Synthesis and Characterization of a Thermally Robust Titanium Dinitrogen Complex. The Crystal Structure of [{[(Me₃Si)₂N]TiCl(pyridine)₂}₂(μ-η:η′-N₂)]

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Reaction of *trans*-[TiCl₂(tmeda)₂] (tmeda = N,N,N',N'-tetramethylethylenediamine) with one equivalent of LiN(Me₃Si)₂, followed by treatment with pyridine, led to the formation of a novel Ti–dinitrogen complex [{TiCl[N(SiMe₃)₂](pyridine)₂}(pyridine)₂}₂(μ-η : η′-N₂)].

Electron-rich divalent titanium is a promising substrate for studying molecular activation processes. The enormous reducing power of this species is in fact the key for understanding the remarkable performances (dinitrogen activation,[1,2] reactivity with unsaturated organic substrates,[3] C–H bond activation,[4] CO chemistry[5] and Ziegler–Natta catalysis[6]) which characterize the chemistry of its metallocenic derivatives. By way of contrast, the chemistry of Ti[II] remains surprisingly poor (apart from the bis-cyclopentadienyl systems) and is limited to only a few cases.[7] To date there is not one clearly demonstrated example where dinitrogen fixation occurs on a non-organometallic Ti[II] system.

The large scale preparation of monomeric and octahedral *trans*-[TiCl₂(tmeda)₂][8] provided us with a versatile starting material for the preparation of new Ti[II] systems *via* mild-condition ligand replacement reactions. In this paper we describe the result of the reaction of *trans*-[TiCl₂(tmeda)₂] with a sterically demanding lithium amide LiN(SiMe₃)₂ to form an unprecedented titanium–amide dinitrogen complex.
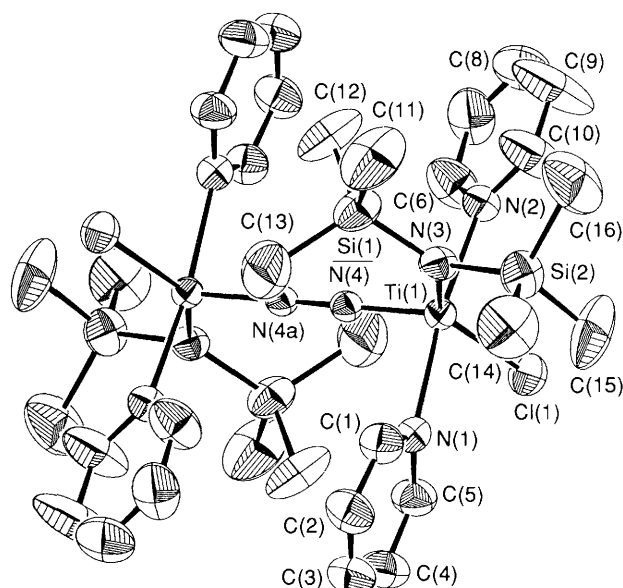
The reaction of *trans*-[TiCl₂(tmeda)₂] with one equivalent of LiN(SiMe₃)₂ in toluene under nitrogen at −80 °C, formed a
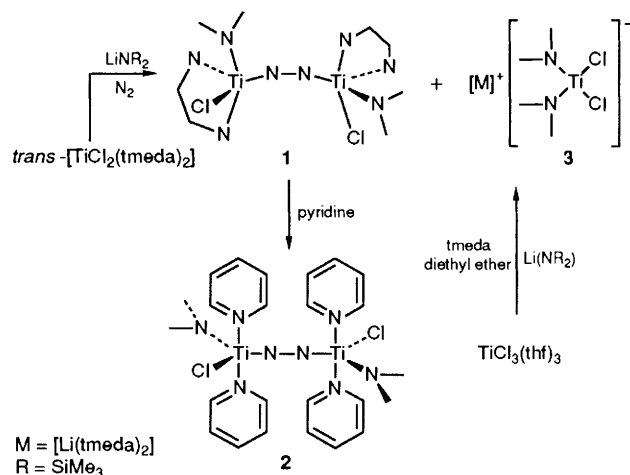
Scheme 1

purple gelatinous suspension which turned into a deep-brown solution upon standing overnight at room temperature.†
Brown crystals of [{TiCl[N(SiMe$_3$)$_2$](pyridine)$_2$}$_2$(μ-η:η'-N$_2$)] **1** were obtained in low yield after solvent evaporation, and crystallization of the residual solid from diethyl ether at −30 °C (Scheme 1). Further treatment of **1** with pyridine in toluene allowed the isolation of well-formed, large deep-green crystals of [{TiCl[N(SiMe$_3$)$_2$](pyridine)$_2$}$_2$(μ-η:η'-N$_2$)] **2**. Variable amounts of colourless crystals of the tetrahedral monomeric [Li(tmeda)$_2$][TiCl$_2${N(SiMe$_3$)$_2$}$_2$] **3** were isolated upon concentration of the mother liquor and further cooling. Conversely, reaction of *trans*-[TiCl$_2$(tmeda)$_2$] with 2.0 equivalents of LiN(SiMe$_3$)$_2$ in the presence of a small excess of tmeda in diethyl ether or in tetrahydrofuran (thf) led to the almost exclusive formation of **3**. Complex **3** could conveniently be prepared in large scale from reaction of TiCl$_3$(thf)$_3$ with two equivalents of LiN(SiMe$_3$)$_2$.‡

The structures of **2** and **3** have been determined by X-ray analysis.§ Complex **2** is binuclear and consists of two identical

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† Complex **1**: solid LiN(SiMe$_3$)$_2$ (2.95 g, 17.7 mmol) was added to a suspension of *trans*-[TiCl$_2$(tmeda)$_2$] (6.2 g, 17.6 mmol) in toluene (75 ml) under a nitrogen atmosphere at −80 °C. The reaction mixture was allowed to slowly warm up to −40 °C giving a thick purple gelatinous suspension which became a deep-brown solution upon standing at room temperature. After 3 days at room temperature, the solution was evaporated to dryness and the residual solid redissolved in diethyl ether. Deep-brown crystals of **1** were obtained upon cooling at −30 °C (1.4 g, 1.9 mmol, 11% yield based on titanium). IR (KBr, Nujol mull) ν/cm^{-1}: 2920s, 1460s, 1380m, 1360w, 1295w, 1290m, 1260s, 1240s, 1195w, 1170w, 1125m, 1100w, 1070m, 1050m, 1020m, 1010m, 100sh, 950s, 840s, 810s, 770s, 760sh, 750sh, 695s, 655s, 620s, 610sh, 505m, 480w, 460w, 430m, 415m, 395m and 380w. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 23 °C) δ: 3.48, 2.80, 2.15, 1.90 (s, 16H, tmeda) and 0.68 (s, 18H, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 75 MHz, 25 °C) δ: 58.33, 57.89 (CH$_2$, tmeda), 53.47, 51.73, 49.20 (Me, tmeda) and 7.51 (Me, SiMe$_3$).

Complex **2**: a suspension of **1** (1.08 g, 1.4 mmol) in toluene (75 ml) was treated with pyridine (2 ml). The resulting deep-green solution was evaporated to dryness and the residual solid redissolved in dry diethyl ether. Large deep-green crystals of **2** (0.65 g, 0.86 mmol, 68% yield) formed upon standing one day at −30 °C. IR (KBr, Nujol mull) ν/cm^{-1}: 1590m, 1435s, 1250s, 1235s, 1210m, 1140m, 1060m, 1030m, 1000m, 950vs, 860s, 830vs, 770s, 750s, 690m, 680m, 655m and 615w. ^{1}H NMR (NC$_5$D$_5$, 200 MHz, 23 °C) δ: 8.71, 7.56, 7.19, (s, pyridine), 0.19 (s, 9H, SiMe$_3$) and 0.04 (s, 9H, SiMe$_3$). ^{13}C NMR (NC$_5$D$_5$, 75 MHz, 25 °C) δ: 150.28, 135.85, 123.85 (CH, pyridine), 6.16 (Me, SiMe$_3$) and 4.12 (Me, SiMe$_3$).

‡ A suspension of TiCl$_3$(thf)$_3$ (20 g, 54 mmol) in thf (200 ml) was treated with tmeda (17 ml). The addition of LiN(SiMe$_3$)$_2$ (18.1 g, 108 mmol) to the resulting light blue solution turned the colour light green. After standing 30 min at room temperature the solvent was evaporated *in vacuo*. The residual solid was redissolved in diethyl ether (500 ml) and insoluble material filtered out. Colourless crystals of **3** (21.9 g, 32 mmol, 59%) separated upon concentration and standing at −30 °C overnight. IR (KBr, Nujol mull) ν/cm^{-1}: 2900s, 2800m, 1460s, 1380m, 1360m, 1290s, 1260sh, 1240s, 1190m, 1170m, 1140m, 1105m, 1070m, 1030s, 1015s, 930s, 890s, 835s, 785s, 760m, 720w, 695s, 670s, 630m, 615w, 500m, 450w, 410m and 390m.

§ Complex **2**: monoclinic, $P2_1/n$ $a = 11.797(2)$ Å, $b = 12.910(1)$ Å, $c = 15.105(2)$ Å, $β = 98.38(1)°$, $V = 2275.9(5)$ Å^3, $Z = 4$, $R = 0.040$ ($R_W = 0.064$), $T = 296$ K for 218 parameters and 2265 significant reflections out of 3552. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were introduced at calculated positions but not refined.

Complex **3**: triclinic, $P\bar{1}$, $a = 13.090(4)$ Å, $b = 14.683(4)$ Å, $c = 11.591(1)$ Å, $α = 102.09(1)$, $β = 91.02(1)$, $γ = 92.80(2)°$, $V = 2174.8(9)$ Å^3, $Z = 2$, $R = 0.072$ ($R_W = 0.058$), $T = 298$ K for 344 parameters and 3503 significant reflections out of 6425. All non-hydrogen atoms were located and anisotropically refined. Hydrogen atom positions were calculated but not refined.

Atomic coordinates, bond lengths and angles, and thermal parameters for complexes **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Fig. 1 ORTEP drawing of **2** showing the labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected values of bond distances (Å) and angles (°): Ti(1)–Cl(1) 2.394(2), Ti(1)–N(1) 2.268(4), Ti(1)–N(2) 2.251(4), Ti(1)–N(3) 2.020(4), Ti(1)–N(4) 1.759(3), N(3)–Si(1) 1.728(4), N(4)–N(4a) 1.263(7); Cl(1)–Ti(1)–N(3) 142.2(1), Cl(1)–Ti(1)–N(4) 108.9(1), N(1)–Ti(1)–N(2) 171.8(2), N(3)–Ti(1)–N(4) 108.7(2), Ti(1)–N(4)–N(4a) 175.5(5), Ti(1)–N(3)–Si(1) 120.2(2).

{TiCl[N(SiMe$_3$)$_2$](pyridine)$_2$} units each bonded to one of the two nitrogen atoms of a bridging dinitrogen moiety (Fig. 1). The two fragments are eclipsed and rotated with respect to each other [torsion angle Cl(1)–Ti(1)–Ti(1a)–Cl(1a) 180.0(9)°]. The coordination geometry of titanium is slightly distorted trigonal bipyramidal with the two pyridine molecules placed on the two axial positions [N(1)–Ti(1)–N(2) 171.8(2)°], and the equatorial plane defined by chlorine and the two nitrogen atoms of amido and dinitrogen groups [N(3)–Ti(1)–N(4) 108.7(2), N(4)–Ti(1)–Cl(1) 108.9(2), Cl(1)–Ti(1)–N(3) 142.2(1)°]. The Ti–N distance formed by titanium with the trigonal planar amido group [Ti(1)–N(3) 2.020(4) Å] is significantly shorter than those formed by the nitrogen atoms of the two pyridine molecules [Ti(1)–N(1) 2.268(4), Ti(1)–N(2) 2.251(4) Å], suggesting the presence of some π-bond character with both silicon and titanium atoms. The remarkably short Ti–N distance [Ti(1)–N(4) 1.759(3) Å] formed by titanium with the dinitrogen moiety, the almost linear arrangement of the Ti–(μ-η:η'-N$_2$)-Ti unit [Ti(1)–N(4)–N(4a) 175.5(5)°] and the rather long N–N distance [N(4)–N(4a) 1.263(7) Å] are in agreement with the presence of electronic delocalization over the Ti$_2$(μ-η:η'-N$_2$) group and possibly with some extent of dinitrogen reduction.

The chemical connectivity of **3** was also demonstrated by X-ray diffraction analysis. The molecule is formed by two separate [Li(tmeda)$_2$]$^+$ and {TiCl$_2$[N(SiMe$_3$)$_2$]$_2$}$^-$ ionic fragments. The titanium-containing anion consists of a distorted tetrahedral Ti^{III} atom surrounded by two amido ligands and two chlorine atoms [Cl(1)–Ti(1)–Cl(2) 102.4(1), C(11)–Ti(1)–N(1) 99.7(3), N(1)–Ti(1)–N(2) 121.9(3)°] (Fig. 2). The distorted geometry is probably a result of the steric bulk of the two N(SiMe$_3$)$_2$ groups. The Ti–Cl bond distances are normal [Ti(1)–Cl(1) 2.349(4), Ti(1)–C(12) 2.326(4) Å]. Conversely, the Ti–N distances [Ti(1)–N(1) 1.933(8), Ti(1)–N(2) 1.989(8) Å] are slightly shorter than in complex **2** and, together with the trigonal planar geometry of the nitrogen atom, indicate a certain character of π-bonding over the Ti–N–Si moiety. No special features are observed for the tetrahedral [Li(tmeda)$_2$]$^+$ cation.
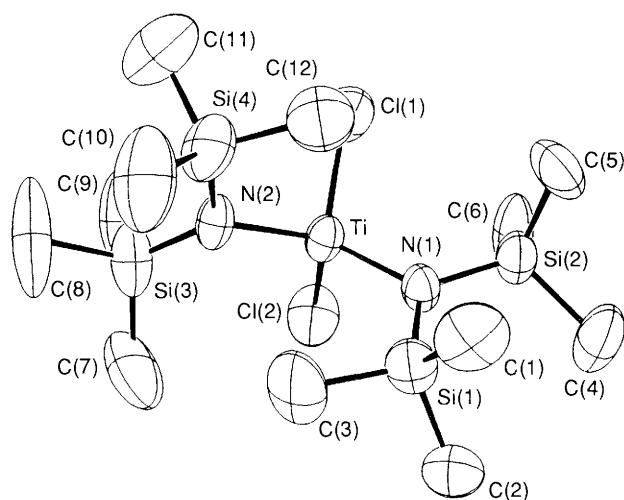
Fig. 2 ORTEP drawing of **3** showing the labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected values of bond distances (Å) and angles (°): Ti(1)–Cl(1) 2.354(3), Ti(1)–Cl(2) 2.338(3), Ti(1)–N(1) 1.962(6), Ti(1)–N(2) 1.989(7), N(1)–Si(1) 1.766(8); N(1)–Ti(1)–N(2) 122.2(3), N(1)–Ti(1)–Cl(1) 100.4(2), N(1)–Ti(1)–Cl(2) 110.7(2), N(2)–Ti(1)–Cl(1) 116.9(2), N(2)–Ti(1)–Cl(2) 102.7(2), Ti(1)–N(1)–Si(1) 119.7(4).

Complexes **1** and **2** are the first examples where dinitrogen fixation occurs on a non-metallocenic titanium system. The two diamagnetic complexes are thermally robust, since no appreciable decomposition has been observed in benzene (80 °C) and in pyridine (90 °C) solutions of **1** and **2**, respectively. Complex **3** is paramagnetic with a magnetic moment as expected for a d^1 species ($\mu_{eff} = 1.75$ μ_B). The ^{1}H and ^{13}C NMR spectra of **2** show two distinct resonances attributable to the two inequivalent SiMe$_3$ groups. The magnetic inequivalence can be explained by assuming that the solid state structure, showing two different orientations of the SiMe$_3$ groups (parallel and perpendicular with respect to the intermetallic vector) is preserved in solution at room temperature. The fluxional behaviour of **2**, with a coalescence temperature of T 57 °C, can be explained with a rather high rotational energy barrier of the SiMe$_3$ groups around the Ti–N vector.

This remarkable short Ti–N distance observed in complex **2**, which is very similar to those observed in the recently reported Ti-imido derivatives,[9] and the surprising stability of the Ti$_2$N$_2$ frame during the pyridine replacement reaction of tmeda in complex **1**¶ are giving some expectation for further reactivity of coordinated dinitrogen. Further work to investigate this point is in progress at the moment.

¶ This behaviour is in striking contrast with the reversibility observed in a V^{II} dinitrogen derivative, possessing a similar V–N$_2$–V array,[10] and which evolved dinitrogen upon reaction with pyridine.

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