2$)$_2$N(*C*H$_2$CH$_2$N(Me)CH$_2$)$_2$), 56.90 (NC(CH$_2$)$_2$N(CH$_2$CH$_2$N(Me)*C*H$_2$)$_2$), 55.75 (NC(CH$_2$)$_2$N(CH$_2$*C*H$_2$N(Me)CH$_2$)$_2$), 54.30 (Me$_2$[9]aneN$_3$(*C*H$_2$CH$_2$CN)), 46.70 ((NCCH$_2$CH$_2$)[9]aneN$_3$(*Me*)$_2$), 16.39 (Me$_2$[9]aneN$_3$(CH$_2$*C*H$_2$CN)). IR (thin film, KBr plates): 2927 (s), 2840 (s), 2795 (s), 2246 [m, ν(C≡N)], 1671 (ms), 1511 (ms), 1452 (s), 1366 (ms), 1318 (m), 1260 (m), 1232 (m), 1109 (s), 1036 (s), 989 (m), 871 (m), 803 (m), 735 (w), 582 (w), 523 (w) cm^{-1}. Accurate mass ES-MS for [L^{2a}•H]$^+$. Found (calcd for C$_{11}$H$_{23}$N$_4$): $m/z = 211.1943$ (211.1923).

1-Cyanoethyl-4,7-diisopropyl-1,4,7-triazacyclononane (L^{2b}; 1b). 1,4-Diisopropyl-1,4,7-triazacyclononane (L^{1b}; 4.3 g, 20 mmol) was transferred to a multineck flask equipped with a reflux condenser and dissolved in degassed acrylonitrile. The mixture was brought to reflux with stirring for 16 h. The volatiles were removed in vacuo, leaving the cyanoethyl compound **1b**. Yield: 5.25 g (98%).

Data for **1b**. ^{1}H NMR (CDCl$_3$, 500.0 MHz, 298 K): δ 2.90 (t, 2H, $J = 7$ Hz, Pr$^i_2$[9]aneN$_3$(C*H*$_2$CH$_2$CN)), 2.89 (sept (signal obscured by overlapping resonance), 2H, [9]aneN$_3$(C*H*Me$_2$)$_2$), 2.87 (m, 4H, NCCH$_2$CH$_2$(NC*H*$_2$CH$_2$N(CHMe$_2$)CH$_2$)$_2$), 2.67 (m, 4H, NCCH$_2$CH$_2$(NCH$_2$C*H*$_2$N(CHMe$_2$)CH$_2$)$_2$), 2.56 (s, 4H, NCCH$_2$CH$_2$(NCH$_2$CH$_2$N(CHMe$_2$)C*H*$_2$)$_2$), 2.47 (t, 2H, $J = 7$ Hz, Pr$^i_2$[9]aneN$_3$(CH$_2$C*H*$_2$CN)), 0.97 (d, 12H, $J = 6.5$ Hz, [9]aneN$_3$(CH*Me*$_2$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.7 MHz, 298 K): δ 119.36 (Pr$^i_2$[9]aneN$_3$(CH$_2$CH$_2$*C*N)), 55.47 (NCCH$_2$CH$_2$(N*C*H$_2$CH$_2$N(CHMe$_2$)CH$_2$)$_2$), 54.65 ([9]aneN$_3$(*C*HMe$_2$)$_2$), 53.58 (Pr$^i_2$[9]aneN$_3$(*C*H$_2$CH$_2$CN)), 52.76 (NCCH$_2$CH$_2$(NCH$_2$*C*H$_2$N(CHMe$_2$)CH$_2$)$_2$), 52.34 (NCCH$_2$CH$_2$(NCH$_2$CH$_2$N(CHMe$_2$)C*H*$_2$)$_2$), 18.34 ([9]aneN$_3$(CH*Me*$_2$)$_2$), 16.51 (Pr$^i_2$[9]aneN$_3$(CH$_2$*C*H$_2$CN)). IR (thin film, KBr plates): 2962 (s), 2922 (s), 2830 (s), 2247 [m, ν(C≡N)], 1670 (mw), 1510 (s), 1462 (s), 1359 (s), 1307 (ms), 1233 (s), 1170 (s), 1116 (s), 1039 (s), 1006 (m), 889 (w), 828 (m), 735 (m), 576 (w), 521 (w) cm^{-1}. Accurate mass electrospray-mass spectrum (ES-MS) for [L^{2b}•H]$^+$. Found (calcd for C$_{15}$H$_{31}$N$_4$): $m/z = 267.2537$ (267.2549).

1-Aminopropyl-4,7-dimethyl-1,4,7-triazacyclononane (H$_2$L^{3a}; 2a). 1-Cyanoethyl-4,7-dimethyl-1,4,7-triazacyclononane (L^{2a}; 0.61 g, 2.9 mmol) was dissolved in BH$_3$•THF (1.0 M, 30 cm^3) and brought to reflux for 24 h. The solution was then cooled below 0 °C for quenching with MeOH (50 cm^3) before the removal of all solvent under reduced pressure. The remaining white solid was dissolved in aqueous HCl (6.0 M, 100 cm^3) and refluxed for 4 h or until the solution lost its turbidity. The mixture was evaporated to dryness and redissolved in deionized water. The solution was basified to pH > 12 with concentrated aqueous NaOH (12 M) and then extracted with CHCl$_3$ (5 × 100 cm^3). The extracts were dried over anhydrous MgSO$_4$, filtered, and reduced to dryness under reduced pressure to leave the crude product as a pale yellow oil. The product was purified by distillation on a Kügelröhr apparatus (95 °C, 0.04 Torr) to give a colorless oil. Yield: 0.36 g (59%).

Data for **2a**. ^{1}H NMR (C$_6$D$_6$, 300.13 MHz, 298 K): δ 2.70 (s, 4H, (NH$_2$(CH$_2$)$_3$)N(CH$_2$CH$_2$N(Me)C*H*$_2$)$_2$), 2.65−2.67 (2 × m, 8H, (NH$_2$(CH$_2$)$_3$)N(C*H*$_2$CH$_2$N(Me)CH$_2$)$_2$ and (NH$_2$(CH$_2$)$_3$)N(CH$_2$C*H*$_2$N(Me)CH$_2$)$_2$), 2.60 (t, 2H, $J = 6.7$ Hz, Me$_2$[9]aneN$_3$(CH$_2$CH$_2$C*H*$_2$NH$_2$)), 2.43 (t, 2H, $J = 7$ Hz, Me$_2$[9]aneN$_3$(C*H*$_2$CH$_2$CH$_2$NH$_2$)), 2.29 (s, 6H, (NH$_2$CH$_2$CH$_2$CH$_2$)[9]aneN$_3$(*Me*$_3$)$_2$), 1.43 (app. quint, 2H, $J = 6.9$ Hz, Me$_2$[9]aneN$_3$(CH$_2$C*H*$_2$CH$_2$NH$_2$)), 0.74 (br s, 2H, Me$_2$[9]aneN$_3$(CH$_2$CH$_2$CH$_2$N*H*$_2$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.47 MHz, 298 K): δ 58.01 (NH$_2$(CH$_2$)$_3$N(CH$_2$CH$_2$N(Me)*C*H$_2$)$_2$), 57.67 (NH$_2$(CH$_2$)$_3$N(CH$_2$*C*H$_2$N(Me)CH$_2$)$_2$), 57.07 (Me$_2$[9]aneN$_3$(CH$_2$CH$_2$*C*H$_2$NH$_2$)), 56.43 (NH$_2$(CH$_2$)$_3$N(*C*H$_2$CH$_2$N(Me)CH$_2$)$_2$), 46.81 (NH$_2$CH$_2$CH$_2$CH$_2$[9]aneN$_3$*Me*$_2$), 40.93 (Me$_2$[9]aneN$_3$(*C*H$_2$CH$_2$CH$_2$NH$_2$)), 32.72 (Me$_2$[9]aneN$_3$(CH$_2$*C*H$_2$CH$_2$NH$_2$)). IR (thin film, KBr plates): 3385 [br ms, ν(N−H)], 3275 [br ms, ν(N−H)], 2932 (s), 2840 (s), 2790 (s), 1682 (ms), 1559 (w), 1542 (w), 1508 (w), 1456 (s), 1366 (s), 1316 (s), 1273 (ms), 1205 (w), 1109 (s), 1034 (s), 987 (ms), 870 (m), 801 (m), 669 (w), 581 (w) cm^{-1}. Accurate mass ES-MS for [H$_2$L^{3a}•H]$^+$. Found (calcd for C$_{11}$H$_{27}$N$_4$): $m/z = 215.3625$ (215.3623).

1-Aminopropyl-4,7-diisopropyl-1,4,7-triazacyclononane (H$_2$L^{3b}; 2b). 1-Cyanoethyl-4,7-diisopropyl-1,4,7-triazacyclononane (L^{2b}; 5.25 g, 19.7 mmol) was dissolved in borane•THF (1.0 M, 140 cm^3) and again brought to reflux for 24 h. The solution was then cooled below 0 °C for quenching with MeOH (150 cm^3) before the removal of all solvent under reduced pressure. The remaining white solid was dissolved in aqueous HCl (6.0 M, 200 cm^3) and refluxed for 4 h or

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(28) Although for ease of representation all titanium−imido linkages are drawn "Ti=NR", the formal Ti−N bond order in the imido complexes described herein is generally best thought of as 3 (pseudo-$\sigma^2\pi^4$ triple bond) rather than as 2.[18]

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until the solution lost its turbidity. The mixture was evaporated to dryness and redissolved in deionized water. The solution was basified to pH > 12 with concentrated aqueous NaOH (12 M) and then extracted with $CHCl_3$ (5 × 200 cm^3). The extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness under reduced pressure to leave the crude product as a pale yellow oil. The product was purified by distillation on a Kügelröhr apparatus (95 °C, 0.04 Torr) to give a colorless oil. Yield: 3.45 g (65%).

Data for **2b**. ^1H NMR (C_6D_6, 500.0 MHz, 298 K): δ 2.80 (m, 4H, $(H_2N(CH_2)_3)N(C\mathit{H}_2CH_2N(Pr^i)CH_2)_2$), 2.79 (sept, 2H, J = 6.5 Hz, $C\mathit{H}Me_2$), 2.66 (t, 2H, J = 8.0 Hz, $Pr^i_2[9]aneN_3(C\mathit{H}_2CH_2CH_2NH_2)$), 2.65 (m, 4H, $H_2N(CH_2)_3)N(CH_2C\mathit{H}_2N(Pr^i)CH_2)_2$), 2.52 (s, 4H, $H_2N(CH_2)_3N(CH_2CH_2N(Pr^i)C\mathit{H}_2)_2$), 2.51 (t, 2H, J = 6.5 Hz, $Pr^i_2[9]aneN_3(CH_2CH_2C\mathit{H}_2NH_2)$), 1.50 (app. quint, 2H, app. J = 6.5 Hz, $Pr^i_2[9]aneN_3(CH_2C\mathit{H}_2CH_2NH_2)$), 0.94 (d, 12H, J = 6.5 Hz, $CH\mathit{Me}_2$), 0.80 (br s, 2H, $N\mathit{H}_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): δ 56.7 ($Pr^i_2[9]aneN_3(\mathit{C}H_2CH_2CH_2NH_2)$), 56.5 ($H_2N(CH_2)_3N(\mathit{C}H_2CH_2N(Pr^i)CH_2)_2$), 54.9 ($\mathit{C}HMe_2$), 53.3 ($H_2N(CH_2)_3N(CH_2\mathit{C}H_2N(Pr^i)CH_2)_2$), 53.1 ($H_2N(CH_2)_3N(CH_2CH_2N(Pr^i)\mathit{C}H_2)_2$), 41.2 ($Pr^i_2[9]aneN_3(CH_2CH_2\mathit{C}H_2NH_2)$), 32.7 ($Pr^i_2[9]aneN_3(CH_2\mathit{C}H_2CH_2NH_2)$), 18.6 ($CH\mathit{Me}_2$). IR (thin film, KBr plates): 3425 [br ms, ν(N−H)], 3285 [br ms, ν(N−H)], 2961 (s), 2930 (s), 2870 (s), 1670 (m), 1509 (m), 1462 (s), 1381 (s), 1359 (s), 1306 (ms), 1260 (m), 1233 (m), 1169 (s), 1115 (s), 1038 (m), 992 (m), 874 (m), 851 (m), 717 (w), 669 (w), 577 (w), 520 (w) cm^{-1}. Accurate mass ES-MS for $[H_2L^{3b}{\bullet}H]^+$. Found (calcd for $C_{15}H_{35}N_4$): m/z = 271.2858 (271.2862).

1-(2-Nitrobenzyl)-4,7-dimethyl-1,4,7-triazacyclononane (L^{4a}; 3a). 1,4-Dimethyl-1,4,7-triazacyclononane (L^{1a}; 1.30 g, 8.3 mmol) was dissolved in dry, degassed toluene (30 cm^3) and stirred for the addition of 2-nitrobenzyl bromide (1.78 g, 8.2 mmol) followed by powdered KOH (0.50 g, 9 mmol). The mixture was heated to 60 °C for 5 h and then allowed to cool to room temperature. The mixture was filtered to remove potassium salts and reduced to dryness, giving the product as a spectroscopically pure yellow oil. Yield: 2.36 g (98%).

Data for **3a**. ^1H NMR ($CDCl_3$, 300.13 MHz, 298 K): δ 7.84 (d, J = 8.0 Hz, 1H, $3\text{-}C_6\mathit{H}_4\text{-}2\text{-}NO_2$), 7.58 (t, J = 8.0 Hz, 1H, $4\text{-}C_6\mathit{H}_4\text{-}2\text{-}NO_2$), 7.53 (d, J = 7.0 Hz, 1H, $6\text{-}C_6\mathit{H}_4\text{-}2\text{-}NO_2$), 7.40 (dt, J = 7.0, 2.0 Hz, 1H, $5\text{-}C_6\mathit{H}_4\text{-}2\text{-}NO_2$), 3.97 (s, 2H, $2\text{-}NO_2C_6H_4C\mathit{H}_2$), 2.75 (m, 4H, $NO_2C_6H_4CH_2N(C\mathit{H}_2CH_2N(Me)CH_2)_2$), 2.68 (s, 4H, $NO_2C_6H_4CH_2N(CH_2CH_2N(Me)C\mathit{H}_2)_2$), 2.64, (m, 4H, $NO_2C_6H_4CH_2N(CH_2C\mathit{H}_2N(Me)CH_2)_2$), 2.34 (s, 6H, $2\text{-}NO_2C_6H_4CH_2[9]aneN_3\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz, 298 K): δ 150.00 ($2\text{-}NO_2\mathit{C}_6H_4$), 135.23 ($1\text{-}\mathit{C}_6H_4$), 132.29 ($5\text{-}\mathit{C}_6H_4$), 131.43 ($4\text{-}\mathit{C}_6H_4$), 127.84 ($6\text{-}\mathit{C}_6H_4$), 124.51 ($3\text{-}\mathit{C}_6H_4$), 59.87 ($2\text{-}NO_2C_6H_4\mathit{C}H_2$), 56.81 ($NO_2C_6H_4CH_2N(CH_2\mathit{C}H_2N(Me)CH_2)_2$), 56.61 ($NO_2C_6H_4CH_2N(\mathit{C}H_2CH_2N(Me)CH_2)_2$), 56.17 ($NO_2C_6H_4CH_2N(CH_2CH_2N(Me)\mathit{C}H_2)_2$), 46.42 ($2\text{-}NO_2C_6H_4CH_2[9]aneN_3\mathit{Me}_2$). IR (thin film, KBr plates): 3066 (m), 2927 (s), 1669 (s), 1610 (ms), 1578 (ms), 1526 [s, $\nu(NO_2)$], 1455 (s), 1360 [s, $\nu(NO_2)$], 1261 (ms), 1205 (m), 1029 (s), 991 (m), 908 (w), 858 (ms), 787 (s), 732 (s), 668 (w), 580 (w), 526 (w) cm^{-1}. Accurate mass ES-MS for $[L^{4a}{\bullet}H]^+$. Found (calcd for $C_{15}H_{25}N_4O_2$): m/z = 293.1960 (293.1978).

1-(2-Nitrobenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane (L^{4b}; 3b). 1,4-Diisopropyl-1,4,7-triazacyclononane (L^{1b}; 2.51 g, 11.8 mmol) was dissolved in dry, degassed toluene (50 cm^3) and stirred for the addition of 2-nitrobenzyl bromide (2.54 g, 11.8 mmol) followed by powdered KOH (0.73 g, 13 mmol). The mixture was heated to 60 °C for 4 h and then stirred at room temperature for a further 16 h. The mixture was filtered to remove potassium salts and reduced to dryness, giving the product as an analytically pure yellow oil. Yield: 4.06 g (99%).

Data for **3b**. ^1H NMR ($CDCl_3$, 300.13 MHz, 298 K): δ 7.81 (2 × overlapping d, J = 8.0 Hz, 2 × 1H, $3\text{-}C_6\mathit{H}_4\text{-}2\text{-}NO_2$ and $6\text{-}C_6\mathit{H}_4\text{-}2\text{-}NO_2$), 7.54 (t, J = 7.5 Hz, 1H, $4\text{-}C_6\mathit{H}_4\text{-}2\text{-}NO_2$), 7.35 (t, J = 7.5 Hz, 1H, $5\text{-}C_6H_4\text{-}2\text{-}NO_2$), 3.96 (s, 2H, $2\text{-}NO_2C_6H_4C\mathit{H}_2$), 2.86 (m, 4H, $2\text{-}NO_2C_6H_4CH_2N(C\mathit{H}_2CH_2N(Pr^i)CH_2)_2$), 2.85 (sept, J = 6.5 Hz, 2H, $C\mathit{H}Me_2$), 2.60 (m, 4H, $2\text{-}NO_2C_6H_4CH_2N(CH_2C\mathit{H}_2N(Pr^i)CH_2)_2$), 2.52 (s, 4H, $2\text{-}NO_2C_6H_4CH_2N(CH_2CH_2N(Pr^i)C\mathit{H}_2)_2$), 0.95 (d, J = 6.5 Hz, 12H, $CH\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz, 298 K): δ 145.16 ($2\text{-}C_6H_4\text{-}2\text{-}NO_2$), 136.50 ($1\text{-}\mathit{C}_6H_4\text{-}2\text{-}NO_2$), 132.20 ($5\text{-}\mathit{C}_6H_4$), 131.24 ($4\text{-}\mathit{C}_6H_4$), 127.31 ($6\text{-}\mathit{C}_6H_4$), 124.16 ($3\text{-}\mathit{C}_6H_4$), 58.67 ($2\text{-}NO_2C_6H_4\mathit{C}H_2$), 55.44 ($2\text{-}NO_2C_6H_4CH_2N(\mathit{C}H_2CH_2N(Pr^i)CH_2)_2$), 54.75 ($\mathit{C}HMe_2$), 52.77 ($2\text{-}NO_2C_6H_4CH_2N(CH_2\mathit{C}H_2N(Pr^i)CH_2)_2$), 52.59 ($2\text{-}NH_2C_6H_4CH_2N(CH_2CH_2N(Pr^i)\mathit{C}H_2)_2$), 18.38 ($CH\mathit{Me}_2$). IR (thin film, KBr plates): 2962 (s), 2922 (s), 2870 (s), 1609 (ms), 1577 (ms), 1559 (ms), 1525 [s, $\nu(NO_2)$], 1458 (s), 1361 [s, $\nu(NO_2)$], 1261 (ms), 1159 (s), 1116 (s), 1032 (s), 858 (m), 790 (m), 730 (s), 713 (m), 696 (m), 679 (w), 669 (w), 643 (w), 575 (w), 549 (m), 518 (w) cm^{-1}. Accurate mass ES-MS for $[L^{4b}{\bullet}H]^+$. Found (calcd for $C_{19}H_{33}N_4O_2$): m/z = 349.2603 (349.2604).

1-(2-Aminobenzyl)-4,7-dimethyl-1,4,7-triazacyclononane (H_2L^{5a}; 4a). 1-(2-Nitrobenzyl)-4,7-dimethyl-1,4,7-triazacyclononane (L^{4a}; 2.86 g, 9.8 mmol) was dissolved in absolute EtOH (40 cm^3) and transferred to an argon-purged flask containing graphite KS-10 (1.80 g) and equipped with a reflux condenser. Hydrazine monohydrate (10 g, 0.2 mol) was added, and the mixture was heated under an argon atmosphere to 90 °C for 24 h. The mixture was cooled, and the graphite was removed by filtration. The solution was evaporated to dryness and the resultant oil redissolved in $CHCl_3$ (30 cm^3), and $MgSO_4$ was added. The dried solution was filtered and reduced in vacuo to give the product as a spectroscopically pure yellow oil. Yield: 1.32 g (47%).

Data for **4a**. ^1H NMR ($CDCl_3$, 500.0 MHz, 298 K): δ 7.07 (t, 1H, J = 8 Hz, $4\text{-}C_6\mathit{H}_4$), 6.97 (d, 1H, J = 7.5 Hz, $6\text{-}C_6\mathit{H}_4$), 6.64 (t, 1H, J = 7.5 Hz, $5\text{-}C_6\mathit{H}_4$), 6.63 (d, 1H, J = 8 Hz, $3\text{-}C_6\mathit{H}_4$), 4.87 (br s, 2H, $N\mathit{H}_2$), 3.58 (s, 2H, $NH_2C_6H_4C\mathit{H}_2[9]aneN_3Me_2$), 2.70 (m, 4H, $NH_2C_6H_4\text{-}CH_2N(C\mathit{H}_2CH_2N(Me)CH_2)_2$), 2.59 (m, 4H, $NH_2C_6H_4\text{-}CH_2N(CH_2C\mathit{H}_2N(Me)CH_2)_2$), 2.58 (s, 4H, $NH_2C_6H_4CH_2N(CH_2CH_2N(Me)C\mathit{H}_2)_2$), 2.30 (s, 6H, $NH_2C_6H_4CH_2[9]aneN_3\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz, 298 K): δ 148.06 ($2\text{-}\mathit{C}_6H_4$), 131.06 ($3\text{-}\mathit{C}_6H_4$), 128.80 ($5\text{-}\mathit{C}_6H_4$), 124.60 ($1\text{-}\mathit{C}_6H_4$), 117.86 ($4\text{-}\mathit{C}_6H_4$), 115.90 ($6\text{-}\mathit{C}_6H_4$), 61.90 ($NH_2C_6H_4\mathit{C}H_2[9]aneN_3Me_2$), 57.60 ($NH_2C_6H_4CH_2N\mathit{C}H_2CH_2N$), 57.54 ($NH_2C_6H_4CH_2NCH_2\mathit{C}H_2N$), 54.69 ($MeN\mathit{C}H_2\mathit{C}H_2NMe$), 46.15 ($NH_2C_6H_4CH_2[9]aneN_3\mathit{Me}_2$). IR (thin film, KBr plates): 3318 [br ms, ν(N−H)], 3200 [br ms, ν(N−H)], 2932 (s), 2840 (s), 2795 (s), 1662 (s), 1615 (s), 1495 (s), 1456 (s), 1367 (s), 1321 (s), 1218 (m), 1157 (m), 1125 (m), 1103 (m), 1027 (ms), 989 (m), 930 (w), 908 (w), 885 (w), 871 (w), 752 (s), 665 (w), 650 (w), 540 (w) cm^{-1}. Accurate mass ES-MS for $[L^{5a}{\bullet}H]^+$. Found (calcd for $C_{15}H_{27}N_4$): m/z = 263.4056 (263.4063).

1-(2-Aminobenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane (H_2L^{5b}; 4b). 1-(2-Nitrobenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane (L^{4b}; 3.20 g, 9.2 mmol) was dissolved in absolute EtOH (60 cm^3) and transferred to a flask containing argon-purged graphite KS-10 (2.4 g). The solution was stirred for the addition of degassed hydrazine monohydrate (20 g, 0.4 mol). The mixture was refluxed under argon at 90 °C for 6 h. The mixture was filtered and the residue washed with $CHCl_3$ (3 × 5 cm^3). The combined organic extracts were reduced to dryness, redissolved in CH_2Cl_2 (50 cm^3), and dried over anhydrous $MgSO_4$ and then over CaH_2. After filtration and removal of solvent, the product was obtained as an analytically pure pale-green oil. Yield: 2.33 g (80%).

Data for **4b**. ^1H NMR ($CDCl_3$, 500.0 MHz, 298 K): δ 7.13 (t, 1H, J = 7.5 Hz, $5\text{-}C_6\mathit{H}_4$), 7.06 (d, 1H, J = 7.5 Hz, $3\text{-}C_6\mathit{H}_4$), 6.75 (t, 1H, J = 6.5 Hz, $4\text{-}C_6\mathit{H}_4$), 6.50 (d, 1H, J = 7.5 Hz, $6\text{-}C_6\mathit{H}_4$), 4.94 (br s, 2H, $N\mathit{H}_2$), 3.64 (s, 2H, $NH_2C_6H_4C\mathit{H}_2$), 2.72 (m, 4H, $2\text{-}NH_2C_6H_4CH_2)N(C\mathit{H}_2CH_2N(Pr^i)CH_2)_2$), 2.70 (sept, 2H, J = 6.5 Hz, $C\mathit{H}Me_2$), 2.49 (m, 4H, $2\text{-}NH_2C_6H_4CH_2N(CH_2C\mathit{H}_2N(Pr^i)CH_2)_2$), 2.34 (s, 4H, $2\text{-}NH_2C_6H_4CH_2N(CH_2CH_2N(Pr^i)C\mathit{H}_2)_2$), 0.86 (d, 12H, J = 6.5 Hz, $CH\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz, 298 K): δ 148.3 ($2\text{-}\mathit{C}_6H_4$), 130.4 ($3\text{-}\mathit{C}_6H_4$), 128.5 ($5\text{-}\mathit{C}_6H_4$), 124.4 ($1\text{-}\mathit{C}_6H_4$), 117.2 ($4\text{-}\mathit{C}_6H_4$), 115.5 ($6\text{-}\mathit{C}_6H_4$), 62.2 ($NH_2C_6H_4\mathit{C}H_2$), 55.5 ($2\text{-}NH_2C_6H_4CH_2N(\mathit{C}H_2CH_2N(Pr^i)CH_2)_2$), 54.7 ($\mathit{C}HMe_2$), 54.1 ($2\text{-}NH_2C_6H_4CH_2N(CH_2\mathit{C}H_2N(Pr^i)CH_2)_2$), 53.7 ($2\text{-}NH_2C_6H_4CH_2N(CH_2CH_2N(Pr^i)\mathit{C}H_2)_2$), 18.5 ($CH\mathit{Me}_2$). IR (thin film, KBr plates): 3300 [br ms, ν(N−H)], 3198 [br ms, ν(N−H)], 2963 (s), 2927 (s), 2870 (s), 1662 (s), 1615 (s), 1516 (ms), 1494 (s), 1462 (s), 1382 (s), 1362 (s), 1324 (s), 1306 (ms), 1261 (s), 1217 (m), 1159 (s), 1116 (s), 1092 (s), 1021 (s), 931 (w), 800 (s), 756 (s), 714 (m), 697 (m), 665 (w), 644 (w), 549 (mw) cm^{-1}. Accurate mass ES-MS for $[L^{5b}{\bullet}H]^+$. Found (calcd for $C_{19}H_{35}N_4$): m/z = 319.2862 (319.2860).

$[Ti(\kappa^4\text{-}L^{3a})Cl_2]$ (5a). $[Ti(NMe_2)_2Cl_2]$ (0.22 g, 1.05 mmol) was dissolved in dry CH_2Cl_2 (30 cm^3) and stirred for the addition of a solution of H_2L^{3a} (**2a**; 0.226 g, 1.05 mmol) in CH_2Cl_2 (10 cm^3). The solution quickly darkened in color. After the solution was stirred for 2 h at room temperature, it was concentrated in vacuo (to ca. 5−10 cm^3) and hexane (12 cm^3) was added, resulting in precipitation of the product.

The product was filtered and dried in vacuo to give an orange/brown solid. Yield: 0.25 g (72%).

Data for **5a**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500.0 MHz, 298 K): δ 3.96 (ddd, 1H, *J* = 17.0, 11.5, 5.5 Hz, 1 × $\mathrm{Ti{=}NC}\mathit{H}_2$), 3.69 (app. dt, 1H, *J* = 13.0, 5.5 Hz, 1 × $\mathrm{Ti{=}NCH_2CH_2C}\mathit{H}_2$), 3.55−3.62 (2 × m, 2H, 2 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.26−3.36 (2 × m, 2H, 2 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.13 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.10 (s, 3H, $\mathrm{N}\mathit{Me}$), 2.98−3.07 (3 × m, 3H, 3 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.78 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.66−2.71 (2 × m, 2H, 1 × $\mathrm{Ti{=}NC}\mathit{H}_2$, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.62 (m, 1H, 1 × $\mathrm{Ti{=}NCH_2CH_2C}\mathit{H}_2$), 2.52 (s, 3H, $\mathrm{N}\mathit{Me}$), 2.49 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.30 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.15 (m, 1H, 1 × $\mathrm{Ti{=}NCH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.02 (m, 1H, 1 × $\mathrm{Ti{=}NCH_2C}\mathit{H}_2\mathrm{CH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 125.7 MHz, 298 K): δ 62.95 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 62.06 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 61.31 ($\mathrm{Ti{=}N}\mathit{C}\mathrm{H_2}$), 60.13 ($\mathrm{Ti{=}NCH_2CH_2}\mathit{C}\mathrm{H_2}$), 57.24 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 53.67 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 52.83 ($\mathrm{N}\mathit{Me}$), 52.30 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 51.99 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 49.48 ($\mathrm{N}\mathit{Me}$), 28.38 ($\mathrm{Ti{=}NCH_2}\mathit{C}\mathrm{H_2CH_2}$). IR (Nujol mull, KBr plates): 1497 (w), 1350 (w), 1306 (w), 1291 (w), 1261 (m), 1231 (mw), 1204 (w), 1178 (s), 1101 (ms), 1065 (s), 1041 (ms), 1011 (s), 897 (w), 787 (ms), 659 (w), 555 (w), 474 (w), 441 (w) cm^{-1}. EI-MS *m/z* (%): 330 (100) [M]$^+$, 294 (80) [M − H − Cl]$^+$, 274 (39) [M − $\mathrm{CH_2CH_2CH_2N}$]$^+$, 259 (18) [M − $\mathrm{CH_2CH_2CH_2N}$ − $\mathrm{CH_3}$]$^+$. Anal. Found (calcd for $\mathrm{C_{11}H_{24}Cl_2N_4Ti{\cdot}0.3CH_2Cl_2}$): C, 37.9 (38.1); H, 7.3 (7.0); N, 15.6 (15.7).

[Ti(κ^4-L^{3b})Cl$_2$] (5b). [Ti(NBu^t)Cl$_2$(py)$_3$] (1.10 g, 2.5 mmol) was slurried in benzene (75 cm^3) and stirred for the addition of H$_2$L^{3b} (**2b**; 0.68 g, 2.5 mmol). The mixture was heated to 65 °C for 4 h, during which time an oily red solid was deposited. The supernatant was decanted, and the solid was dried to give **5b** as an orange powder, which could be recrystallized from $\mathrm{CH_2Cl_2}$ at −25 °C. Yield: 0.74 g (74%).

Data for **5b**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500.0 MHz, 298 K): δ 3.98 (ddd, 1H, *J* = 17.0, 11.5, 6.0 Hz, 1 × $\mathrm{Ti{=}NC}\mathit{H}_2$), 3.82 (app. sept, 1H, app. *J* = 6.5 Hz, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.61 (m, 1H, 1 × $\mathrm{Ti{=}NCH_2CH_2C}\mathit{H}_2$), 3.58 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.48 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.37 (app. sept, 1H, app. *J* = 6.5 Hz, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.06−3.19 (3 × m, 3H, 3 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.91 (dt, 1H, *J* = 12.0, 3.0 Hz, 1 × $\mathrm{Ti{=}NCH_2CH_2C}\mathit{H}_2$), 2.71−2.87 (4 × m, 4H, 4 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.56−2.64 (3 × m, 3H, 2 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$, 1 × $\mathrm{Ti{=}NC}\mathit{H}_2$), 2.24 (ddd, 1H, *J* = 13.0, 4.0, 2.5 Hz, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.06 (m, 1H, 1 × $\mathrm{Ti{=}NCH_2C}\mathit{H}_2$), 1.96 (m, 1H, 1 × $\mathrm{Ti{=}NCH_2C}\mathit{H}_2$), 1.81 (d, 3H, *J* = 6.5 Hz, 1 × $\mathrm{CH}\mathit{Me}_2$), 1.30 (d, 3H, *J* = 6.5 Hz, 1 × $\mathrm{CH}\mathit{Me}_2$), 1.20 (d, 3H, *J* = 6.5 Hz, 1 × $\mathrm{CH}\mathit{Me}_2$), 1.04 (d, 3H, *J* = 6.5 Hz, 1 × $\mathrm{CH}\mathit{Me}_2$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 125.7 MHz, 298 K): δ 62.7 ($\mathrm{Ti{=}NCH_2CH_2}\mathit{C}\mathrm{H_2}$), 61.6 ($\mathrm{Ti{=}N}\mathit{C}\mathrm{H_2CH_2CH_2}$), 61.4 ($\mathit{C}\mathrm{HMe_2}$), 60.6 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 57.7 ($\mathit{C}\mathrm{HMe_2}$), 52.0 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 51.1 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 49.6 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 48.0 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 45.8 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 28.0 ($\mathrm{Ti{=}NCH_2}\mathit{C}\mathrm{H_2CH_2}$), 21.9 ($\mathrm{CH}\mathit{Me}_2$), 21.6 ($\mathrm{CH}\mathit{Me}_2$), 16.5 ($\mathrm{CH}\mathit{Me}_2$), 16.4 ($\mathrm{CH}\mathit{Me}_2$). IR (Nujol mull, KBr plates): 1499 (w), 1292 (w), 1262 (w), 1234 (m), 1206 (w), 1195 (s), 1163 (m), 1118 (s), 1087 (s), 1041 (s), 963 (m), 937 (w), 801 (w), 772 (w), 653 (w), 604 (w), 565 (w) cm^{-1}. EI-MS *m/z* (%): 386 (46) [M]$^+$, 350 (42) [M − H − Cl]$^+$, 343 (100) [M − Pr^i]$^+$, 307 (62) [M − H − Cl − Pr^i]$^+$, 265 (16) [M − 2Pr^i]$^+$. Anal. Found (calcd for $\mathrm{C_{15}H_{32}Cl_2N_4Ti}$): C, 47.1 (46.5); H, 8.5 (8.3); N, 14.1 (14.5).

NMR Tube Scale Synthesis of [Ti(κ^4-L^{3b})Cl$_2$] (5b) from [Ti(NMe$_2$)$_2$Cl$_2$] and H$_2$L^{3b}. [Ti(NMe$_2$)$_2$Cl$_2$] (10 mg, 0.048 mmol) and H$_2$L^{3b} (**2b**; 13 mg, 0.048 mmol) were dissolved in $\mathrm{CD_2Cl_2}$ (0.4 cm^3) and transferred to a 5 mm J. Young NMR tube. The ^{1}H NMR spectrum showed the immediate formation of **5b** with evolution of Me$_2$NH.

[Ti(κ^4-L^{5a})Cl$_2$] (6a). [Ti(NMe$_2$)$_2$Cl$_2$] (0.24 g, 1.1 mmol) was dissolved in dry $\mathrm{CH_2Cl_2}$ (30 cm^3) and stirred for the addition of a solution of H$_2$L^{5a} (**4a**; 0.30 g, 1.1 mmol) in $\mathrm{CH_2Cl_2}$ (10 cm^3). The solution quickly darkened and was concentrated in vacuo (to ca. 5−10 cm^3). After 2 h, hexane (12 cm^3) was added, resulting in the precipitation of the product. The product was filtered and dried in vacuo to give a brown solid. Yield: 0.25 g (58%).

Data for **6a**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500.0 MHz, 298 K): δ 7.22 (d, 1H, *J* = 7.0 Hz, 6-$\mathrm{C_6}\mathit{H}_4$), 7.11 (m, 1H, 4-$\mathrm{C_6}\mathit{H}_4$), 6.80 (dt, 1H, *J* = 7.5, 1.0 Hz, 5-$\mathrm{C_6}\mathit{H}_4$), 5.93 (dd, 1H, *J* = 7.5, 1.0 Hz, 3-$\mathrm{C_6}\mathit{H}_4$), 4.86 (d, 1H, *J* = 13.0 Hz, 1 × $\mathrm{C}\mathit{H}_2\mathrm{C_6H_4}$), 3.87 (app. dt, 1H, *J* = 13.0, 5.5 Hz, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.73 (d, 1H, *J* = 13.0 Hz, 1 × $\mathrm{C}\mathit{H}_2\mathrm{C_6H_4}$), 3.49 (app. dt, 1H, *J* = 13.0, 5.5 Hz, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.08−3.22 (overlapping 3 × m, 3H, 3 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.01 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.00 (s, 3H, $\mathrm{N}\mathit{Me}$), 2.92 (app. dt, 1H, *J* = 13.0, 6.5 Hz, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.71−2.81 (overlapping 2 × m, 2H, 2 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.72 (s, 3H, $\mathrm{N}\mathit{Me}$), 2.67 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.46 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.43 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 125.7 MHz, 298 K): δ 156.40 (2-$\mathrm{N}\mathit{C}_6\mathrm{H_4}$), 136.38 (1-$\mathit{C}_6\mathrm{H_4}$), 129.26 (6-$\mathit{C}_6\mathrm{H_4}$), 129.18 (4-$\mathit{C}_6\mathrm{H_4}$), 121.52 (5-$\mathit{C}_6\mathrm{H_4}$), 110.28 (3-$\mathit{C}_6\mathrm{H_4}$), 66.64 ($\mathit{C}\mathrm{H_2C_6H_4}$), 61.33 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 59.12 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 56.79 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 54.04 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 52.03 ($\mathrm{N}\mathit{Me}$), 51.76 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 51.51 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 49.29 ($\mathrm{N}\mathit{Me}$). IR (Nujol mull, KBr plates): 1584 (w), 1341 (w), 1322 (m), 1301 (s), 1280 (m), 1261 (w), 1156 (w), 1090 (w), 1065 (m), 1026 (w), 1002 (w), 983 (w), 954 (w), 800 (m), 763 (ms), 687 (w), 541 (w) cm^{-1}. EI-MS *m/z* (%): 378 (100) [M]$^+$, 342 (94) [M − H − Cl]$^+$, 327 (12) [M − Me − H − Cl]$^+$. Anal. Found (calcd for $\mathrm{C_{15}H_{24}Cl_2N_4Ti{\cdot}0.4CH_2Cl_2}$): C, 44.5 (44.8); H, 6.5 (6.1); N, 14.1 (13.6).

[Ti(κ^4-L^{5b})Cl$_2$] (6b). [Ti(NBu^t)Cl$_2$(py)$_3$] (0.80 g, 1.9 mmol) was slurried in benzene (30 cm^3) and stirred for the dropwise addition of H$_2$L^{5b} (**4b**; 0.60 g, 1.9 mmol) in benzene (20 cm^3). The reaction occurred rapidly, giving a dark-orange solution and a dark-ocher precipitate. After the solution was stirred for 5 h, the solid was filtered and dried in vacuo to give **6b** as a benzene solvate. Yield: 0.53 g (64%).

Data for **6b**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500.0 MHz, 298 K): δ 7.18 (d, 1H, *J* = 7.5 Hz, 6-$\mathrm{C_6}\mathit{H}_4$), 7.09 (t, 1H, *J* = 7.5 Hz, 4-$\mathrm{C_6}\mathit{H}_4$), 6.80 (t, 1H, *J* = 7.5 Hz, 5-$\mathrm{C_6}\mathit{H}_4$), 5.90 (d, 1H, *J* = 7.5 Hz, 3-$\mathrm{C_6}\mathit{H}_4$), 4.96 (d, 1H, *J* = 13.5 Hz, 1 × $\mathrm{C}\mathit{H}_2\mathrm{C_6H_4}$), 3.94 (app. sept, 1H, *J* = 6.5 Hz, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.71 (d, 1H, *J* = 13.5, 1 × $\mathrm{C}\mathit{H}_2\mathrm{C_6H_4}$), 3.68 (app. sept, 1H, *J* = 6.5 Hz, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.52 (m, 1H, 1 × $\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 3.15−3.27 (overlapping 3 × m, 3H, 3 × $\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 2.99−3.09 (overlapping 2 × m, 2H, 2 × $\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 2.75−2.93 (overlapping 4 × m, 4H, 4 × $\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 2.45−2.52 (overlapping 2 × m, 2H, 2 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 1.70 (d, 3H, *J* = 6.5 Hz, $\mathrm{CH}\mathit{Me}_2$), 1.44 (d, 3H, *J* = 6.5 Hz, $\mathrm{CH}\mathit{Me}_2$), 1.12 (d, 3H, *J* = 6.5 Hz, $\mathrm{CH}\mathit{Me}_2$), 1.11 (d, 3H, *J* = 6.5 Hz, $\mathrm{CH}\mathit{Me}_2$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 125.7 MHz, 298 K): δ 137.1 (2-$\mathrm{N}\mathit{C}_6\mathrm{H_4}$), 129.0 (4-$\mathit{C}_6\mathrm{H_4}$), 128.9 (6-$\mathit{C}_6\mathrm{H_4}$), 121.9 (5-$\mathit{C}_6\mathrm{H_4}$), 110.6 (3-$\mathit{C}_6\mathrm{H_4}$), 67.9 ($\mathit{C}\mathrm{H_2C_6H_4}$), 62.1 ($\mathit{C}\mathrm{HMe_2}$), 59.3 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 57.7 ($\mathit{C}\mathrm{HMe_2}$), 53.8 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 53.6 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 50.0 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 47.8 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 45.4 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 21.58 ($\mathrm{CH}\mathit{Me}_2$), 21.56 ($\mathrm{CH}\mathit{Me}_2$), 16.71 ($\mathrm{CH}\mathit{Me}_2$), 16.27 ($\mathrm{CH}\mathit{Me}_2$) (note: unobserved, 1-$\mathit{C}_6\mathrm{H_4}$). IR (Nujol mull, KBr plates): 1490 (w), 1405 (w), 1325 (m), 1306 (s), 1265 (m), 1155 (w), 1118 (m), 1080 (m), 1066 (m), 1040 (w), 1017 (m), 962 (m), 940 (w), 801 (m), 768 (ms), 680 (ms), 602 (w), 560 (w) cm^{-1}. EI-MS *m/z* (%): 34 (82) [M]$^+$, 399 (100) [M − Cl]$^+$, 391 (43) [M − Pr^i]$^+$, 355 (43) [M − H − Cl − Pr^i]$^+$. Anal. Found (calcd for $\mathrm{C_{19}H_{32}Cl_2N_4Ti{\cdot}0.75CH_2Cl_2}$): C, 56.9 (57.2); H, 7.9 (7.5); N, 11.2 (11.3).

NMR Tube Scale Synthesis of [Ti(κ^4-L^{5b})Cl$_2$] (6b) from [Ti(NMe$_2$)$_2$Cl$_2$] and H$_2$L^{5b}. [Ti(NMe$_2$)$_2$Cl$_2$] (10 mg, 0.048 mmol) and H$_2$L^{5b} (**4b**; 15 mg, 0.048 mmol) were dissolved in $\mathrm{CD_2Cl_2}$ (0.4 cm^3) and transferred to a 5 mm J. Young NMR tube. The ^{1}H NMR spectrum showed the immediate formation of **6b** with evolution of Me$_2$NH.

[Ti(NBu^t)(κ^3-H$_2$L^{3a})Cl$_2$] (7). [Ti(NBu^t)Cl$_2$(py)$_3$] (0.09 g, 0.2 mmol) was dissolved in dry $\mathrm{CH_2Cl_2}$ (20 cm^3) and stirred for the addition of H$_2$L^{3a} (**2a**; 0.044 g, 0.2 mmol) via a syringe. The solution was stirred for 2 h at room temperature and then concentrated in vacuo to ca. $^1/_4$ of its volume. Hexane (5 cm^3) was added to give an orange precipitate, which was filtered and dried in vacuo. Yield: 0.05 g (61%).

Data for **7**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500.0 MHz, 298 K): δ 5.59 (br t, 1H, 1 × $\mathrm{N}\mathit{H}_2$), 4.15 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.80 (m, 1H, 1 × $\mathrm{NH_2C}\mathit{H}_2\mathrm{CH_2CH_2N}$), 3.76 (overlapping 2 × m, 2H, 1 × $\mathrm{NH_2CH_2CH_2C}\mathit{H}_2\mathrm{N}$ and 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.60 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.35−3.50 (overlapping 4 × m, 4H, 1 × $\mathrm{N}\mathit{H}_2$, 1 × $\mathrm{NH_2C}\mathit{H}_2\mathrm{CH_2CH_2N}$ and 2 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.26 (s, 3H, $\mathrm{N}\mathit{Me}$), 3.15−3.25 (overlapping 2 × m, 2H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$ and 1 × $\mathrm{NH_2CH_2CH_2C}\mathit{H}_2\mathrm{N}$), 3.06 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.98 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.87 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.56 (s, 3H, $\mathrm{N}\mathit{Me}$), 2.50−2.58 (overlapping 2 × m, 2H, 2 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.36 (m, 1H, 1 × $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 2.28 (m, 1H, 1 × $\mathrm{TiNH_2CH_2C}\mathit{H}_2\mathrm{CH_2N}$), 1.96 (m, 1H, 1 × $\mathrm{TiNH_2CH_2C}\mathit{H}_2\mathrm{CH_2N}$), 1.09 (s, 9H, $\mathrm{C}\mathit{Me}_3$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 125.7 MHz, 298 K): δ 70.17 ($\mathrm{N}\mathit{C}\mathrm{Me_3}$), 65.22 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 59.20 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 58.83 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 55.19 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 54.36 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 54.05 ($\mathrm{NH_2CH_2CH_2}\mathit{C}\mathrm{H_2N}$), 53.84 ($\mathrm{N}\mathit{Me}$), 52.36 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 49.36 ($\mathrm{N}\mathit{Me}$), 45.48 ($\mathrm{NH_2}\mathit{C}\mathrm{H_2CH_2CH_2N}$), 31.86 ($\mathrm{NC}\mathit{Me}_3$), 26.33 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2NH_2}$). IR (Nujol mull, KBr plates): 3176 [w, ν(N−H)], 1587 (w), 1352 (m), 1297 (w), 1261 (w), 1238 (s), 1208 (w), 1150 (w), 1064 (s), 1031 (m), 1008 (s), 921 (w), 890 (w), 801 (m), 785 (m), 741 (w), 596 (w), 542 (w), 446 (w) cm^{-1}. EI-MS *m/z* (%): 388 (65) $[M - Me]^+$, 330 (100) $[M - Bu^tNH_2]^+$, 294 (77) $[M - Bu^tNH_2 - H - Cl]^+$. Anal. Found (calcd for $C_{15}H_{35}Cl_2N_5Ti$): C, 44.5 (44.6); H, 7.8 (8.7); N, 14.9 (17.3).

[Ti(κ^4-L^{3b})(OTf)Cl] (8). [Ti(κ^4-L^{3b})Cl$_2$] (**5b**; 0.12 g, 0.3 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and stirred at room temperature for the addition of a suspension of AgOTf (0.080 g, 0.3 mmol) in CH_2Cl_2 (5 cm^3). The mixture was stirred for 16 h with the exclusion of light before filtration. The filtrate was evaporated to dryness under reduced pressure to leave the crude product. Yield: 0.096 g (62%). Recrystallization from CH_2Cl_2 layered with hexane yielded a mixture of red and yellow crystals, from which yellow crystals of **8** suitable for single-crystal X-ray analysis could be selected.

Data for **8**. ^{1}H NMR (CD_2Cl_2, 500.0 MHz, 298 K): δ 3.79−3.85 (overlapping 2 × m, 2H, 1 × Ti═NC*H*$_2$ and 1 × C*H*Me$_2$), 3.55−3.65 (overlapping 2 × m, 2H, 1 × NC*H*$_2$CH$_2$N and 1 × Ti═NCH$_2$CH$_2$C*H*$_2$), 3.28−3.35 (overlapping 2 × m, 2H, 2 × NC*H*$_2$CH$_2$N), 3.09−3.17 (overlapping 3 × m, 3H, 3 × NC*H*$_2$CH$_2$N), 3.05 (app. dt, 1H, *J* = 12.0, 3.0 Hz, 1 × Ti═NCH$_2$CH$_2$C*H*$_2$), 3.01 (app. sept, 1H, *J* = 6.5 Hz, C*H*Me$_2$), 2.60−2.90 (overlapping 6 × m, 6H, 5 × NC*H*$_2$CH$_2$N and 1 × Ti═NC*H*$_2$), 2.21 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 2.12 (m, 1H, 1 × Ti═NCH$_2$C*H*$_2$CH$_2$), 2.07 (m, 1H, 1 × Ti═NCH$_2$C*H*$_2$CH$_2$), 1.82 (d, 3H, *J* = 6.5 Hz, CH*Me*$_2$), 1.23 (d, 3H, *J* = 6.5 Hz, CH*Me*$_2$), 1.16 (d, 3H, *J* = 6.5 Hz, CH*Me*$_2$), 1.04 (d, 3H, *J* = 6.5 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, 298 K): δ 62.5 (*C*HMe$_2$), 61.8 (Ti═NCH$_2$CH$_2$*C*H$_2$), 60.7 (Ti═N*C*H$_2$), 60.3 (1 × N*C*H$_2$CH$_2$N), 57.5 (*C*HMe$_2$), 51.6 (1 × N*C*H$_2$CH$_2$N), 50.9 (1 × N*C*H$_2$CH$_2$N), 50.5 (1 × N*C*H$_2$CH$_2$N), 46.7 (1 × N*C*H$_2$CH$_2$N), 46.6 (1 × N*C*H$_2$CH$_2$N), 27.6 (Ti═NCH$_2$*C*H$_2$CH$_2$), 21.7 (CH*Me*$_2$), 20.7 (CH*Me*$_2$), 17.1 (CH*Me*$_2$), 16.6 (CH*Me*$_2$). ^{19}F{^{1}H} NMR (CD_2Cl_2, 282.2 MHz, 298 K): δ −78.54 (OSO$_2$C*F*$_3$). IR (Nujol mull, KBr plates): 1500 (w), 1333 (w), 1260 (s), 1240 (m), 1200 (m), 1150 (m), 1090 (w), 1060 (w), 1030 (s), 955 (w), 805 (w), 772 (w), 640 (m), 575 (w), 520 (w) cm^{-1}. Anal. Found (calcd for $C_{16}H_{32}ClF_3N_4O_3STi$): C, 37.5 (38.4); H, 8.2 (6.4); N, 10.3 (11.2).

[Ti(κ^4-L^{5b})Me$_2$] (9). [Ti(κ^4-L^{5b})Cl$_2$] (**6b**; 0.44 g, 1.0 mmol) was slurried in benzene (30 cm^3) and stirred for the addition of MeLi (1.4 cm^3, 1.6 M solution in Et$_2$O, 2.2 mmol). The reaction was stirred with the exclusion of light for 12 h. The mixture was filtered and the filtrate concentrated in vacuo to ca. $^1/_3$ of its volume. Hexane (8 cm^3) was added, resulting in precipitation of a brown solid product which was filtered and dried in vacuo. Yield: 0.21 g (53%).

Data for **9**. ^{1}H NMR (CD_2Cl_2, 500.0 MHz, 298 K): δ 7.08 (t, 1H, *J* = 7.5 Hz, 4-C$_6$*H*$_4$), 7.04 (d, 1H, *J* = 7.0 Hz, 6-C$_6$*H*$_4$), 6.54 (dt, 1H, *J* = 7.5, 1.5 Hz, 5-C$_6$*H*$_4$), 6.02 (d, 1H, *J* = 6.5 Hz, 3-C$_6$*H*$_4$), 4.42 (d, 1H, *J* = 13.0 Hz, C*H*$_a$H$_b$C$_6$H$_4$), 3.73 (app. sept, 1H, *J* = 6.5 Hz, C*H*Me$_2$), 3.37 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 3.33 (d, 1H, *J* = 13.0 Hz, CH$_a$*H*$_b$C$_6$H$_4$), 3.04−3.16 (3 × m, 3H, 3 × NC*H*$_2$CH$_2$N), 2.83−2.95 (3 × m, 3H, 3 × NC*H*$_2$CH$_2$N), 2.69−2.75 (2 × m, 2H, 2 × NC*H*$_2$CH$_2$N), 2.58 (app. sept, 1H, *J* = 6.5 Hz, C*H*Me$_2$), 2.47 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 2.22−2.32 (2 × m, 2H, 2 × NC*H*$_2$CH$_2$N), 1.54 (d, 3H, *J* = 6.5 Hz, CH*Me*$_2$), 1.43 (d, 3H, *J* = 6.5 Hz, CH*Me*$_2$), 1.19 (d, 3H, *J* = 6.5 Hz, CH*Me*$_2$), 0.92 (d, 3H, *J* = 6.5 Hz, CH*Me*$_2$), 0.08 (s, 3H, *J* = 6.5 Hz, Ti*Me*), −0.03 (s, 3H, *J* = 6.5 Hz, Ti*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, 298 K): δ 157.70 (2-N*C*$_6$H$_4$), 135.79 (1-*C*$_6$H$_4$), 129.02 (4-*C*$_6$H$_4$), 128.53 (6-*C*$_6$H$_4$), 116.64 (5-*C*$_6$H$_4$), 110.18 (3-*C*$_6$H$_4$), 66.66 (*C*H$_2$C$_6$H$_4$), 57.82 (*C*HMe$_2$), 57.60 (*C*HMe$_2$), 56.56 (N*C*H$_2$CH$_2$N), 53.70 (N*C*H$_2$CH$_2$N), 53.26 (N*C*H$_2$CH$_2$N), 51.78 (N*C*H$_2$CH$_2$N), 45.60 (N*C*H$_2$CH$_2$N), 45.45 (N*C*H$_2$CH$_2$N), 34.52 (Ti*C*H$_3$), 33.86 (Ti*C*H$_3$), 21.66 (CH*Me*$_2$), 21.06 (CH*Me*$_2$), 15.58 (CH*Me*$_2$), 14.99 (CH*Me*$_2$). Anal. Found (calcd for $C_{21}H_{38}N_4Ti$): C, 62.6 (63.9); H, 9.8 (9.7); N, 14.1 (14.2).

[Ti(κ^4-L^{5b})(CH$_2$SiMe$_3$)$_2$] (10). [Ti(κ^4-L^{5b})Cl$_2$] (**6b**; 0.20 g, 0.45 mmol) was slurried in benzene (20 cm^3) and stirred for the addition of LiCH$_2$SiMe$_3$ (0.9 g, 1 mmol) as a solution in benzene (10 cm^3). The mixture was stirred for 12 h, filtered, and dried in vacuo to give the crude product as an orange/yellow powder, which could not be recrystallized without significant decomposition. Yield: 0.11 g (45%).

Data for **10**. ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K): δ 7.21 (t, 1H, *J* = 7.0 Hz, 4-C$_6$*H*$_4$), 7.04 (d, 1H, *J* = 7.0 Hz, 6-C$_6$*H*$_4$), 6.72 (t, 1H, *J* = 7.5 Hz, 5-C$_6$*H*$_4$), 6.54 (d, 1H, *J* = 8.0 Hz, 3-C$_6$*H*$_4$), 4.55 (d, 1H, *J* = 12.5 Hz, C*H*$_a$H$_b$C$_6$H$_4$), 3.48 (app. sept, 1H, *J* = 6.0 Hz, C*H*Me$_2$), 3.23 (app. sept, 1H, *J* = 6.0 Hz, C*H*Me$_2$), 2.95 (d, 1H, *J* = 12.5 Hz, CH$_a$*H*$_b$C$_6$H$_4$), 2.55 (ddd, 1H, *J* = 13.5, 10.5, 6.0 Hz, 1 × NC*H*$_2$CH$_2$N), 2.29−2.46 (3 × m, 3H, 3 × NC*H*$_2$CH$_2$N), 2.15 (dt, 1H, *J* = 15.0, 10.5 Hz, 1 × NC*H*$_2$CH$_2$N), 2.00−2.06 (2 × m, 2H, 2 × NC*H*$_2$CH$_2$N), 1.84−1.89 (2 × m, 2H, 2 × NC*H*$_2$CH$_2$N), 1.76 (dt, 1H, *J* = 13.0, 5.0 Hz, 1 × NC*H*$_2$CH$_2$N), 1.70 (dt, 1H, *J* = 13.0, 4.0 Hz, 1 × NC*H*$_2$CH$_2$N), 1.62 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 1.40 (d, 3H, *J* = 6.0 Hz, CH*Me*$_2$), 1.24 (d, 3H, *J* = 6.0 Hz, CH*Me*$_2$), 0.73 (s, 9H, Si*Me*$_3$), 0.63 (d, 3H, *J* = 6.0 Hz, CH*Me*$_2$), 0.48 (d, 3H, CH*Me*$_2$), 0.39 (s, 9H, Si*Me*$_3$), 0.14 (d, 1H, *J* = 11.0 Hz, Ti(C*H*$_c$H$_d$SiMe$_3$)), −0.03 (d, 1H, *J* = 10.5 Hz, Ti(C*H*$_e$H$_f$SiMe$_3$)), −0.21 (d, 1H, *J* = 11.0 Hz, Ti(CH$_c$*H*$_d$SiMe$_3$); one Ti(CH$_e$*H*$_f$SiMe$_3$) was not observed due to overlapping signals). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): δ 158.23 (2-N*C*$_6$H$_4$), 136.20 (1-*C*$_6$H$_4$), 129.68 (4-*C*$_6$H$_4$), 128.28 (6-*C*$_6$H$_4$), 117.54 (5-*C*$_6$H$_4$), 111.33 (3-*C*$_6$H$_4$), 67.36 (*C*H$_2$C$_6$H$_4$), 60.92 (Ti*C*H$_2$SiMe$_3$), 57.17 (*C*HMe$_2$), 56.69 (*C*HMe$_2$), 55.70 (N*C*H$_2$CH$_2$N), 54.70 (N*C*H$_2$CH$_2$N), 54.19 (N*C*H$_2$CH$_2$N), 52.01 (N*C*H$_2$CH$_2$N), 48.37 (Ti*C*H$_2$SiMe$_3$), 44.21 (N*C*H$_2$CH$_2$N), 43.71 (N*C*H$_2$CH$_2$N), 21.85 (CH*Me*$_2$), 21.81 (CH*Me*$_2$), 15.04 (CH*Me*$_2$), 14.21 (CH*Me*$_2$), 4.60 (SiMe$_3$), 3.51 (SiMe$_3$). Anal. Found (calcd for $C_{27}H_{54}N_4Si_2Ti$): C, 59.7 (60.1); H, 9.9 (10.1); N, 11.0 (10.4).

[Ti(NBu^t)(κ^3-L^{1a})Cl$_2$] (11a). [Ti(NBu^t)Cl$_2$(py)$_3$] (0.37 g, 0.86 mmol) was slurried in dry benzene (25 cm^3) and stirred for the addition of 1,4-dimethyl-1,4,7-triazacyclononane (L^{1a}; 0.136 g, 0.86 mmol). The solution quickly turned yellow, and a precipitate began to form. After the solution was stirred for 6 h, the product was filtered off and dried in vacuo. Yield: 0.22 g (73%).

Data for **11a**. The compound **11a** exists as a mixture of cis (major) and trans isomers (cis and trans refer to the position of the macrocycle N−H group with respect to NBu^t) in a ca. 4:1 ratio (by ^{1}H NMR integration). ^{1}H NMR for cis (major) isomer (CD_2Cl_2, 500.0 MHz, 298 K): δ 4.70 (br s, 1H, N*H)*, 4.01 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 3.61 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 3.42 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 3.20 (s, 3H, N*Me*), 3.13 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 3.03 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 2.92−2.97 (2 × m, 2H, 2 × NC*H*$_2$CH$_2$N), 2.85 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 2.75 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 2.67 (m, 1H, 1 × NC*H*$_2$CH$_2$N), 2.45−2.56 (overlapping 2 × m, 2H, 2 × NC*H*$_2$CH$_2$N), 2.43 (s, 3H, N*Me*), 1.09 (s, 9H, C*Me*$_3$). ^{1}H NMR for trans (minor) isomer (CD_2Cl_2, 500.0 MHz, 298 K): δ 3.25 (s, 6H, N*Me*), 1.92 (br s, 1H, N*H*), 1.10 (s, 9H, Bu^t), all macrocyclic CH$_2$ groups obscured by major isomer. ^{13}C{^{1}H} NMR for cis (major) isomer only (CD_2Cl_2, 125.7 MHz, 298 K): δ 57.58 (N*C*H$_2$CH$_2$N), 56.96 (N*C*H$_2$CH$_2$N), 54.69 (N*C*H$_2$CH$_2$N), 54.52 (N*C*H$_2$CH$_2$N), 53.26 (N*Me*), 48.06 (N*C*H$_2$CH$_2$N), 47.97 (N*C*H$_2$CH$_2$N), 47.34 (N*Me*), 31.15 (NC*Me*$_3$), the N*C*Me$_3$ resonance was not observed. IR (Nujol mull, KBr plates): 3249 [mw, ν(N−H)], 1494 (w), 1351 (w), 1300 (w), 1287 (w), 1247 (s), 1208 (w), 1153 (w), 1122 (w), 1095 (m), 1067 (w), 1049 (w), 1032 (ms), 1009 (m), 994 (w), 901 (w), 877 (w), 856 (w), 823 (m), 804 (w), 759 (w), 602 (w), 580 (w), 528 (w), 425 (w) cm^{-1}. EI-MS *m/z* (%): 331 (100) $[M - Me]^+$, 295 (6) $[M - Me - H - Cl]^+$, 274 (67) $[M - NCMe_3 - H]^+$, 239 (7) $[M - NCMe_3 - 2H - Cl]^+$, 204 (17). Anal. Found (calcd for $C_{12}H_{28}Cl_2N_4Ti$): C, 42.0 (41.5); H, 7.9 (8.1); N, 15.8 (16.1).

General Procedure for Ethylene Polymerization Studies. A Fisher−Porter bottle with a pressure gauge and a seal was taken into an inert atmosphere glovebox and charged with a catalyst (10 μmol) and a magnetic stir bar. The vessel was sealed and attached to a Schlenk line with a combined N$_2$ and C$_2$H$_4$ gas manifold. Dry toluene (50 cm^3) was added followed by methylaluminoxane (MAO; 10 cm^3 of a 10% w/w solution in toluene, 15 mmol) in further toluene (50 cm^3). Ethylene was then added to 7 bar pressure and the reaction vigorously stirred for 1 h. The reaction was then quenched with acidified MeOH (300 cm^3, 10% v/v HCl, 1 M) and the polymer filtered at the pump, washed with water and MeOH, and oven-dried (60 °C) to constant weight.

Crystal Structure Determination of [Ti(κ^4-L^{1b})(OTf)Cl] (8). Crystal data collection and processing parameters are given in Table 1. A crystal of **8** was immersed in a film of perfluoropolyether oil on a glass fiber and transferred to an Enraf-Nonius DIP2000 image plate diffractometer equipped with an Oxford Cryosystems low-temperature device.[33] Data were collected at −103 °C using Mo Kα radiation;

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Table 1. X-ray Data Collection and Processing Parameters for $[Ti(\kappa^4\text{-}L^{3b})(OTf)Cl]$ (**8**)

empirical formula	$C_{16}H_{32}ClF_3N_4O_3SiTi$
fw	500.86
temp/°C	−103(1)
wavelength/Å	0.710 69
space group	$P2_1/n$
a/Å	9.2840(6)
b/Å	19.097(2)
c/Å	12.7810(7)
β/deg	99.091(4)
V/Å^3	2237.6
Z	4
d(calcd)/(mg m^{-3})	1.49
abs coeff/mm^{-1}	0.64
R indices $[I > 3\sigma(I)]^{a,b}$	$R = 0.0526$ $R_w = 0.0359$

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

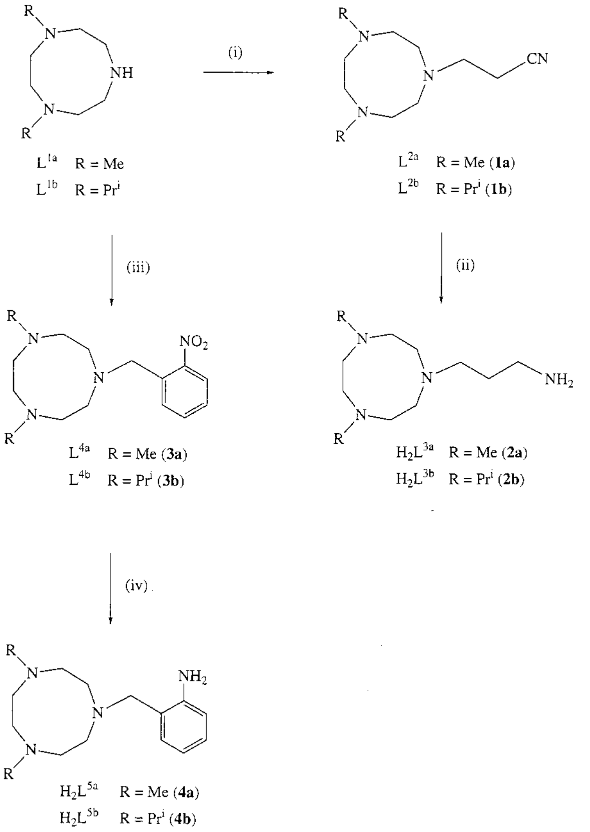
equivalent reflections were merged, and the images were processed with the DENZO and SCALEPACK programs.[34] Corrections for Lorentz polarization effects and absorption were performed, and the structures were solved by direct methods using SIR92.[35] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were placed geometrically and their positions allowed to vary using a riding model. Examination of the refined extinction parameters and agreement analyses suggested that no extinction correction was required. All crystallographic calculations were performed using SIR92 and CRYSTALS-PC.[36]

Results and Discussion

We found previously that the reaction of $[Ti(NBu^t)Cl_2(py)_3]$[31] with $R_3[9]aneN_3$ ($R_3[9]aneN_3$ = 1,4,7-tri-R-1,4,7-triazacyclononane; R = H or Me) affords the corresponding macrocyclic derivatives $[Ti(NBu^t)(R_3[9]aneN_3)Cl_2]$ of type **III**.[23] This general approach therefore appeared suitable for the synthesis of ansa-linked analogues by using appropriately functionalized triazacyclononane ligands that would allow for the simultaneous incorporation of the new macrocyclic and imido functionalities into the titanium coordination sphere. Analogous protocols are generally used for the synthesis of cyclopentadienyl ansa compounds **I** and **II**.[1] Scheme 1 shows the syntheses of the new ligands $H_2L^{3a,b}$ (**2a,b**) and $H_2L^{5a,b}$ (**4a,b**), which were prepared using methodologies based on those previously described for functionalized triazacyclononanes.[37−39]

The compounds 1,4-dimethyl-1,4,7-triazacyclononane (L^{1a}) and 1,4-diisopropyl-1,4,7-triazacyclononane (L^{1b}) were prepared according to literature methods.[29,30] Refluxing of $L^{1a,b}$ in neat acrylonitrile gives the cyano compounds **1a,b** via a Michael addition in >95% yield. Subsequent reduction with $BH_3 \cdot THF$ forms the 1-aminopropyl-4,7-di-R-1,4,7-triazacyclononane compounds **2a** (R = Me) and **2b** (R = Pr^i) in 59−65% yield after Kügelröhr distillation. The aniline-based analogues of **2a,b**, namely, 1-(2-aminobenzyl)-4,7-di-R-1,4,7-triazacyclononane **4a** (R = Me) and **4b** (R = Pr^i), were prepared via the nitrobenzyl intermediates **3a,b**, which were obtained in >98% yield. Reduction of **3a,b** with an excess of hydrazine monohydrate in the presence of graphite KS-10 catalyst in hot EtOH afforded **4a,b** in 47−80% yield. The compounds **2a,b** and **4a,b** are all pale-colored or colorless oils and were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR, IR spectroscopy, and accurate mass spectrometry. They are precursors to ansa-linked macrocycle−imido complexes as shown in Scheme 2.

Scheme 1[a]



[a] Reagents and conditions: (i) CH_2CHCN, reflux, 16 h, >95%; (ii) $BH_3 \cdot THF$, reflux, 24 h, 59% (**2a**) or 65%; (iii) 2-nitrobenzyl bromide, KOH, toluene, 60 °C, 4−5 h, >98%; (iv) hydrazine monohydrate, graphite KS-10, EtOH, 90 °C, 6−24 h, 47% (**4a**) or 80%.

Protonolysis reactions between amines and metal alkyls, amides, or imides are well-established general routes to transition-metal imido complexes.[16,40−42] Thus, reaction of H_2L^{3a} (**2a**) and H_2L^{5a} (**4a**) with $[Ti(NMe_2)_2Cl_2]$ in CH_2Cl_2 gave good yields of the ring *N*-methyl-substituted imido complexes $[Ti(\kappa^4\text{-}L^{3a})Cl_2]$ (**5a**) and $[Ti(\kappa^4\text{-}L^{5a})Cl_2]$ (**6a**), respectively, and $HNMe_2$ as summarized in Scheme 2. NMR tube scale reactions showed that the ring *N*-isopropyl-substituted analogues $[Ti(\kappa^4\text{-}L^{3b})Cl_2]$ (**5b**) and $[Ti(\kappa^4\text{-}L^{5b})Cl_2]$ (**6b**) could be prepared from the reaction of H_2L^{3b} (**2b**) and H_2L^{5b} (**4b**), respectively, with $[Ti(NMe_2)_2Cl_2]$. However, these compounds are more conveniently prepared by amine/*tert*-butylimide exchange reactions between H_2L^{3b} or H_2L^{5b} and $[Ti(NBu^t)Cl_2(py)_3]$ in benzene. We have shown previously that $[Ti(NBu^t)Cl_2(py)_3]$ readily undergoes such exchange reactions.[31] Interestingly, attempts to prepare $[Ti(\kappa^4\text{-}L^{3a})Cl_2]$ (**5a**) via an analogous amine/imide exchange route gave only $[Ti(NBu^t)(\kappa^3\text{-}H_2L^{3a})Cl_2]$ (**7**), which possesses a pendant alkylamine group. The compound **7** does not eliminate Bu^tNH_2 even on prolonged heating in C_6D_6. There was no NMR

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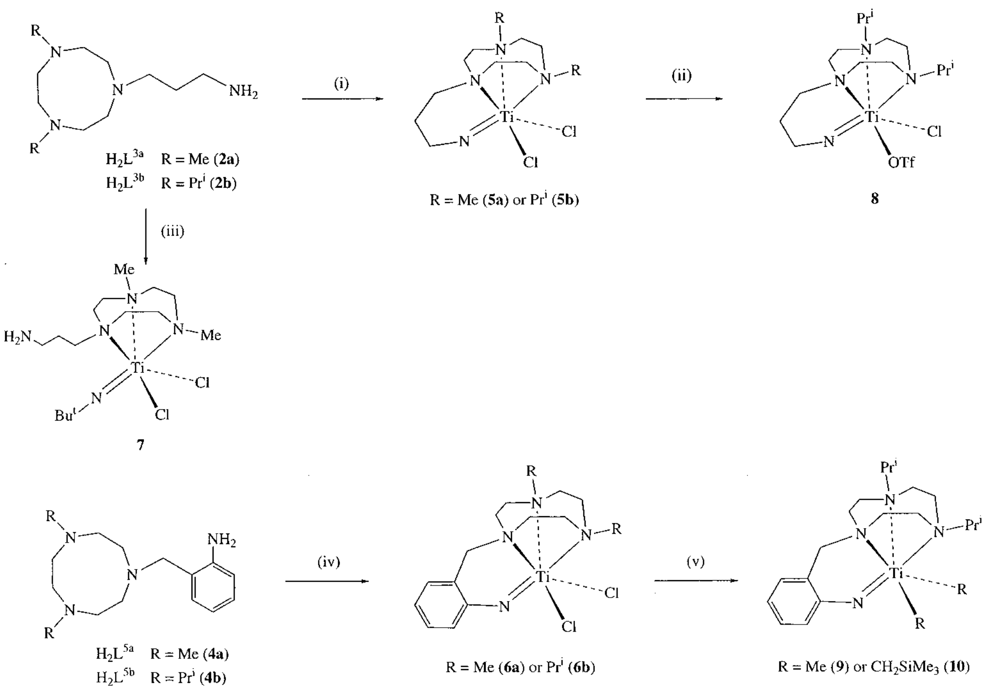
Scheme 2[a]



[a] Reagents and conditions: (i) (for **5a**) $[Ti(NMe_2)_2Cl_2]$, CH_2Cl_2, 2 h, rt, 72%; (for **5b**) $[Ti(NBu^t)Cl_2(py)_3]$, benzene, 65 °C, 4 h, 74%; (ii) AgOTf, CH_2Cl_2, rt, 16 h, 62% (crude); (iii) $[Ti(NBu^t)Cl_2(py)_3]$, CH_2Cl_2, 2 h, rt, 61%; (iv) (for **6a**) $[Ti(NMe_2)_2Cl_2]$, CH_2Cl_2, rt, 2 h, 58%; (for **6b**) $[Ti(NBu^t)Cl_2(py)_3]$, benzene, rt, 5 h, 64%; (v) (for **9**) MeLi/Et_2O, benzene, rt (dark), 12 h, 53%; (for **10**) $LiCH_2SiMe_3$, benzene, rt, 12 h, 45%.

spectroscopic evidence for the other possible isomer of **7**, that is, with the propylamino-substituted nitrogen trans to the imido group. Indeed, it is possible that the isomer shown in Scheme 2 is favored by formation of an intramolecular N(amine)−H···N(imide) hydrogen bond, because the ^1H NMR spectrum of **7** confirms that the two H atoms of the amino NH_2 group are inequivalent. The compounds **5**−**7** were fully characterized by NMR, IR spectroscopy, EI-MS, and elemental analysis. The data given in the Experimental Section fully support the structures proposed in Scheme 2. For example, the ^1H NMR spectrum of $[Ti(\kappa^4\text{-}L^{5b})Cl_2]$ (**6b**) shows four doublets for the diastereotopic isopropyl groups of the macrocycle, as well as individual signals for the hydrogens of the diastereotopic methylene of the benzyl ansa link, as required by C_1 symmetry.

Unfortunately, repeated attempts to obtain diffraction-quality crystals of any of the ansa-linked dichloride complexes **5a,b** or **6a,b** were unsuccessful. We therefore prepared the mono(triflate) derivative $[Ti(\kappa^4\text{-}L^{3b})(OTf)Cl]$ (**8**) (Scheme 2) in order to establish unambiguously the mononuclear, ansa-linked geometry. In the bulk, **8** cannot be completely freed from impurities tentatively assigned as the bis(triflate) analogue $[Ti(\kappa^4\text{-}L^{3b})(OTf)_2]$, as previously found for other titanium mono(triflate) complexes.[43] Nonetheless, careful selection yielded a diffraction-quality crystal of **8**. The molecular structure is shown in Figure 1. Table 1 summarizes data collection and processing parameters, and Table 2 lists selected bond lengths and angles.

$[Ti(\kappa^4\text{-}L^{3b})(OTf)Cl]$ (**8**) is mononuclear in the solid state and contains six-coordinate Ti(IV) facially coordinated to a triazacyclic ring, which is itself linked via a 1,3-propanediyl C_3 linker to the imido group also bound to titanium. The coordination sphere at Ti(IV) is completed by mutually cis chloride and triflate ligands. The $Ti{=}N_{imide}$ bond length of 1.699(3) Å is typical of a “normal” imidotitanium linkage (i.e., a pseudo-$\sigma^2\pi^4$ triple bond),[18] and indeed the Ti−Cl, $Ti{=}N_{imide}$, and $Ti{-}N_{macrocycle}$ distances are not significantly different from those of the non-ansa-linked complex $[Ti(NBu^t)(Me_3[9]aneN_3)Cl_2]$.[23]

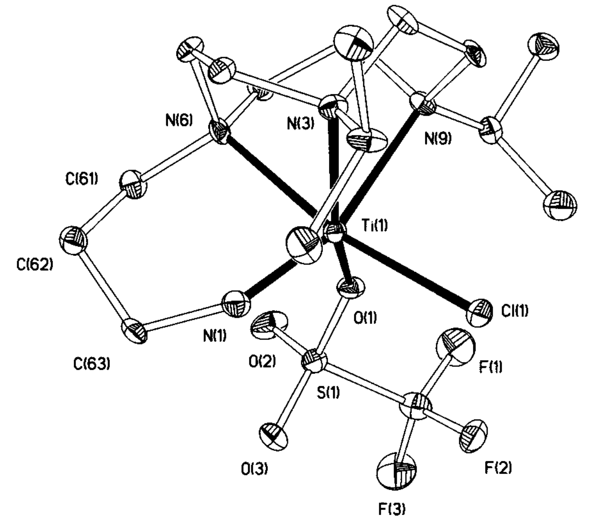


Figure 1. Displacement ellipsoid (25% probability) plot for $[Ti(L^{3b})Cl(OTf)]$ (**8**) with H atoms omitted.

In contrast, the propanediyl ansa link has a substantial constraining effect on the *angular* metric parameters of **8**. The 150.5(2)° angle subtended at the imido nitrogen, N(63), is at the low end of the range of values for which an imide may still be considered a four-electron donor[16] and is considerably less than that for $[Ti(NBu^t)(R_3[9]aneN_3)Cl_2]$ [Ti=N−Bu^t = 164.3(2)° (R = H) or 171.0(2)° (R = Me)].[23] Nevertheless, despite the flexibility of the $C{-}N_{imide}{=}Ti$ unit, the ansa link in **8** clearly “ties back” the $[9]aneN_3$ ring and imido groups, leading to a more “open” reaction center as evidenced by (i) a substantial *decrease* in the angle between the N_{imide}−Ti bond vector and the normal to the macrocycle nitrogens [N(3)−N(6)−N(9)]

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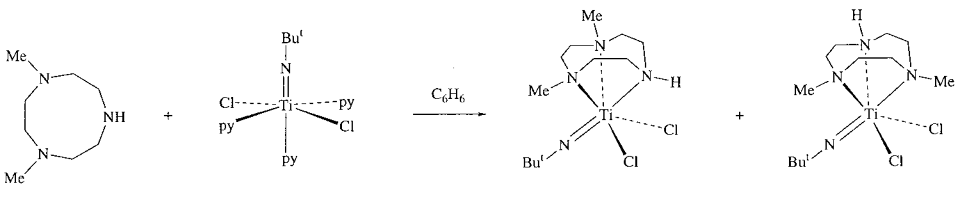
Scheme 3



trans-**11a**
(Minor product)

cis-**11a**
(Major product)

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ti(κ^4-L^{3b})(OTf)Cl] (**8**)

Ti(1)−N(1)	1.699(3)	Ti(1)−N(9)	2.449(3)
Ti(1)−N(3)	2.278(2)	Ti(1)−O(1)	2.070(2)
Ti(1)−N(6)	2.259(3)	Ti(1)−Cl(1)	2.3817(9)
N(1)−C(63)	1.430(4)		
N(1)−Ti(1)−N(3)	100.1(1)	N(6)−Ti(1)−O(1)	90.50(9)
N(1)−Ti(1)−N(6)	84.1(1)	N(9)−Ti(1)−O(1)	79.85(8)
N(3)−Ti(1)−N(6)	79.11(9)	N(1)−Ti(1)−Cl(1)	104.26(9)
N(1)−Ti(1)−N(9)	159.6(1)	N(3)−Ti(1)−Cl(1)	91.10(7)
N(3)−Ti(1)−N(9)	79.29(9)	N(6)−Ti(1)−Cl(1)	168.19(7)
N(6)−Ti(1)−N(9)	75.71(9)	N(9)−Ti(1)−Cl(1)	96.12(6)
N(1)−Ti(1)−O(1)	97.5(1)	O(1)−Ti(1)−Cl(1)	96.51(6)
N(3)−Ti(1)−O(1)	158.44(9)	Ti(1)−N(1)−C(63)	150.5(2)
Ti(1)−O(1)−S(1)	138.9(1)		

least-squares plane (116.5° in **8** compared with 123.7° in non-ansa-bridged [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$]) and (ii) an *increase* in the angle between the N$_{\mathrm{imide}}$−Ti bond vector and the [Ti(1)−Cl(1)−O(1)] plane (104.2° in **8** compared with 98.1° for the corresponding value in [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$]).

The X-ray structure of [Ti(κ^4-L^{3b})(OTf)Cl] (**8**) supports those proposed for [Ti(κ^4-L^{3a,b})Cl$_2$] (**5a,b**) and [Ti(κ^4-L^{5a,b})Cl$_2$] (**6a,b**) and establishes these compounds as the first ansa-linked macrocycle−imido complexes. The dianionic ligands L^{3a,b} and L^{5a,b} are isoelectronic analogues of the dianionic ansa-bis(cyclopentadienyl) ligand set. In addition, the compounds **5**, **6**, and **8** are the first examples of any pendant-arm macrocyclic complex bearing an imido donor group, although other types of compounds with chelating imido linkages have been described recently.[44−47]

Attempts to prepare dialkyl derivatives of the new compounds **5a,b** and **6a,b** were complicated by side reactions and low compound stability. This is in contrast to the fairly well-behaved alkylation chemistry of non-ansa-linked R$_3$[9]aneN$_3$ and R$_3$[6]aneN$_3$-supported species [Ti(NBu^t)(R$_3$[*n*]aneN$_3$)Cl$_2$] ($n = 9$ or 6).[24,48] Of the ansa compounds studied, only [Ti(κ^4-L^{5b})Cl$_2$] (**6b**) afforded tractable dialkyl derivatives, namely, [Ti(κ^4-L^{5b})(R)$_2$] [R = Me (**9**) or CH$_2$SiMe$_3$ (**10**); Scheme 2]. They were characterized by NMR spectroscopy and elemental analysis.

As mentioned above, one of the main current interests in ansa-metallocenes (**I**) and constrained geometry cyclopentadienyl−amide systems (**II**) is their use in olefin polymerization. A range of “alternative” ligand environments (to those exemplified by **I** and **II**) are currently under investigation[49] and among these have been groups 5 and 6 mono- and bisimido complexes.[50−53] Triazacyclononane complexes of Sc, Y, and Rh have also been studied in this context.[54−56] Group 4 imides have only recently been studied in this regard,[48] and so it was of interest to assess the polymerization capability of the new ansa-linked compounds. For the purposes of comparison with non-ansa-linked analogues, we also prepared the ring *N*-methyl-substituted complex [Ti(NBu^t)(κ^3-L^{1a})Cl$_2$] (**11a**) from L^{1a} and [Ti(NBu^t)Cl$_2$(py)$_3$] in 73% isolated yield (Scheme 3). The ring *N*-isopropyl-substituted homologue [Ti(NBu^t)(κ^3-L^{1b})Cl$_2$] (**11b**) was also prepared for the purposes of comparison with the corresponding ring isopropyl-substituted ansa compounds **5b** and **6b**.[57]

Table 3. Summary of Ethylene Polymerization Data^a

procatalyst	yield/ mg	$10^{-5}M_w$	$10^{-5}M_n$	M_w/M_n	activity/ g(mmol bar h)$^{-1}$
5a	180	*b*	*b*	*b*	2.6
5b	83	*b*	*b*	*b*	1.2
6a	265	*b*	*b*	*b*	3.8
6b	54	8.8	0.13	70	0.8
9^c	48	*b*	*b*	*b*	0.7
11a	280	3.3	0.067	50	4.0
11b	140	7.5	0.15	50	2.0

^{a} Conditions: ambient temperature in toluene over 60 min, 10 μmol of procatalyst, MAO cocatalyst with Al:Ti ratio of ca. 1500, 7 bar C_2H_4. ^{b} Samples are of very high M_w and only partly soluble under GPC conditions used. Reliable measurements could not be obtained. ^{c} No activity was observed with B(C$_6$F$_5$)$_3$ activator.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **11a** show that it exists as a mixture of isomers, *cis*-**11a** (major product, 80%) and *trans*-**11a** (minor product, 20%), where cis and trans refer to the relative coordination sites of the macrocycle N−H and imido N groups. On statistical grounds, the product distribution would be *cis*-**11a**:*trans*-**11a** = 2:1. The nonstatistical preference of **11** for the cis isomer presumably reflects steric effects of alternative neighboring groups.

The polymerization results for **5a,b**, **6a,b**, **9**, and **11a,b** are listed in Table 3, and further details are given in the Experimental Section. All of the complexes show low activity, giving very high molecular weight polymers. GPC analysis of these polymers was hampered by the low solubility. Where measurements could be made, the polymer had very poor polydispersity

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indices (M_w/M_n), suggesting multiple types of active sites. Attempts to obtain better-defined catalyst formulations by using $B(C_6F_5)_3$ as an activator[58] with either of the dialkyl complexes **9** or **10** gave no polymerization activity at all. The magnitude of the activities in Table 3 make more than a very qualitative interpretation inappropriate. Briefly, it appears that compounds with ring *N*-methyl substituents (in **5a**, **6a**, and **11a**) afford better activities than those with *N*-isopropyl groups (**5b**, **6b**, and **11b**). There is no obvious activity enhancement for the ansa-linked compounds **5a,b** and **6a,b** compared to that of the non-ansa-linked **11a,b**.

Concluding Remarks

We have described ligand precursors to the first ansa-linked macrocycle−imido complexes. Two exchange routes to these compounds have been identified, namely, via $[Ti(NMe_2)_2Cl_2]$ and $[Ti(NBu^t)Cl_2(py)_3]$. The X-ray structure of $[Ti(\kappa^4\text{-}L^{3b})(OTf)Cl]$ (**8**) confirmed the presence of the ansa linkage and revealed significant angular constraints at the metal center when compared with those of related non-ansa-linked analogues. However, no significant ethylene polymerization activity gain was observed in comparison with that of the non-ansa-linked systems **11a,b**.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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