Titanium *tert*-Butyl- and Trimethylsilyl-imido Complexes with Monopendant Arm Triazacyclononane Ligands

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Received August 22, 2000

Introduction

Titanium imido compounds are a topic of current interest[1−9] and have also been postulated[9,10] as transient intermediates in the conversion of other titanium−nitrogen compounds to titanium nitride (TiN), a material with a number of important uses.[11,12] A number of titanium imides have been isolated and tested as single-source CVD (chemical vapor deposition) precursors to TiN.[9,13−15] There is also continuing interest in the synthesis and properties of molecular titanium nitride derivatives,[16,17−24] driven in part by the insight that such compounds may give into the chemistry behind the CVD of TiN. Furthermore, transition metal nitrido compounds in general also represent an area of continuing activity.[10,25,26] Terminal transition metal molecular nitrides (i.e., $L_nM{\equiv}N$) have been structurally characterized for V, Cr, Mn, and some second- and third-row mid-transition metals, but not for titanium.[10,25−28] Further efforts toward a terminal titanium nitride are potentially worthwhile and form the subject of this contribution. In this regard we noted that the octameric titanium imide $[Ti(NSiMe_3)Cl_2]_8$ decomposes via the isomeric polymer $[Ti(NSiMe_3)Cl_2]_n$ to TiNCl and Me_3SiCl at temperatures above 250 °C.[29] In related chemistry, the conversion of a vanadium trimethylsilyl imido complex to a terminal nitrido derivative was reported by Doherty and coworkers whereby reaction of $[V(NSiMe_3)Cl_3]$ with $4\text{-}NC_5H_4R$ ($R = Et, Bu^t$) or quinuclidine forms the corresponding monomeric nitrides $[V(N)Cl_2(L)_2]$.[30] It therefore seemed possible that reaction of octameric $[Ti(NSiMe_3)Cl_2]_8$ with suitable, polydentate monoanionic or neutral ligands might give rise to trimethylsilyl imido complexes that could be converted to well-defined titanium nitrides. Here, we describe the syntheses and structures of new trimethylsilyl- and *tert*-butylimidotitanium complexes with monopendant arm triazacyclononane ligands, along with our efforts to prepare molecular titanium nitrides.

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 protio-solvents and commercially available reagents were predried over activated molecular sieves and 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 rt (CD_2Cl_2) or molten potassium (C_6D_6), distilled under reduced pressure, and stored under N_2 in J. Young ampules. NMR samples of air- and moisture-sensitive compounds were prepared in the drybox in 5 mm Wilmad tubes equipped with a Young's Teflon valve.

^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 500 or Mercry 300 spectrometer and referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances. Chemical shifts are reported relative to tetramethylsilane ($\delta = 0$ ppm) in δ (ppm) and coupling constants in hertz. ^1H and ^{13}C NMR shift assignments were supported by DEPT-135 and DEPT-90, homo- and heteronuclear, one- and two-dimensional experiments as appropriate. Infrared samples were recorded as Nujol mulls using a Perkin-Elmer 1710 spectrophotometer. Mass spectra were recorded on an AEI MS902, Micromass LC Tof ESI or Micromass Autospec 500 mass spectrometer. Elemental analyses were carried out by the analysis laboratory of this department.

Literature Preparations. KL^1 was prepared[31] from HL^1.[32] L^2,[33] $[Ti(NBu^t)Cl_2(py)_3]$,[34] and $[Ti(NSiMe_3)Cl_2]_8$[35] were prepared according to literature methods. All other starting materials were purchased commercially.

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10.1021/ic0009728 CCC: $20.00

$[Ti(NBu^t)(L^1)Cl]$ (1). To a solution of $[Ti(NBu^t)Cl_2(py)_3]$ (0.46 g, 1.07 mmol) in toluene (25 mL) at −78 °C was added a solution of KL^1 (0.50 g, 1.07 mmol) in toluene dropwise with stirring. An orange solution, which contained a white precipitate, was formed, and the mixture was allowed to warm slowly to rt. Stirring was continued for a further 2 h. The mixture was filtered, and the volatiles were removed under reduced pressure. The resulting orange oil was dissolved in diethyl ether (25 mL) and cooled to −30 °C to give **1** as a yellow solid which was dried in vacuo. Yield: 0.15 g, 24%.

Data for 1. ^1H NMR (C_6D_6, 500.0 MHz, 298 K): δ 7.64 (1 H, s, $C_6\mathit{H}_2Bu^t_2O$), 7.08 (1 H, s, $C_6\mathit{H}_2Bu^t_2O$), 5.24 (1 H, d, J = 14 Hz, $ArC\mathit{H}_aH_b$), 4.33 (1 H, m, $C\mathit{H}Me_2$), 3.72 (1 H, m, $C\mathit{H}Me_2$), 3.48 (1 H, d, J = 14 Hz, $ArCH_a\mathit{H}_b$), 3.44 (1 H, m, $NC\mathit{H}_2CH_2$), 2.78 (1 H, m, $NC\mathit{H}_2CH_2$), 2.43 (1 H, m, $NC\mathit{H}_2CH_2$), 2.31 (3 H, m, $NC\mathit{H}_2CH_2$), 1.97−1.85 (2 H, m, $NC\mathit{H}_2CH_2$), 1.92 (9 H, s, CBu^t), 1.70 (3 H, d, J = 6.5 Hz, $CH\mathit{Me}_2$), 1.60−0.82 (4 H, m, $NC\mathit{H}_2CH_2$), 1.42 (9 H, s, Bu^t), 1.07 (3 H, d, J = 6.5 Hz, $CH\mathit{Me}_2$), 1.04 (9 H, s, Bu^t), 0.81 (3 H, d, J = 6.5 Hz, $CH\mathit{Me}_2$), 0.57 (3 H, d, J = 6.0 Hz, $CH\mathit{Me}_2$). ^{13}C-{^1H} NMR (C_6D_6, 125.7 MHz, 298 K): δ 161.8 (2-$\mathit{C}_6H_2Bu^t_2O$), 137.7 ($\mathit{C}Bu^t$ of $\mathit{C}_6H_2Bu^t_2O$), 137.3 ($\mathit{C}Bu^t$ of $\mathit{C}_6H_2Bu^t_2O$), 123.6 (4- or 6- $\mathit{C}_6H_2Bu^t_2O$), 122.7 (6- or 4- $\mathit{C}_6H_2Bu^t_2O$), 121.5 (1-$\mathit{C}_6H_2Bu^t_2O$), 69.9 ($Ar\mathit{C}H_2$), 69.0 ($N\mathit{C}Me_3$), 58.9 ($N\mathit{C}H_2CH_2$), 57.4 ($\mathit{C}HMe_2$), 55.6 ($N\mathit{C}H_2CH_2$), 54.4 ($\mathit{C}HMe_2$), 53.0 ($N\mathit{C}H_2CH_2$), 44.2 ($N\mathit{C}H_2CH_2$), 42.4 ($N\mathit{C}H_2CH_2$), 35.8 ($\mathit{C}Me_3$), 34.3 ($\mathit{C}Me_3$), 32.2 ($C\mathit{Me}_3$), 32.0 ($C\mathit{Me}_3$), 31.7 ($C\mathit{Me}_3$), 21.6 ($CH\mathit{Me}_2$), 20.7 ($CH\mathit{Me}_2$), 16.4 ($CH\mathit{Me}_2$), 15.2 ($CH\mathit{Me}_2$). IR (CsBr plates): 1600 (m), 1498 (w), 1413 (w), 1296 (m), 1231 (s), 1203 (m), 1132 (w), 1109 (w), 1058 (w), 965 (w), 940 (w), 896 (w), 874(s), 843 (s), 768 (w), 752 (w), 615 (w), 603 (w), 585 (w), 546 (s), 512(w), 465 (m) cm^{-1}. EI-mass spectrum: m/z = 584. ($[M]^+$, 100), 569 ($[M - Me]^+$, 44). Anal. Found (calcd for $C_{31}H_{57}ClN_4OTi$): C, 63.5 (63.6); H, 9.5 (9.8); N, 9.3 (9.6).

$[Ti(NSiMe_3)(L^1)Cl]$ (2). To a solution of $[Ti(NSiMe_3)Cl_2]_8$ (0.177 g, 0.107 mmol) in toluene (25 mL) at −78 °C was added a solution of KL^1 (0.400 g, 0.858 mmol) in toluene (20 mL) dropwise with stirring. A dark orange solution, which contained a white precipitate, was formed, and the mixture was allowed to warm slowly to rt. Stirring was continued for further 2 h. The mixture was filtered and the volatiles were removed under reduced pressure. The resulting orange oil was dissolved in diethyl ether (25 mL) and cooled to −30 °C to give **2** as light orange crystals that were dried in vacuo. Yield: 0.21 g, 40%.

Data for 2. ^1H NMR (C_6D_6, 500.0 MHz, 298 K): δ 7.61 (1 H, s, $C_6\mathit{H}_2Bu^t_2O$), 7.06 (1 H, d, $C_6\mathit{H}_2Bu^t_2O$), 5.20 (1 H, d, J = 14 Hz, $ArC\mathit{H}_aH_b$), 4.43 (1 H, app. sept., J = 6.5 Hz, $C\mathit{H}Me_2$), 3.66 (1 H, app sept, J = 6.5 Hz, $C\mathit{H}Me_2$), 3.64 (1 H, m, $NC\mathit{H}_2CH_2$), 3.49 (1 H, d, J = 14 Hz, $ArCH_a\mathit{H}_b$), 2.78 (1 H, m, $NC\mathit{H}_2CH_2$), 2.43−2.32 (4 H, m, $NC\mathit{H}_2CH_2$), 1.92 (2 H, m, $NC\mathit{H}_2CH_2$), 1.89 (9 H, s, Bu^t), 1.66 (3 H, d, J = 6.5 Hz, $CH\mathit{Me}_2$), 1.63−1.42 (3 H, m, $NC\mathit{H}_2CH_2$), 1.41 (9 H, s, Bu^t), 1.39 (1 H, m, $NC\mathit{H}_2CH_2$), 1.04 (3 H, d J = 6.5 Hz, $CH\mathit{Me}_2$), 0.92 (3 H, d J = 6.5 Hz, $CH\mathit{Me}_2$), 0.55 (3 H, d J = 6.5 Hz, $CH\mathit{Me}_2$), −0.05 (9 H, s, $SiMe_3$). ^{13}C-{^1H} NMR (C_6D_6, 125.7 MHz, 298 K): δ 161.0 (2-$\mathit{C}_6H_2Bu^t_2O$), 138.6 ($\mathit{C}Bu^t$ of $C_6H_2Bu^t_2O$), 137.0 ($\mathit{C}Bu^t$ of $C_6H_2Bu^t_2O$), 128.2 (4- or 6-$\mathit{C}_6H_2Bu^t_2O$), 128.1 (6- or 4-$\mathit{C}_6H_2Bu^t_2O$), 127.9 (*1*-$C_6H_2Bu^t_2O$), 70.0 ($Ar\mathit{C}H_2N$), 58.9 ($\mathit{C}HMe_2$), 57.7 ($N\mathit{C}H_2CH_2$), 55.7 ($N\mathit{C}H_2CH_2$), 54.5 ($\mathit{C}HMe_2$), 53.2 ($N\mathit{C}H_2CH_2$), 53.1 ($N\mathit{C}H_2CH_2$), 44.5 ($N\mathit{C}H_2CH_2$), 42.0 ($N\mathit{C}H_2CH_2$), 35.7 ($\mathit{C}Me_3$), 34.2 ($\mathit{C}Me_3$), 32.0 ($C\mathit{Me}_3$), 31.4 ($C\mathit{Me}_3$), 21.3 ($CH\mathit{Me}_2$), 20.4 ($CH\mathit{Me}_2$), 16.7 ($CH\mathit{Me}_2$), 15.0 ($CH\mathit{Me}_2$), 2.16 ($SiMe_3$). IR (CsBr plates): 1238 (m), 1203 (w), 1132 (m), 1097 (s), 966 (w), 941 (w), 833 (s), 751 (m), 730 (m), 584 (w), 551 (w), 465 (w) cm^{-1}. EI-mass spectrum: m/z = 600 ($[M]^+$, 100). Anal. Found (calcd for $C_{30}H_{57}ClN_4SiTi$): C, 60.1 (60.0); H, 9.4 (9.3); N, 9.1 (9.3).

$[Ti(NBu^t)(L^2)Cl]Cl$ (3). To a solution of $[Ti(NBu^t)Cl_2(py)_3]$ (0.644 g, 1.51 mmol) in toluene (20 mL) was added a solution of L^2 in toluene dropwise with stirring. Initially a clear orange solution was formed which on stirring for a further 2 h. produced a yellow precipitate. The volatiles were removed under reduced pressure, and the resulting sandy yellow solid was dissolved in dichloromethane (25 mL) and filtered. The solution was reduced in volume, layered with hexane and cooled to −30 °C to give **3** as a sandy yellow solid which was dried in vacuo. Yield: 0.49 g, 66%.

Data for 3. ^1H NMR ($CDCl_3$, 500.0 MHz, 298 K): δ 9.30 (1 H, d, J = 6 Hz, 1-NC_5H_4), 7.98 (1 H, t, J = 8 Hz, 3-NC_5H_4), 7.73 (1 H, d, J = 8 Hz, 4-NC_5H_4), 7.48 (1 H, t, J = 7 Hz, 2-NC_5H_4), 5.14 (1 H, d, J = 15 Hz, $ArC\mathit{H}_aH_b$), 4.95 (1 H, d, J = 15.5 Hz, $ArCH_a\mathit{H}_b$), 4.49 (1 H, m, $NC\mathit{H}_2CH_2$), 4.18 (1 H, m, $NC\mathit{H}_2CH_2$), 4.05 (1 H, m, $NC\mathit{H}_2CH_2$), 3.87 (1 H, m, $NC\mathit{H}_2CH_2$), 3.60−3.52 (2 H, m, $NC\mathit{H}_2CH_2$), 3.33 (2 H, m, $NC\mathit{H}_2CH_2$), 3.06 (1 H, m, $NC\mathit{H}_2CH_2$), 2.68 (1 H, m, $NC\mathit{H}_2CH_2$), 2.56 (1 H, m, $NC\mathit{H}_2CH_2$), 2.47 (1 H, m, $NC\mathit{H}_2CH_2$), 1.59 (3 H, d, J = 6.5 Hz, $CH\mathit{Me}_2$), 1.21 (3 H, d, J = 6.5 Hz, $CH\mathit{Me}_2$), 0.79 (3 H, d, J = 6.5 Hz, $CH\mathit{Me}_2$), 0.63 (3 H, d, J = 6 Hz, $CH\mathit{Me}_2$), 0.63 (9 H, s, Bu^t). ^{13}C-{^1H} NMR ($CDCl_3$, 125.7 MHz, 298 K): δ 157.3 (5-C_5H_4N), 151.1 (*1*−C_5H_4N), 140.0 (*3*-C_5H_4N), 124.2 (4- or 2-C_5H_4N), 123.6 (2- or 4-C_5H_4N), 71.1 ($N\mathit{C}Me_3$), 66.0 ($Ar\mathit{C}H_2N$), 62.3 ($\mathit{C}HMe_2$), 59.3 ($N\mathit{C}H_2CH_2$), 55.5 ($N\mathit{C}H_2CH_2$), 55.3 ($N\mathit{C}H_2CH_2$), 54.8 ($\mathit{C}HMe_2$), 53.2 ($N\mathit{C}H_2CH_2$), 43.3 ($N\mathit{C}H_2CH_2$), 41.4 ($N\mathit{C}H_2CH_2$), 29.8 ($C\mathit{Me}_3$), 22.2 ($CH\mathit{Me}_2$), 21.2 ($CH\mathit{Me}_2$), 15.4 ($CH\mathit{Me}_2$), 13.6 ($CH\mathit{Me}_2$). IR (KBr plates): 1608 (m), 1238 (m), 1210 (w), 1124 (w), 1062 (w), 957 (w), 940 (w), 837 (w), 689 (w), 664 (w), 601 (m), 568 (m), 548 (w), 472 (w), 453 (w) cm^{-1}. ES-mass spectrum: m/z = 458 ($[M]^+$, 100). Anal. Found [calcd for $C_{22}H_{41}Cl_2N_4Ti{\cdot}0.8(CH_2Cl_2)$]: C, 48.6 (48.7); H, 8.1 (7.6); N, 12.3 (12.5).

$[Ti(NSiMe_3)(L^2)Cl]Cl$ (4). To a slurry of $[Ti(NSiMe_3)Cl_2]_8$ (0.750 g, 0.455 mmol) in toluene (40 mL) at −78 °C was added a solution of L^2 (1.10 g, 3.64 mmol) in toluene (20 mL) dropwise with stirring. The initially formed, clear orange solution produced a yellow precipitate on warming slowly to room temperature and stirring for 2 h. The sandy yellow precipitate was isolated by filtration, washed with toluene (20 mL) and dried under reduced pressure. Yield: 1.15 g, 62%.

Data for 4. ^1H NMR ($CDCl_3$, 500.0 MHz, 298 K): δ 9.26 (1 H, d, J = 7 Hz, 1-NC_5H_4), 8.00 (1 H, t, J = 7 Hz, 3-NC_5H_4), 7.73 (1 H, d, J = 7 Hz, 4-NC_5H_4), 7.50 (1 H, t, J = 7 Hz, 2-NC_5H_4), 5.17 (1 H, d, J = 15.5 Hz, $ArC\mathit{H}_aH_b$), 5.01 (1 H, d, J = 15.5 Hz, $ArCH_a\mathit{H}_b$), 4.52 (1 H, m, $NC\mathit{H}_2CH_2$), 4.16 (1 H, m, $NC\mathit{H}_2CH_2$), 4.16 (1 H, m, $C\mathit{H}Me_2$), 3.87 (1 H, m, $NC\mathit{H}_2CH_2$), 3.59 (1 H, m, $NC\mathit{H}_2CH_2$), 3.52 (1 H, m, $C\mathit{H}Me_2$), 3.48 (2 H, m, $NC\mathit{H}_2CH_2$), 3.08−2.39 (5 H, m, $NC\mathit{H}_2CH_2$), 1.59 (3 H, d, J = 7 Hz, $CH\mathit{Me}_2$), 1.20 (3 H, d, J = 7 Hz, $CH\mathit{Me}_2$), 1.20−1.07 (1 H, m, $NC\mathit{H}_2CH_2$), 0.78 (3 H, d, J = 7 Hz, $CH\mathit{Me}_2$), 0.60 (3 H, d, J = 7 Hz, $CH\mathit{Me}_2$), 0.80−0.60 (1 H, m, $NC\mathit{H}_2CH_2$), −0.44 (9 H, s, $SiMe_3$). ^{13}C-{^1H} NMR ($CDCl_3$, 125.7 MHz, 298 K): δ 157.6 (5-C_5H_4N), 151.2 (1-C_5H_4N), 140.3 (3-C_5H_4N), 124.4 (4- or 2-C_5H_4N), 123.7 (2- or 4-C_5H_4N), 66.3 ($Ar\mathit{C}H_2N$), 63.0 ($\mathit{C}HMe_2$), 59.5 ($N\mathit{C}H_2CH_2$), 55.9 ($N\mathit{C}H_2CH_2$), 55.3 ($N\mathit{C}H_2CH_2$), 55.1 ($\mathit{C}HMe_2$), 53.8 ($N\mathit{C}H_2CH_2$), 43.8 ($N\mathit{C}H_2CH_2$), 41.2 ($N\mathit{C}H_2CH_2$), 22.1 ($CH\mathit{Me}_2$), 21.3 ($CH\mathit{Me}_2$), 15.6 ($CH\mathit{Me}_2$), 13.7 ($CH\mathit{Me}_2$), 0.1 ($SiMe_3$). IR (KBr plates): 1607 (m), 1340 (m), 1242 (w), 956 (w), 939 (w), 838 (m), 799 (s), 739 (w), 635 (w), 595 (w), 458 (w) cm^{-1}. ES-mass spectrum: m/z = 474 ($[M]^+$, 100). Anal. Found [calcd for $C_{21}H_{41}Cl_2N_5SiTi \cdot 0.7(CH_2Cl_2)$]: C, 45.4 (45.7); H, 7.7 (7.5); N, 13.0 (12.3).

Crystal Structure Determination of $[Ti(NSiMe_3)(L^1)Cl]$ (2) and $[Ti(NBu^t)(L^2)Cl]Cl$ (3). Crystal data collection and processing parameters are given in Table 1. Crystals were 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.[36] Data were collected at 150 K using Mo Kα radiation; equivalent reflections were merged and the images were processed with the DENZO and SCALEPACK programs.[37] Corrections for Lorentz-polarization effects and absorption were performed and the structures were solved by direct methods using SIR92.[38] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were placed geometrically. Crystallographic calculations were performed using SIR92 and CRYSTALS-PC.[39]

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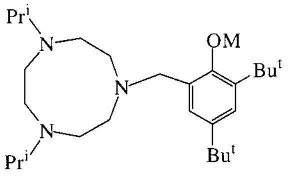
Table 1. X-ray Data Collection and Processing Parameters for $[Ti(NSiMe_3)(L^1)Cl]\cdot OEt_2$ (**2·OEt₂**) and $[Ti(NBu^t)(L^2)Cl]Cl\cdot CH_2Cl_2$ (**3·CH₂Cl₂**)

	2·OEt₂	**3·CH₂Cl₂**
emp formula	$C_{34}H_{67}ClN_4O_2SiTi$	$C_{25}H_{47}Cl_8N_5Ti$
fw	675.37	749.21
T/°C	−123(1)	−123(1)
wavelength/Å	0.71069	0.71069
space group	$P2_1/c$	$P2_1/n$
a/Å	11.000(4)	17.034(7)
b/Å	14.735(3)	11.534(5)
c/Å	24.752(9)	19.534(4)
β/°	103.128(6)	108.49(6)
V/Å^3	3907.1(5)	36.39.7(5)
Z	4	4
d (calcd)/Mg.m^{-3}	1.15	1.37
abs coeff/mm^{-1}	0.35	0.85
R indices $[I > 3\sigma(I)]^{a,b}$	$R_1 = 0.0603$, $R_w = 0.0580$	$R_1 = 0.0523$, $R_w = 0.0539$

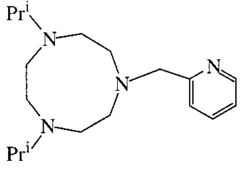
^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \sqrt{\{\sum w\,(F_o - F_c)^2/\sum(w(F_o)^2\}}$.

Results and Discussion

Molecular titanium nitrido chemistry is dominated by the formation of μ-N bridged species,[16−23] and so to reduce the likelihood of forming such compounds we used the pendant arm 1,4,7-triazacyclononane ligands shown below. The syntheses of HL^1 and L^2 have been reported by Tolman and co-workers,[32,33] and the conversion of the phenol HL^1 to its potassium salt KL^1 is straightforwardly achieved with potassium hydride.[31] Ligand L^1 typically acts as a tetradentate, monoanionic donor, and L^2 is potentially a tetradentate, neutral donor. In general, L^1 and its homologues have been used mainly with the later transition metals,[32,40−45] and the coordination chemistry of L^2 has been limitted to copper.[41,46] Such pendant armtriazacyclononane ligands in general form kinetically and thermodynamically stable complexes through the benefits of the so-called chelate- and macrocyclic-effects.[47,48]



M = H (HL^1) or K (KL^1)



L^2

We have recently reported that 1,4,7-trimethyl-1,4,7-triazacyclononane ($Me_3[9]aneN_3$) reacts smoothly with $[Ti(NR)Cl_2(py)_3]$ (R = Bu^t or aryl)[34] to form titanium imido derivatives $[Ti(NR)(Me_3[9]aneN_3)Cl_2]$.[49,50] A number of other titanium triazacyclononane complexes have also been described, some of which feature rings with three pendant arms.[51,52,53] We also very recently reported the mono-pendant arm complex $[Ti\{1\text{-}(NCH_2CH_2CH_2)\text{-}4,7\text{-}Pr^i_2[9]aneN_3\}Cl_2]$ in which the imido moiety forms part of the pendant arm.[54] Octameric $[Ti(NSiMe_3)Cl_2]_8$ was first prepared by reaction of $TiCl_4$ with $N(SiMe_3)_3$ in sealed glass tubes.[29] A more convenient preparation of $[Ti(NSiMe_3)Cl_2]_8$ from $TiCl_4$ and $HN(SiMe_3)_2$ in CH_2Cl_2 was recently reported by Schnick and co-workers.[35] In addition to the reactions of KL^1 and L^2 with $[Ti(NSiMe_3)Cl_2]_8$, we also report here, for the purposes of comparison, the corresponding reactions with $[Ti(NBu^t)Cl_2(py)_3]$.

The syntheses and proposed structures of the new compounds are summarized in Scheme 1. We will first consider the reactions of $[Ti(NBu^t)Cl_2(py)_3]$ and $[Ti(NSiMe_3)Cl_2]_8$ with KL^1. Reaction of KL^1 with either imido complex in toluene at −78 °C affords the macrocycle-supported complexes $[Ti(NBu^t)(L^1)Cl]$ (**1**) and $[Ti(NSiMe_3)(L^1)Cl]$ (**2**) in 24−40% yield after crystallization from Et_2O. It is probably the high solubility of these products that accounts for the relatively poor isolated yields since the corresponding NMR tube scale reactions in C_6D_6 are quantitative. The moderately air- and moisture-sensitive, yellow-orange compounds **1** and **2** are highly soluble in hydrocarbon solvents. Diffraction-quality crystals of $[Ti(NSiMe_3)(L^1)Cl]\cdot Et_2O$ (**2**·Et_2O) were grown from Et_2O at −30 °C. Data collection and processing parameters are given in Table 1, selected bond lengths and angles are listed in Table 2, and a displacement ellipsoid plot of **2** is given in Figure 1.

Molecules of **2** contain approximately octahedral Ti (IV) centers coordinated by a κ^4-bound L^1 ligand. The coordination sphere is completed by mutually cis chloride and trimethylsilyl imido groups. The overall geometry is broadly similar to that of the nonpendant arm complexes $[Ti(NR)(Me_3[9]aneN_3)Cl_2]$ (R = Bu^t or aryl),[49,50] and the bond lengths and angles within the L^1 moiety are similar to those found in previous complexes of this ligand.[27,28] The $Ti{=}N_{imido}$ distance of 1.718(2) Å is within the range expected for a triple bond (*pseudo*-$\sigma^2\pi^4$) and the $Ti{=}N_{imido}{-}Si$ angle of 168.9(1)° is also consistent with the $NSiMe_3$ acting as a 4-electron donor.[27,28,55] Among the $Ti{-}N_{macrocycle}$ distances, the Ti(1)−N(1) (i.e. trans to chloride) bond length of 2.246(2) Å is comparable to those previously found in $[Ti(NR)(Me_3[9]aneN_3)Cl_2]$ (R = Bu^t or aryl) for macrocycle N-donors trans to Cl. The Ti(1)−N(3) (trans to imide) and Ti(1)−N(6) (trans to aryloxide) distances of 2.552(2) and 2.376(2) Å are substantially longer than Ti(1)−N(1), and in the case of Ti(1)−N(3), longer than any found previously in $[Ti(NR)(Me_3[9]aneN_3)Cl_2]$ (R = Bu^t or aryl). The general lengthening of the $Ti{-}N_{macrocycle}$ bonds trans to the imido and aryloxide grous is consistent with the larger trans influence of these ligands compared with that of chloride, and the particularly long Ti(1)−N(3) distance might be additionally a consequence of the high steric crowding around titanium. The Ti−O and Ti−Cl distances are comparable to those of related structures.[27,28]

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Scheme 1

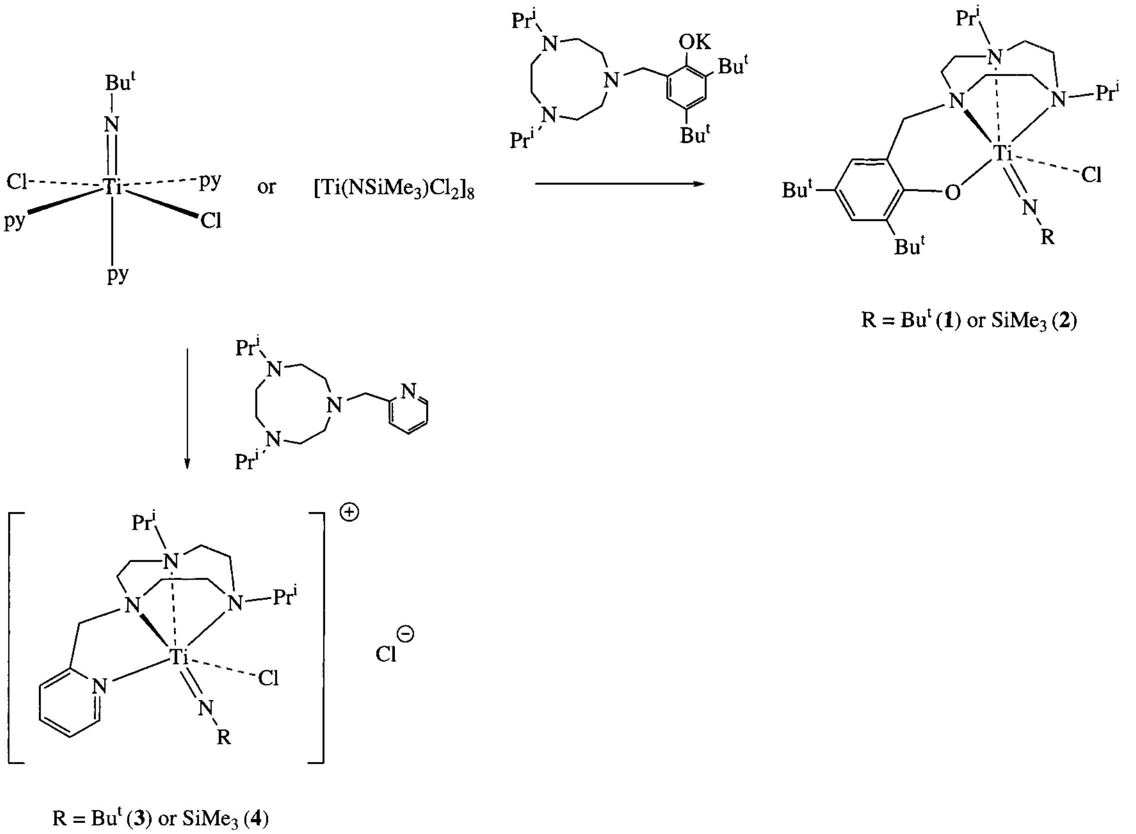

Table 2. Selected Bond Lengths (Å) and Angles (Deg) for $[Ti(NSiMe_3)(L^1)Cl]$ (**2**)

Ti(1)−Cl(1)	2.3872(7)	Ti(1)−N(1)	2.246(2)
Ti(1)−N(6)	2.376(2)	Ti(1)−N(21)	1.718(2)
Ti(1)−O(18)	1.9067(17)	Ti(1)−N(3)	2.552(2)
N(21)−Si(1)	1.714(2)		
Cl(1)−Ti(1)−N(1)	157.73(6)	Cl(1)−Ti(1)−N(6)	103.39(6)
N(1)−Ti(1)−N(6)	77.07(7)	Cl(1)−Ti(1)−N(21)	104.90(8)
N(1)−Ti(1)−N(21)	97.4(1)	N(6)−Ti(1)−N(21)	88.68(9)
Cl(1)−Ti(1)−O(18)	93.84(6)	N(1)−Ti(1)−O(18)	81.59(7)
N(6)−Ti(1)−O(18)	157.64(8)	N(21)−Ti(1)−O(18)	100.70(9)
Cl(1)−Ti(1)−N(3)	84.86(5)	N(21)−Ti(1)−N(3)	162.22(9)
N(3)−Ti(1)−O(18)	93.31(7)	N(3)−Ti(1)−N(1)	73.73(7)
N(3)−Ti(1)−N(6)	74.45(7)	Ti(1)−N(21)−Si(1)	168.9(1)
Ti(1)−O(18)−C(17)	129.6(2)		

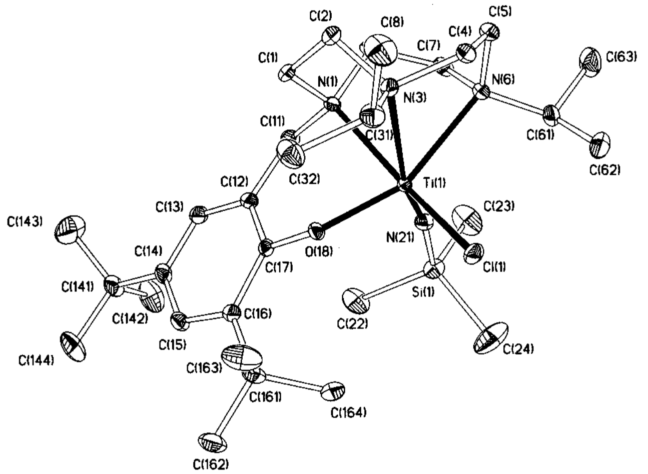

Figure 1. Displacement ellipsoid plot (40% probability) of $[Ti(NSiMe_3)(L^1)Cl]$ (**2**). Hydrogen atoms and Et_2O molecule of crystallization are omitted.

The solution ^1H and ^{13}C NMR data for $[Ti(NBu^t)(L^1)Cl]$ (**1**) and $[Ti(NSiMe_3)(L^1)Cl]$ (**2**) are fully consistent with the structure of **2** found in the solid state. The sets of spectra for the two compounds only differ substantially in the signals attributed to the imido *tert*-butyl group in **1** and the trimethylsilyl group in **2**. The absence of any molecular symmetry elements is revealed in the ^1H NMR spectra by, for example, four doublets and two apparent septets for the two inequivalent N-*iso*-propyl groups, and by a pair of mutually coupled doublets for the diastereotopic benzylic CH_2 linker of the L^1 ligand. Both compounds show the expected molecular ion envelopes in their EI mass spectra; the spectrum of **2** does not show any fragments corresponding to loss of Me_3SiCl. The compounds **1** and **2** are the first reported examples of any Group 4 complex of L^1 or any of its homologues. There has been one report of a structurally related vanadium oxo derivative of the N- and aryl ring-unsubstituted ligand 1-(2-oxybenzyl)-4,7-triazacyclononane.[45] Compound **2** is the first structurally authenticated terminal trimethylsilyl imido derivative of titanium, although compounds with μ-$NSiMe_3$ groups[27,28] and terminal $NSiBu^t_3$ and $NSi(C_2Ph)Me_2$ groups have recently been structurally characterized.[3,56] No imido complexes at all of L^1 or its homologues have been reported previously.

In NMR tube scale experiments (not illustrated in Scheme 1) we examined the reactions of $[Ti(NSiMe_3)Cl_2]_8$ with 4-substituted pyridines and also with $Me_3[9]aneN_3$. With the pyridines there was evidence of formation of Me_3SiCl but on scale-up no single product could be isolated. With $Me_3[9]aneN_3$ alone no reaction occurred even on heating, in contrast to the reaction of $[Ti(NBu^t)Cl_2(py)_3]$ with this macrocycle to form $[Ti(NBu^t)(Me_3[9]aneN_3)Cl_2]$.[34] Reaction of $[Ti(NSiMe_3)Cl_2]_8$ with py-

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Table 3. Selected Bond Lengths (Å) and Angles (Deg) for [Ti(NBu^t)(L^2)Cl]Cl (**3**)

Ti(1)−Cl(1)	2.3669(12)	Ti(1)−N(1)	2.234(3)
Ti(1)−N(4)	2.266(3)	Ti(1)−N(7)	2.505(3)
Ti(1)−N(17)	2.195(3)	Ti(1)−N(18)	1.699(3)

Cl(1)−Ti(1)−N(1)	153.82(9)	Cl(1)−Ti(1)−N(4)	113.90(9)
N(1)−Ti(1)−N(4)	78.59(11)	Cl(1)−Ti(1)−N(7)	85.97(9)
N(1)−Ti(1)−N(7)	73.97(12)	N(4)−Ti(1)−N(7)	77.73(11)
Cl(1)−Ti(1)−N(17)	94.63(9)	N(1)−Ti(1)−N(17)	73.24(12)
N(4)−Ti(1)−N(17)	151.03(12)	N(7)−Ti(1)−N(17)	100.43(11)
Cl(1)−Ti(1)−N(18)	98.81(11)	N(1)−Ti(1)−N(18)	103.50(14)
N(4)−Ti(1)−N(18)	93.15(13)	N(7)−Ti(1)−N(18)	170.83(13)
N(17)−Ti(1)−N(18)	87.05(13)	Ti(1)−N(18)−C(19)	168.7(3)

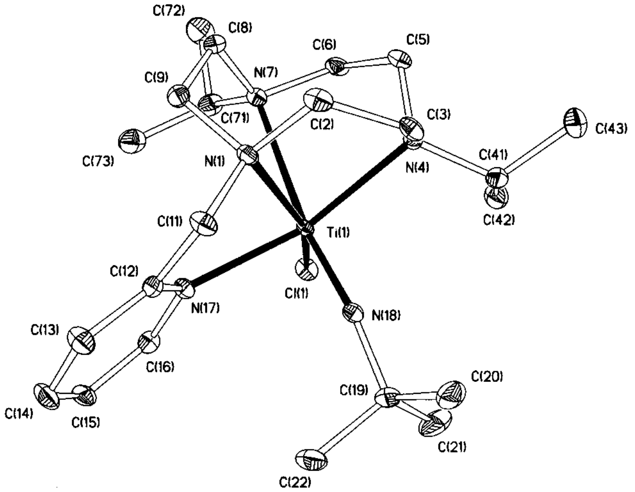

Figure 2. Displacement ellipsoid plot (35% probability) of [Ti(NBu^t)(L^2)Cl]Cl (**3**). Hydrogen atoms, chloride counteranion, and CH_2Cl_2 molecule of crystallization are omitted.

ridines in the presence of Me$_3$[9]aneN$_3$ led to ill-defined products. It was hoped, however, that use of the L^2 ligand (which combines chelating pyridyl and triazacyclononane functional groups) would allow for isolation of a single product.

Scheme 1 shows the reactions of [Ti(NBu^t)Cl$_2$(py)$_3$]and [Ti(NSiMe$_3$)Cl$_2$]$_8$ with the neutral donor L^2. These afford the ionic macrocycle-supported complexes [Ti(NBu^t)(L^2)Cl]Cl (**3**) and [Ti(NSiMe$_3$)(L^2)Cl]Cl (**4**) in 62−66% crystallized yield. The sandy-yellow colored products are soluble only in polar, aprotic solvents. As for **1** and **2**, NMR tube scale reactions (in CD_2Cl_2) showed that the reactions were quantitative and clean. Diffraction-quality crystals of {[Ti(NBu^t)(L^2)Cl]Cl}·CH_2Cl_2 (**3**·CH_2Cl_2) were grown at −30 °C from a CH_2Cl_2 solution layered with hexanes. Data collection and processing parameters are given in Table 1, selected bond lengths and angles are listed in Table 3, and a displacement ellipsoid plot of **3** is given in Figure 2.

The structure of **3** comprises well-separated [Ti(NBu^t)(L^2)Cl]$^+$ cations and Cl$^-$ anions, with no close contacts between them. The titanium is approximately octahedrally coordinated by a κ^4-L^2 ligand, a *tert*-butyl imido group and a chloride ligand. The distances and angles within the L^2 ligand are comparable to the previous examples. The Ti═N$_{\text{imide}}$ bond length of 1.699(3) Å and Ti═N$_{\text{imide}}$-Bu^t angle of 168.7(3)° are within the expected ranges and consistent with a titanium-nitrogen triple bond. The Ti(1)−N(7) distance of 2.505(3) Å still implies a substantial trans influence of NBu^t but the Ti−N$_{\text{macrocycle}}$ distances for the nitrogens trans to Cl and pyridyl nitrogen are very similar to each other. The titanium-ligand bond lengths in **3** mostly show a general decrease with respect to the comparable values for **2** above or the nonpendant arm relative [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$]. The greatest shortening is found for the Ti−Cl values, consistent with the formal positive charge on titanium in **3** and the greater anticipated ionic contribution to the Ti−Cl bonds compared to the Ti−N$_{\text{amine}}$ or Ti═N$_{\text{imide}}$ in complexes of this type.

The solution NMR data for [Ti(NBu^t)(L^2)Cl]Cl (**3**) and [Ti(NSiMe$_3$)(L^2)Cl]Cl (**4**) are consistent with the solid-state structure of **3**. The spectra show many of the features described above for the L^1 analogues **1** and **2**. Evidence for coordination of the pyridyl group of L^2 in solution comes from the ^{1}H shift of δ ca. 9.3 for the NC$_5$H$_4$ moiety ortho H atom; this shift is ca. 0.8 ppm downfield of that found in free L^2 in the same solvent. The positive ion electrospray mass spectra of **3** and **4** in MeCN solution both show the expected parent ion envelopes for [Ti(NR)(L^2)Cl]$^+$ (R = Bu^t or SiMe$_3$) cations. The compounds **3** and **4** are the first early transition metal complexes of the L^2 ligand, and **3** is the first structurally characterized cationic Group 4 imido complex. No imido complexes of L^2 have been reported previously. The formation of [Ti(NR)(L^2)Cl]$^+$ (R = Bu^t or SiMe$_3$) cations, rather than analogues of neutral [Ti(NR)(Me$_3$[9]aneN$_3$)Cl$_2$] with κ^3-coordinated L^2 ligands, is attributed to the chelate effect since the chloride ligands in [Ti(NR)(Me$_3$[9]aneN$_3$)Cl$_2$] are not displaced by pyridine.[49,50] The L^2 ligand could, in principle, adopt a κ^3-coordination as found recently for a Cu derivative.[41,46]

The original purpose of this work was to explore possible Me$_3$SiCl-elimination routes to triazacyclononane-supported titanium nitrido complexes. The potential precursors [Ti(NSiMe$_3$)(L^1)Cl] (**2**) and [Ti(NSiMe$_3$)(L^2)Cl]Cl (**4**) clearly do not eliminate Me$_3$SiCl under ambient conditions and a wide number of attempts have been made to promote this process. These include attempted sublimation of the compounds (yielding ill-defined titanium products and free ligand L^{1,2}) and heating samples in the presence of pyridine (no reaction). Ammonolysis of nitrogen precursors has been widely used as an entry point to titanium nitrides, but none of complexes studied here undergo reaction with NH$_3$. Given the high affinity of silicon for fluorine, a number of reactions of **2** and **4** with fluoride sources (including CsF, Me$_4$NF, Et$_3$N·3HF, tris(dimethylamino)sulfur (trimethylsilyl)difluoride were attempted). Although in some instances there was NMR evidence for elimination of Me$_3$SiF, we were unable to isolate any single titanium complex.

Concluding Remarks

We have described the first examples of complexes of the ligand L^1 (or its homologues) or L^2 for Group 4, or of any imido complex at all. Neither of the trimethylsilyl imido complexes **2** or **4** are entry points to isolable titanium nitrido products.

Acknowledgment. This work was supported by the EPSRC, Leverhulme Trust and Royal Society. We thank Dr. Claire J. Carmalt (University College London) for helpful discussions and disclosing results prior to publication.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org. A full listing of atomic coordinates, bond lengths and angles and displacement parameters for **2** and **3** have also been deposited at the Cambridge Crystallographic Data Centre.

IC0009728